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Plastics — Ethylene/vinyl acetate copolymer (E/VAC) thermoplastics — Determination of vinyl acetate content

*Plastiques — Copolymères éthylène/acétate de vinyle (E/VAC) thermoplastiques —
Dosage de l'acétate de vinyle*



Reference number
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Foreword

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Plastics — Ethylene/vinyl acetate copolymer (E/VAC) thermoplastics — Determination of vinyl acetate content

1 Scope

1.1 This International Standard specifies two categories of methods for the determination of the vinyl acetate (VAC) content in ethylene/vinyl acetate (E/VAC) copolymers for their designation in accordance with ISO 4613-1. The first category comprises "reference methods", the second comprises "control methods".

"Reference methods" are used for the calibration of the method used for the determination of the vinyl acetate content of ethylene/vinyl acetate copolymers.

"Control methods" can be used for the determination if calibrated with one of the "reference methods" described in clause 3 and if the repeatability is acceptable.

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 listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 4613-1 : 1985, *Plastics — Ethylene/vinyl acetate copolymer thermoplastics (E/VAC) — Part 1: Designation*.

ISO 4799 : 1978, *Laboratory glassware — Condensers*.

3 Reference methods

3.1 Reference method 1 : Hydrolysis and back-titration

3.1.1 Principle

Dissolution of a test portion in xylene and hydrolysis of the acetate groups by potassium hydroxide in alcoholic solution. Addition of excess of sulfuric or hydrochloric acid. Back-titration of the acid with a standard volumetric solution of sodium hydroxide, using phenolphthalein as indicator.

3.1.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.1.2.1 Xylene.

3.1.2.2 Sulfuric acid, approximately 5 g/l solution, or **hydrochloric acid**, approximately 3,7 g/l solution.

3.1.2.3 Potassium hydroxide, ethanolic solution, approximately 5,6 g/l.

Dissolve 5,6 g of solid potassium hydroxide (KOH) in 500 ml of ethanol. Make up to 1 000 ml, allow to stand overnight and decant the clear portion of the solution.

3.1.2.4 Sodium hydroxide, standard volumetric solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$.

3.1.2.5 Phenolphthalein, indicator solution.

Dissolve 0,7 g of phenolphthalein in 100 ml of ethanol.

3.1.3 Apparatus

Ordinary laboratory apparatus and

3.1.3.1 Burette, of capacity 50 ml, for the sodium hydroxide solution (3.1.2.4).

3.1.3.2 Pipette, of capacity 30 ml, for the acid solution (3.1.2.2).

3.1.3.3 Pipette, of capacity 25 ml, for the potassium hydroxide solution (3.1.2.3).

3.1.3.4 Cylinder, of capacity 50 ml, for the xylene (3.1.2.1).

3.1.3.5 Conical flask, of capacity 250 ml or 300 ml, with stopper.

3.1.3.6 Dropping bottle, for the phenolphthalein indicator solution (3.1.2.5).

3.1.3.7 Reflux condenser, of length at least 500 mm, complying with the requirements of ISO 4799.

3.1.3.8 Heating device: sand bath or heating mantle, capable of being maintained at 200 °C.

3.1.3.9 Analytical balance, accurate to the nearest 0,1 mg.

3.1.4 Procedure

3.1.4.1 Determination

3.1.4.1.1 Into the flask (3.1.3.5), weigh, to the nearest 0,1 mg, a quantity of dry copolymer as indicated in table 1. The mass of each particle of the sample shall be less than 0,05 g approximately.

Table 1

Estimated vinyl acetate content $w(\text{VAC})$ % (m/m)	Approximate mass of test portion g
$w(\text{VAC}) < 10$	1
$10 < w(\text{VAC}) < 20$	0,5
$20 < w(\text{VAC}) < 40$	0,3
$40 < w(\text{VAC})$	0,2

When analysing an unknown sample, carry out a preliminary test under conditions valid for a copolymer containing 20 % (m/m) to 40 % (m/m) of vinyl acetate.

