INTERNATIONAL STANDARD

ISO 182-3

Second edition
2023-12

Plastics — Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures —

Part 3: Conductometric method

Plastiques — Détermination de la tendance des compositions et produits à base d'homopolymères et de copolymères du chlorure de vinyle à dégager du chlorure d'hydrogène et éventuellement d'autres produits acides à températures élevées —

Partie 3: Méthode conductimétrique

Reference number
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Foreword

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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).

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 9, *Thermoplastic materials*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 182-3:1993), which has been technically revised.

The main changes are as follows:

- adding the use of alternative heating baths such as metal blocks.

A list of all parts in the ISO 182 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.

Plastics — Determination of the tendency of compounds and products based on vinyl chloride homopolymers and copolymers to evolve hydrogen chloride and any other acidic products at elevated temperatures —

Part 3:
Conductometric method

WARNING — The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

1.1 This document specifies a method for the determination of the thermal stability at elevated temperature of compounds and products based on vinyl chloride homopolymers and copolymers (in the following text abbreviated as PVC) which undergo dehydrochlorination (the evolution of hydrogen chloride).

1.2 This document is applicable to the characterization of PVC compounds and products, especially with regard to the effectiveness of their heat-stabilizing systems.

It is applicable to coloured PVC compounds and products where a discolouration test under the action of heat may be unsatisfactory.

1.3 This document is applicable to compounded PVC materials and products. It can be applicable to polymers in powder form under appropriate conditions, to be agreed upon between the interested parties.

This document does not apply to PVC compounds in the form of dry blends, since such materials can be not sufficiently homogeneous.

1.4 This document does not apply to PVC compounds and products which evolve other decomposition products, in addition to hydrogen chloride, at elevated temperatures that can affect the conductivity of water when they are absorbed into it. In this case, a method suitable for the determination of chloride ion (Cl^-) in the absorbing solution shall be used (see ISO 182-4[2]).

1.5 This document can also be applied to other plastics materials which can evolve hydrogen chloride or other hydrogen halides when heated under the conditions prescribed by the relevant specifications, or as agreed upon between the interested parties.

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 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

ISO 6353-2, *Reagents for chemical analysis — Part 2: Specifications — First series*

3 Terms and definitions

For the purposes of this document, the following terms and definitions 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/

3.1
stability time
t_s
time, measured by reference to a predetermined change in the conductivity of absorbing demineralized water, required for a certain amount of hydrogen chloride to be evolved when a prescribed mass of PVC compound or product is maintained at an elevated temperature under the test conditions specified in this document

4 Principle

A test portion of the PVC compound or product is maintained at an agreed temperature in a nitrogen gas stream and the hydrogen chloride evolved is absorbed in a given amount of demineralized water. The amount of hydrogen chloride evolved is determined in relation to the recorded change in conductivity of the water.

5 Reagents

During the test, use only reagents of recognized analytical grade in accordance with ISO 6353-2.

5.1 Pure nitrogen, containing less than 6 ppm oxygen and less than 0,1 ppm carbon dioxide by volume. The purity shall be such that when the gas is passed through demineralized water (see 5.2) for 1 h at a rate of (7,2 ± 0,1) l/h, the conductivity of the water remains unchanged.

The gas shall be dried by passing it through a suitable drying agent, and the flow-rate through the dehydrochlorination cell adjusted by means of a needle valve and measured using a suitable flowmeter.

5.2 Demineralized water, with a conductivity not higher than 5 µS/cm.

6 Apparatus

The general arrangement of the apparatus is shown in Figure 1.

6.1 Dehydrochlorination cells.

6.1.1 Glass Cell A (re-usable), with shape and dimensions as shown in Figure 2.

A recommended procedure for cleaning the cell is given in Annex A.