3.1.4.1.2 Add 50 ml of the xylene (3.1.2.1) to the flask and 25 ml of the potassium hydroxide solution (3.1.2.3) by means of the pipette (3.1.3.3). Heat the flask fitted with the condenser (3.1.3.7) for 2 h on the heating device (3.1.3.8), maintained at 200 °C. After hydrolysis is complete, remove the flask from the heating device and allow to cool to ambient temperature. Add 30 ml of the sulfuric or hydrochloric acid solution (3.1.2.2) by means of the pipette (3.1.3.2), stopper the flask and shake vigorously. Add a few drops of the phenolphthalein solution (3.1.2.5) and titrate the excess acid, while stirring, with the standard volumetric sodium hydroxide solution (3.1.2.4).

3.1.4.2 Blank test

Carry out a blank test at the same time as the determination, following the same procedure and using the same reagents as used for the determination, but omitting the test portion.

3.1.5 Expression of results

3.1.5.1 The vinyl acetate content, expressed as a percentage by mass, is given by the formula

$$\frac{0,8609 (V_1 - V_2) c_1}{m}$$

where

V_1 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (3.1.2.4) used in the determination;

V_2 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (3.1.2.4) used in the blank test;

c_1 is the actual concentration, expressed in moles per litre, of the standard volumetric sodium hydroxide solution (3.1.2.4);

m is the mass, in grams, of the test portion (see 3.1.4.1.1);

0,8609 is the mass, in grams, of vinyl acetate corresponding to 1,00 ml of sodium hydroxide solution, $c(\text{NaOH}) = 0,100 \text{ mol/l}$.

3.1.5.2 Carry out two determinations. If the results differ by more than 1,0 % (m/m), repeat the determination. Report the result as the arithmetic mean of two determinations.

3.1.6 Test report

The test report shall include the following particulars:

- a reference to this International Standard and the method used;
- full identification of the sample;
- the result expressed in accordance with 3.1.5.2.

3.2 Reference method 2: Saponification and potentiometric titration

3.2.1 Principle

Dissolution of a test portion in a mixture of xylene and hexan-1-ol, and hydrolysis of the acetate groups by alcoholic potassium hydroxide solution. Addition of acetone to prevent the precipitation of copolymer. Titration of the excess alkali with a standard volumetric hydrochloric acid solution, using a potentiometric titrator.

3.2.2 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

3.2.2.1 Xylene, or *p*-xylene.

3.2.2.2 Hexan-1-ol.

3.2.2.3 Potassium hydroxide, ethanolic solution, approximately 28 g/l.

3.2.2.4 Acetone.

3.2.2.5 Hydrochloric acid, standard volumetric solution, $c(\text{HCl}) = 0,3 \text{ mol/l}$.

3.2.2.6 Lithium chloride, 40 g/l ethanolic solution.

3.2.3 Apparatus

Ordinary laboratory apparatus and

3.2.3.1 Potentiometric titrator, equipped with a burette of capacity 10 ml (each division 0,02 ml), a millivoltmeter or any other suitable type of voltmeter, a glass measuring electrode and a silver/silver chloride reference electrode filled with the ethanolic lithium chloride solution (3.2.2.6), a connecting bridge filled with the same lithium chloride solution and a beaker filled with the same lithium chloride solution.

Any other suitable type of potentiometric titrator may be used.

3.2.3.2 Cylinder, of capacity 50 ml, for the xylene (3.2.2.1) and the acetone (3.2.2.4).

3.2.3.3 Pipette, of capacity 5 ml, for the potassium hydroxide solution (3.2.2.3).

3.2.3.4 Pipette, of capacity 10 ml, for the hexan-1-ol (3.2.2.2).

3.2.3.5 Conical flask, of capacity 100 ml, of chemically stable glass.

3.2.3.6 Reflux condenser, of length at least 300 mm, complying with the requirements of ISO 4799.

3.2.3.7 Heating device: sand bath or heating mantle, capable of being maintained at about 200 °C.

3.2.3.8 Analytical balance, accurate to the nearest 0,1 mg.

3.2.3.9 Magnetic stirrer.

3.2.4 Procedure

3.2.4.1 Determination

3.2.4.1.1 Into the flask (3.2.3.5), weigh, to the nearest 0,1 mg, a quantity of dry copolymer as indicated in table 2. The mass of each particle of the sample shall be less than 0,05 g approximately.

Table 2

Estimated vinyl acetate content $w(\text{VAC})$ % (m/m)	Approximate mass of test portion g
$w(\text{VAC}) < 2$	1
$2 < w(\text{VAC}) < 5$	0,5
$5 < w(\text{VAC}) < 30$	0,2
$30 < w(\text{VAC})$	0,1

When analysing an unknown sample, carry out a preliminary test under conditions valid for a copolymer containing 5 % (m/m) to 30 % (m/m) of vinyl acetate.

3.2.4.1.2 Add 215 ml of the xylene (3.2.2.1), 10 ml of the hexan-1-ol (3.2.2.2) and 5 ml of the potassium hydroxide solution (3.2.2.3). Heat the flask fitted with the reflux condenser (3.2.3.6) for 30 min on the heating device (3.2.3.7), maintained at the boiling point. After hydrolysis is complete, remove the flask from the heating device and allow to cool for 5 min to 6 min, then introduce 35 ml of the acetone (3.2.2.4) through the top of the condenser. Disconnect the flask from the condenser and place it on the magnetic stirrer (3.2.3.9). Immerse the glass electrode (see 3.2.3.1) and the end of the connecting bridge (see 3.2.3.1) in the solution in the flask, and immerse the other end of the connecting bridge and the silver/silver chloride reference electrode (see 3.2.3.1) in the beaker filled with the ethanolic lithium chloride solution (3.2.2.6).

Carry out the potentiometric titration with the standard volumetric hydrochloric acid solution (3.2.2.5), while stirring, up to the first drop in potential. At first, add the titrant quickly from the burette; when approaching the equivalence point, add it by 0,04 ml to 0,06 ml additions.

When the equilibrium potential is reached, read the voltage, in millivolts, of the potentiometer (3.2.3.1) as well as the added volume.

NOTE — The end-point is taken to be the point at which the greatest change in potential occurs on introducing the above-mentioned volume of titrant. In the case of two similar high values of the change, the first value is taken as the end-point. The end-point can also be determined graphically.

3.2.4.2 Blank test

Carry out a blank test in parallel with the determination, by the same procedure, using the same reagents as in the determination, but omitting the test portion. Prepare the titration curve. The middle point of the sharply rising part of the titration curve is taken as the end-point of the titration.

3.2.5 Expression of results

3.2.5.1 The vinyl acetate content, expressed as a percentage by mass, is given by the formula

$$\frac{2,56 (V_3 - V_4) c_2}{m}$$

where

V_3 is the volume, in millilitres, of the standard volumetric hydrochloric acid solution (3.2.2.5) used in the blank test;

V_4 is the volume, in millilitres, of the standard volumetric hydrochloric acid solution (3.2.2.5) used in the determination;

c_2 is the actual concentration, expressed in moles per litre, of the standard volumetric hydrochloric acid solution (3.2.2.5);

m is the mass, in grams, of the test portion (see 3.2.4.1.1);

2,56 is the mass, in grams, of vinyl acetate corresponding to 1,00 ml of hydrochloric acid solution, $c(\text{HCl}) = 0,300 \text{ mol/l}$.

3.2.5.2 Carry out two determinations. If the results differ by more than 1 % (*m/m*), repeat the determination. Report the result as the arithmetic mean of two determinations.

3.2.6 Test report

The test report shall include the following particulars:

- a) a reference to this International Standard and the method used;
- b) full identification of the sample;
- c) the result expressed in accordance with 3.2.5.2.

4 Control methods (examples)

4.1 Infrared spectrometric method

4.1.1 Principle

The vinyl acetate content is determined by infrared spectrometry. This method consists in the determination of the ratio of the absorbance of the $\nu(\text{CH}_2)$ band at $2\,678\text{ cm}^{-1}$ to that of $2\nu(\text{CO})$ at $3\,460\text{ cm}^{-1}$ in an E/VAC film of thickness $50\text{ }\mu\text{m}$ to $300\text{ }\mu\text{m}$. The ratio of the absorbances is converted to vinyl acetate content using a calibration curve established with E/VAC standard samples of known vinyl acetate contents.

It is not necessary to know the exact thickness of the film; an infrared band is used as an internal standard.