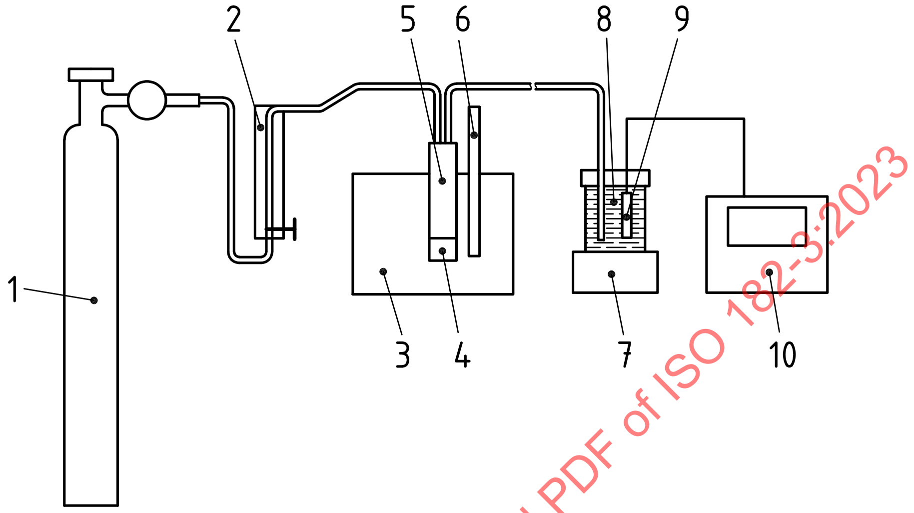
6.1.2 Glass Cell B (disposable), with shape and dimensions as shown in Figure 3.

NOTE Other types of cell can be employed if it has been proved that the results obtained are equivalent to those obtained with one of the cells described in 6.1.1 and 6.1.2.

6.2 Test portion holder, for use with cell A. The test portion is supported on a porous sintered-glass disc grade P 100 specified in ISO 4793, 10 mm in diameter.

To prevent blocking of the porous disc, it is advisable to place a thin, soft layer of glass wool between it and the test portion.

A recommended procedure for cleaning the disc support is given in Annex A.

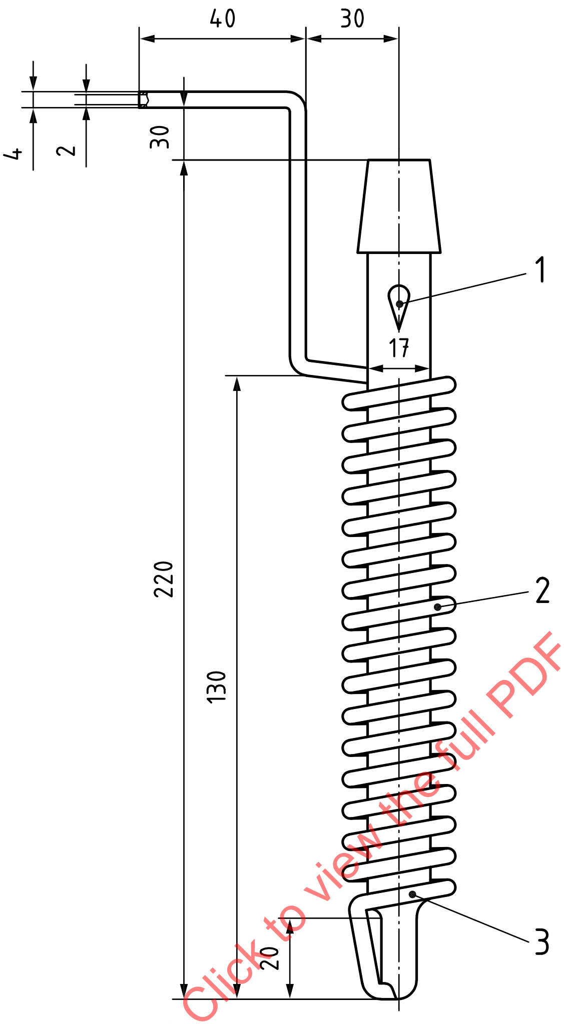


Key

1	N_2 cylinder with pure nitrogen
2	flowmeter
3	heating bath/heating block including temperature controller (resolution 0,1 °C)
4	PVC test portion
5	dehydrochlorination cell (details see Figure 2 and 3)
6	thermometer (resolution 0,1 °C)
7	magnetic stirrer (in case using heating oil bath)
8	absorbing solution
9	measuring electrode(s)
10	conductance meter