NOTES

- 1 This method is suitable for samples with VAC contents of 10 % (*m/m*) and above.
- 2 The internal standard peak at $3\,605\text{ cm}^{-1}$ can also be used for thick samples ($> 200\text{ }\mu\text{m}$) instead of the peak at $2\,678\text{ cm}^{-1}$. If the sample thickness can be measured manually, this can be used instead of the absorbance of the internal standard peaks.
- 3 Other CO peaks, for example 610 cm^{-1} , $1\,020\text{ cm}^{-1}$, $1\,250\text{ cm}^{-1}$ and $1\,743\text{ cm}^{-1}$, can be used instead of $3\,460\text{ cm}^{-1}$, with a sample thickness appropriate to the content of the sample.

4.1.2 Apparatus and materials

Ordinary laboratory apparatus and

4.1.2.1 Infrared spectrometer, of wave number range $4\,000\text{ cm}^{-1}$ to 600 cm^{-1} , capable of resolution to 1 cm^{-1} .

4.1.2.2 Film holder.

4.1.2.3 Beam shutter.

4.1.2.4 Compression moulding press, having a clamping force corresponding to an applied pressure of at least 10 MPa, and having platens capable of being heated to at least $150\text{ }^\circ\text{C}$.

4.1.2.5 E/VAC standard samples, having vinyl acetate contents determined by one of the reference methods described in clause 3.

4.1.3 Procedure

4.1.3.1 Preparation of films

Mould films of constant thickness with the compression moulding press (4.1.2.4), at about $150\text{ }^\circ\text{C}$. The thickness of the films shall be

- $200\text{ }\mu\text{m}$ to $300\text{ }\mu\text{m}$, when the VAC content is $\leq 10\text{ }\%$ (*m/m*);
- $50\text{ }\mu\text{m}$ to $150\text{ }\mu\text{m}$, when the VAC content is $> 10\text{ }\%$ (*m/m*).

NOTES

1 To facilitate the moulding and to avoid sticking of the E/VAC, a thin film of polytetrafluoroethylene (PTFE) may be placed between the E/VAC and the mould.

2 When the VAC content is $< 20\text{ }\%$ (*m/m*), the PTFE film may be replaced with aluminium foil.

4.1.3.2 Measurement

4.1.3.2.1 Select the appropriate wave number scale and adjust the zero absorbance [for 100 % transmission of the infrared spectrometer (4.1.2.1)].

4.1.3.2.2 Introduce a film, prepared as in 4.1.3.1, of an E/VAC standard sample (4.1.2.5) into the film holder (4.1.2.2), and place it in the beam of the spectrometer.

4.1.3.2.3 Adjust the base line with the shutter (4.1.2.3) of the reference beam.

4.1.3.2.4 Record the spectrum from $4\,000\text{ cm}^{-1}$ to $2\,000\text{ cm}^{-1}$.

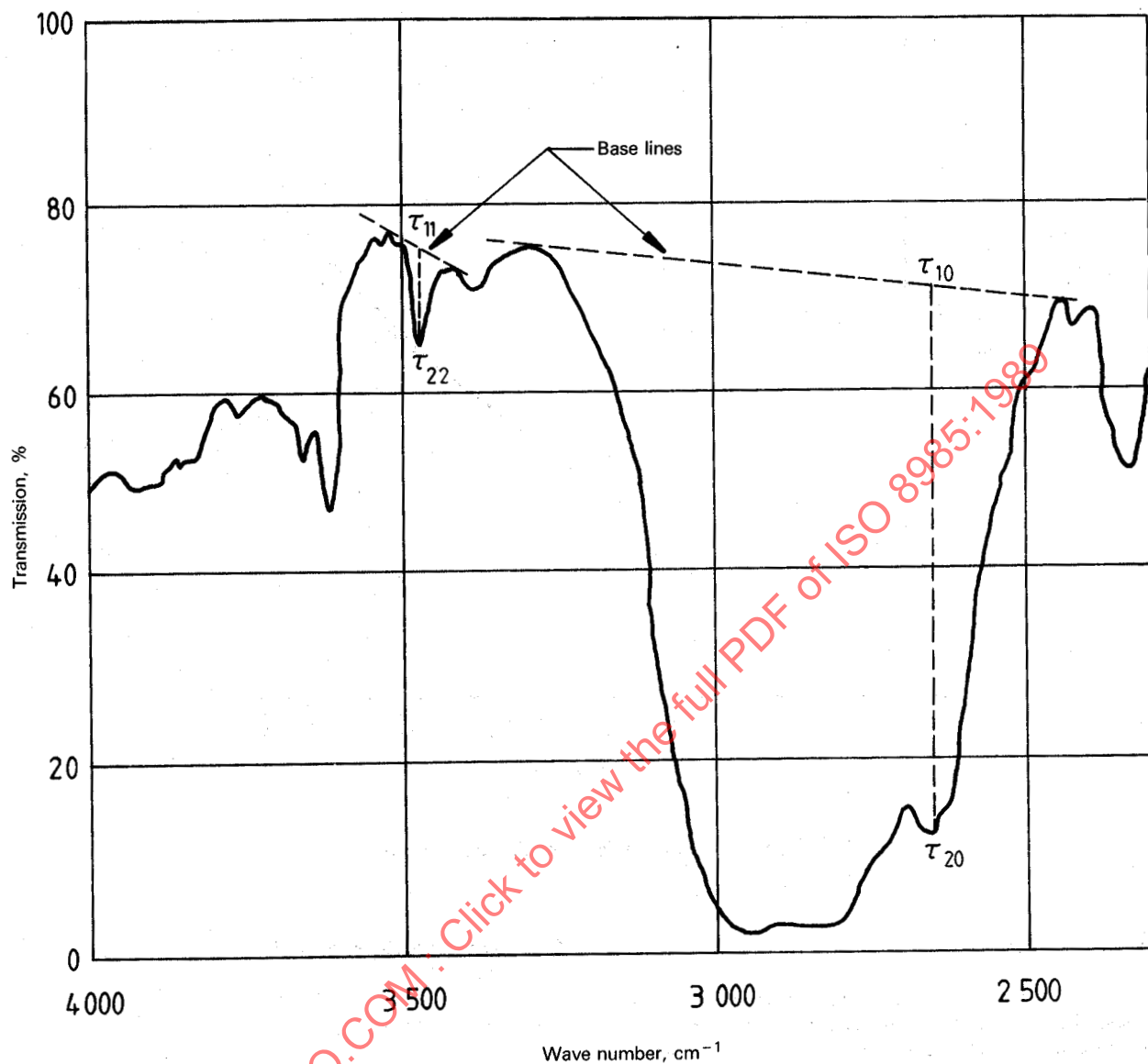
4.1.3.2.5 Draw lines tangential to the peaks at $3\,520\text{ cm}^{-1}$ and $3\,400\text{ cm}^{-1}$ and at $3\,280\text{ cm}^{-1}$ and $2\,430\text{ cm}^{-1}$, as shown in figure 1.

4.1.3.2.6 Determine the absorbances at $3\,460\text{ cm}^{-1}$ and $2\,678\text{ cm}^{-1}$. (See the example of the determination of optical density shown in figure 1.)

4.1.3.2.7 Repeat the operations in 4.1.3.2.2 to 4.1.3.2.6 for films, prepared as in 4.1.3.1, of the other E/VAC standard samples (4.1.2.5), and subsequently for a film, also prepared as in 4.1.3.1, of the sample for which the VAC content is to be determined, without changing the operating conditions (for example scan speed, span, balance, slit, sensitivity, etc.) of the spectrometer.

4.1.3.3 Calibration curve

Draw the calibration curve by plotting the values of VAC content obtained from the reference method (3.1 or 3.2) against the corresponding values of the ratio absorbance ($3\,460$)/absorbance ($2\,678$) determined by the procedure (4.1.3.1 and 4.1.3.2) on the E/VAC standard samples. An example of a calibration curve is shown in figure 2.