Figure 1 — General arrangement of apparatus

Dimensions in millimetres

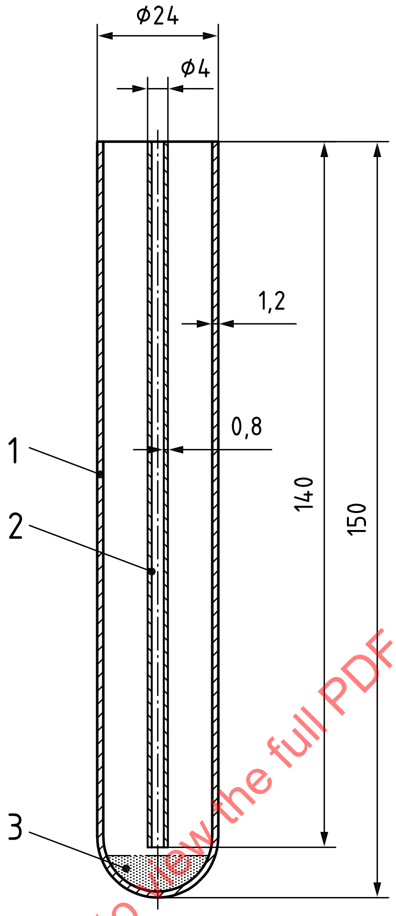


Key

1	spurs
2	17 coils
3	sintered-glass disc, 10 mm diameter (removable)