$$\text{Absorbance (2 678)} = \log_{10} \tau_{10} - \log_{10} \tau_{20} = A_{10} - A_{20} = 0,857$$

$$\text{Absorbance (3 460)} = \log_{10} \tau_{11} - \log_{10} \tau_{22} = A_{11} - A_{22} = 0,062$$

$$\frac{\text{Absorbance (3 460)}}{\text{Absorbance (2 678)}} = 0,072$$

Figure 1 — Example of IR spectrum and determination of absorbance

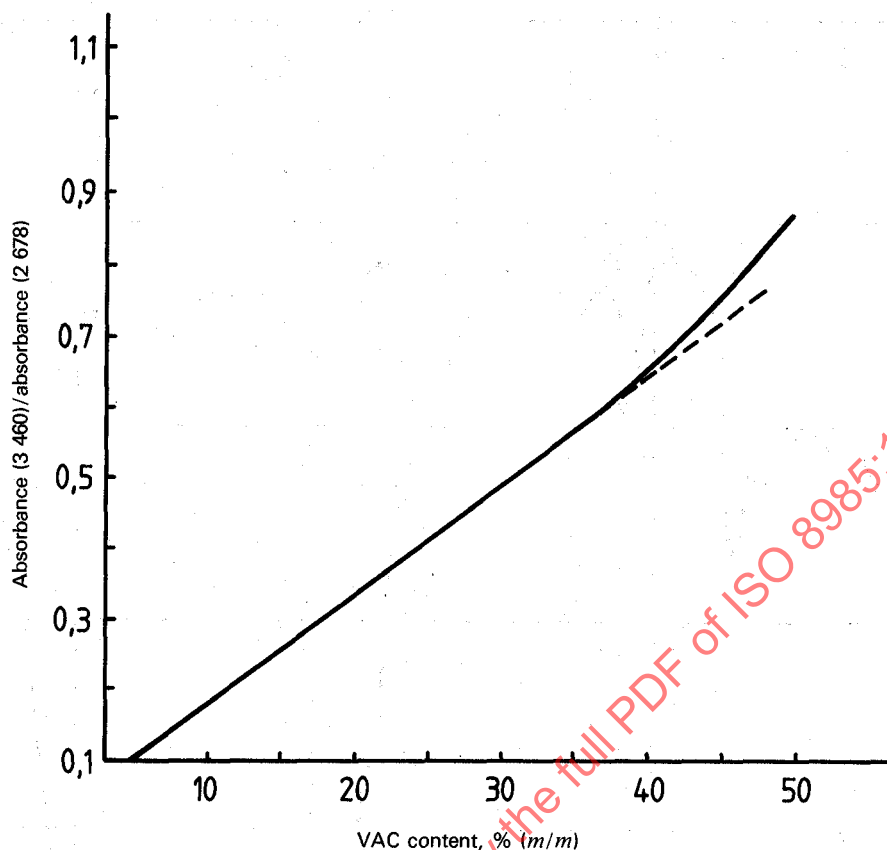


Figure 2 — Example of calibration curve

4.1.4 Expression of results

The vinyl acetate content, expressed as a percentage by mass, is determined by reading, from the calibration curve, the VAC content corresponding to the value of absorbance (3 460)/absorbance (2 678) for the sample (figure 2). If absorbance (3 460)/absorbance (2 678) for the sample lies on the straight-line portion of the calibration curve, the vinyl acetate content is given by the formula

$$K \times \frac{\text{absorbance (3 460)}}{\text{absorbance (2 678)}}$$

where K is the ratio of VAC content to absorbance (3 460)/absorbance (2 678) for the straight-line portion, as determined by the least-squares method on the calibration curve.

4.1.5 Test report

The test report shall include the following particulars:

- a reference to this International Standard and the method used;
- full identification of the sample;
- the results expressed in accordance with 4.1.4;
- experimental details and incidents that may have affected the results.

4.2 Acidimetric method

4.2.1 Principle

A test portion is placed in an oven at a temperature of 350 °C. The interior of the oven is connected through a glass tube to a washing bottle containing a potassium hydroxide solution. By means of a warm nitrogen flow, the pyrolyzates are transferred to the washing bottle in which the acidic decomposition gases are absorbed by the potassium hydroxide solution. The volume of potassium hydroxide solution necessary for the absorption process is then determined by titration with a standard volumetric hydrochloric acid solution, using phenolphthalein as indicator.

4.2.2 Reagents and material

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.2.2.1 Potassium hydroxide, solution,
 $c(\text{KOH}) = 0,1 \text{ mol/l}$.

4.2.2.2 Hydrochloric acid, standard volumetric solution,
 $c(\text{HCl}) = 0,1 \text{ mol/l}$.

4.2.2.3 Phenolphthalein, indicator solution.

Dissolve 0,1 g of phenolphthalein in 100 ml of ethanol.