Figure 2 — Cell A (re-usable) for dehydrochlorination of PVC samples

Dimensions in millimetres

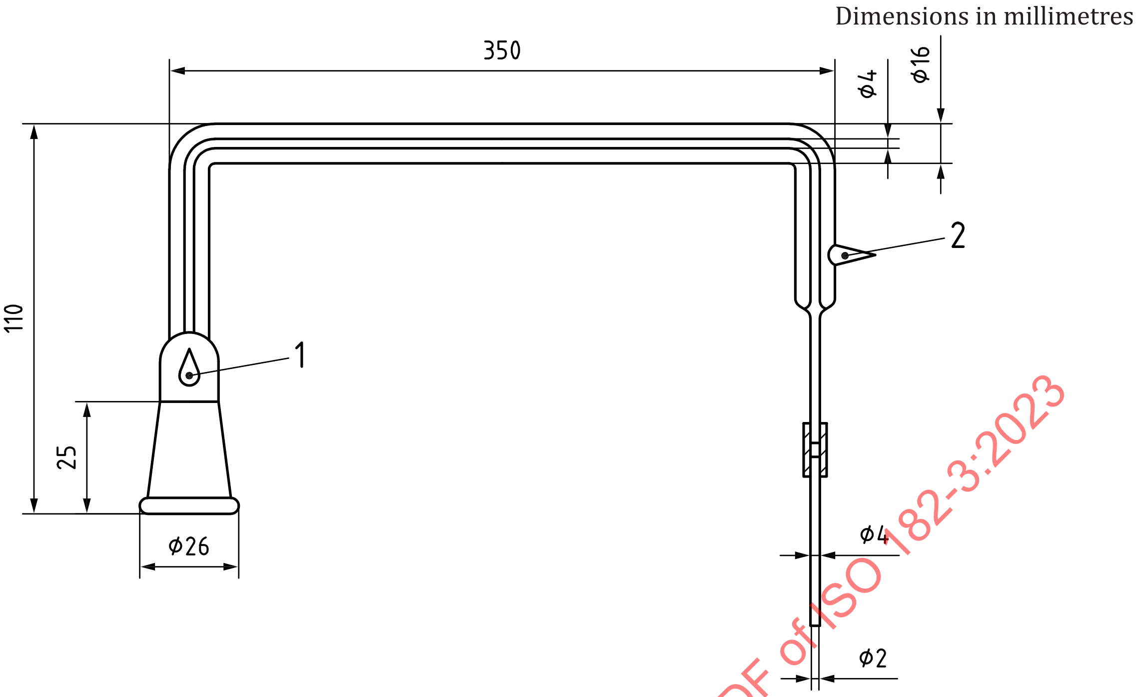


Key

1	disposable glass
2	disposable nitrogen inlet tube
3	sample

Figure 3 — Cell B (disposable) for dehydrochlorination of PVC samples

6.3 Glass connection tube, for use with cell A, connecting the dehydrochlorination cell to the measurement cell and having dimensions as shown in Figure 4. The connection tube is secured to cell A by two springs fixed to hooks on the ground-glass joints. The tube shall be provided with an insulating jacket.



Key

1, 2 spurs

Figure 4 — Glass tubes for connecting the dehydrochlorination cell to the measurement cell (use for cell A)

6.4 Heating bath (e.g. oil bath)/Heating block (e.g. metal block) including temperature controller with a capacity of at least 10 l. The bath / block shall be capable of operating in the temperature range 170 °C to 210 °C and of maintaining the test temperature with an accuracy of ±0,1 °C.

The bath/block shall be designed so that the temperature distribution is even throughout, and shall have a thermal capacity sufficient to avoid temperature change when the dehydrochlorination cell is immersed in it.

6.5 Thermometer, with a scale suitable for reading the heating bath/heating block temperature in the range 170 °C to 210 °C and with a resolution of 0,1 °C.

6.6 Balance, with a resolution of 1 mg.

6.7 Measurement cell.

In general, the measurement cell is a glass vessel with lid and with the relevant openings for the measurement electrode and the feed tube and it shall look like in Figure 1. If the diameters of the measurement electrode and the feed tube for the gases from decomposition of the test portion are sufficiently small, a 300 ml Erlenmeyer flask is a suitable alternative measurement cell.

A recommended procedure for cleaning the cell is given in Annex A.

6.8 Magnetic stirrer, capable of providing gentle agitation within the measurement cell. Only necessary in case using an oil bath.

6.9 Conductance meter, with a conductivity probe constant of 1,0 cm^{-1} to 1,2 cm^{-1}, giving direct readings in µS/cm, and preferably equipped with an automatic temperature compensating device.

The cell constants should be determined by means of a specified standard solution, e.g. a conductivity standard of 100 µS/cm, because in general electrodes are not always stable.

NOTE Graphite electrodes have been shown to operate in a more trouble-free manner than platinized platinum electrodes.

6.10 Stopclock, or other suitable timing device, if not included in the recorder.

6.11 Flowmeter, for example a rotameter, or other suitable device capable of measuring a gas flow-rate within the range (7,2 ± 0,1) l/h.

7 Preparation of test samples

7.1 General

The measured stability times t_s depend to some extent on the surface area of the prepared test portions as well as on their thermal history. Any cutting or grinding of a material necessary to produce the test portions shall be conducted in a uniform manner, avoiding heating of the material.

Cryogenic grinding is recommended.

7.2 PVC plastisols

Spread these materials on glass plates and gel them in an oven at an agreed temperature so that sheets 0,5 mm thick are formed. Cut these sheets into squares approximately 2 mm on a side.

7.3 PVC pellets, extrudates, mouldings, thick sheet, etc.

Cut or grind these materials so that more than 80 % of the material passes through a 2 mm sieve in accordance with R 20/3 series, specified in ISO 565, and an amount adequate to prepare the test portions is retained on a 1,4 mm sieve.

7.4 PVC film and sheet

Cut these materials into squares or cubes having sides no longer than 2 mm.

7.5 PVC coatings

Separate these materials from the substrate and then treat as in 7.2 or 7.3.

7.6 Cable and conductor insulation or sheating

Cut thin slivers of the dimensions indicated in 7.2.

8 Number of tests

Conduct at least two determinations on each sample.

9 Temperatures for dehydrochlorination

The test temperatures are preferably:

— 200 °C for unplasticized compounds and products;

- 200 °C for compounds and products for cable insulation and sheathing;
- 180 °C to 200 °C for plasticized compounds and products, depending on their stabilization.