4.2.2.4 Nitrogen.**4.2.3 Apparatus**

Ordinary laboratory apparatus and

4.2.3.1 Pyrolysis oven, capable of being maintained at 350 °C.

4.2.3.2 Vitrified porcelain combustion boats, 110 mm long, 12 mm wide, 8 mm high.

4.2.3.3 Durand gas washing bottle, capacity 250 ml, fitted with washing bottle insert and fritted glass plate¹⁾. An example is shown in figure 3.

4.2.3.4 Schellbach automatic zero burette, capacity 50 ml.

4.2.3.5 One-mark bulb burettes, capacity 50 ml and 100 ml.

4.2.3.6 Erlenmeyer flask, capacity 250 ml.

4.2.3.7 Balance, accurate to 0,1 mg.

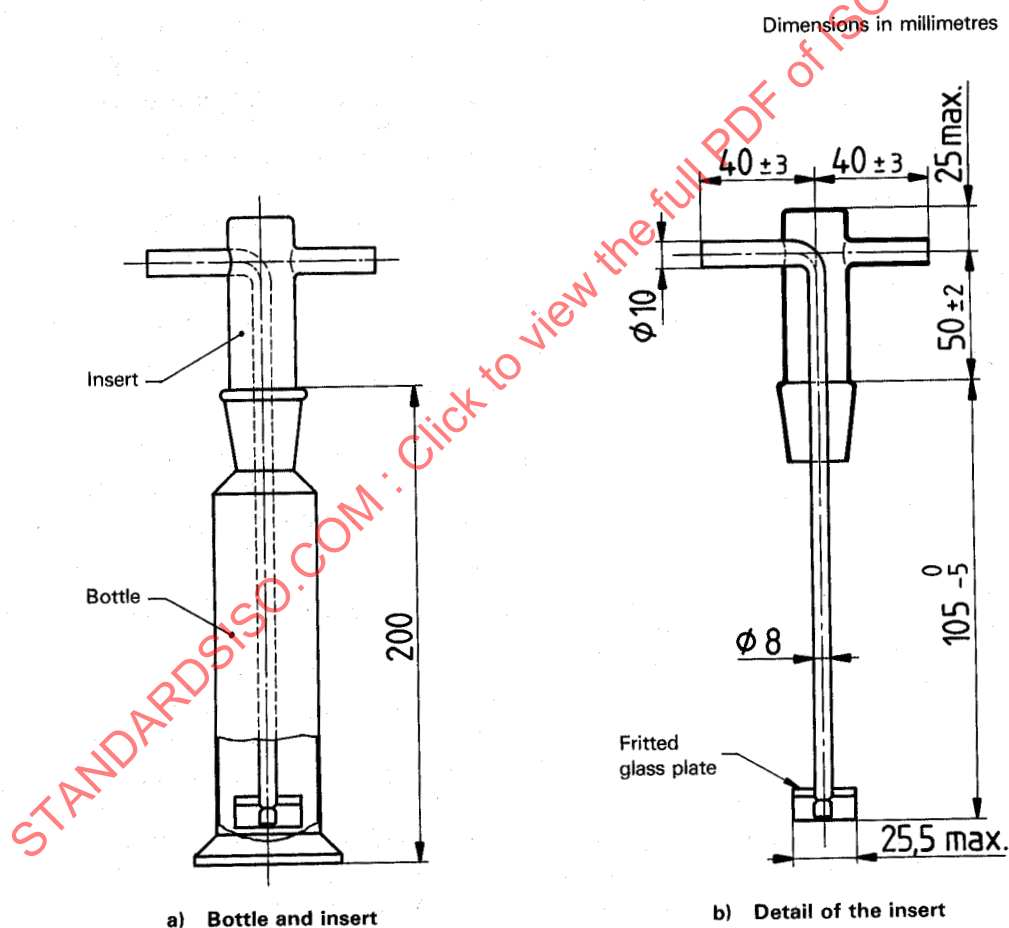


Figure 3 — Durand gas washing bottle

1) Corresponds to the commercially available type D1 fritted glass plate. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this particular product. Equivalent products may be used if they can be shown to lead to the same results.