10 Test procedure

10.1 Preparation of test portion

When working with Cell A, (2 ± 0,01) g of the test sample are weighted in the dehydrochlorination cell and 180 ml of demineralised water in the measuring cell are used.

When working with Cell B, (0,5 ± 0,01) g of the test sample are weighted in the dehydrochlorination cell and 60 ml of demineralised water in the measuring cell are used.

Introduce this test portion into the chosen dehydrochlorination cell (6.1) and connect the cell to the remainder of the apparatus, taking particular care to ensure that all joints are tightly closed and, where appropriate, that all ground glass joints are sealed with a suitable stopcock grease.

10.2 Preliminary operations

Heat the heating bath/heating block (6.4) to the agreed test temperature. Start the flow of nitrogen through the dehydrochlorination cell, adjust to a flow-rate of (7,2 ± 0,1) l/h and flush the cell for about 5 min to eliminate air. During this period, the dehydrochlorination cell shall not be heated.

If cell B is used, a temperature adjustment shall be made beforehand. This temperature adjustment is necessary because the nitrogen stream is not preheated and cools the sample accordingly.

This temperature adjustment compensates for this effect.

(5,0 ± 0,1) g of silicone oil is weighed into cell B, then the nitrogen tube and the thermometer (6.5) are inserted. The gas flow is set to (7,2 ± 0,1) l/h and the cell is inserted into the heating bath or heating block. The temperature of the heating bath or heating block is now gradually increased until the temperature at the thermometer indicates the desired test temperature. The temperature difference determined in this way shall be subtracted from the displayed temperature of the heating bath or heating block to obtain the correct sample temperature.

10.3 Special precautions when using dehydrochlorination cell A

When using cell A (6.1.1), all spirals of the preheating tube shall be completely immersed in the heating bath. The end of the gas-outlet tube shall be positioned about 5 mm from the bottom of the measurement cell.

10.4 Preparation of the measurement cell

Unless specified otherwise for the particular instrument used, introduce 180 ml of demineralized water as specified in 5.2 if cell A is used, or 60 ml if cell B is used and start the stirrer if one is available and mixing with the nitrogen flow is not sufficient. Allow the measurement cell to reach thermal equilibrium in the range (23 ± 2) °C and maintain it at that temperature.

Insert the conductivity probe into the demineralized water to the depth recommended by its manufacturer.

It may be necessary to conduct the test in a temperature-controlled room. Alternatively, it may be necessary to surround the measuring cell with a water bath in order to maintain the temperature at (23 ± 2) °C, or a narrower interval if required by the supplier of the conductance meter.

10.5 Decomposition of the test portion

Immerse the dehydrochlorination cell rapidly in the heating bath/heating block and immediately place the end of the connecting tube into the demineralized water contained in the measurement cell.

Start the stopclock at the moment when the tube is immersed in the demineralized water and continue the test at least until a change of 50 µS/cm is observed in the conductivity of the water.

11 Expression of results

Record the stability time t_s, in minutes, as the time taken to achieve a 50 µS/cm change in conductivity.

12 Test report

The test report shall include at least the following information:

a) a reference to this document, including the year of publication, i.e. ISO 182-3:2023;

b) the nature, form and designation of the PVC compound or product tested;

c) if appropriate, the PVC compound or product manufacturer's name, where sampled and the degree of comminution of the test portion;

d) type of dehydrochlorination cell used (cell A, cell B or other);

e) the test temperature;

f) the stability time t_s, in minutes, to the nearest 0,5 min (include individual values and the arithmetic mean);

g) any deviation from the procedure specified in this document;

h) any unusual features observed;

i) if required, the curve of conductivity plotted against time;

j) the date of the test.

13 Precision

13.1 General

In a two-year period (1989 and 1990), interlaboratory tests were carried out to evaluate the precision of the method described in this document, in comparison with the pH-meter method[1]. Three different PVC compounds were tested:

1	Unplasticized PVC	compound for pipes;
2	Plasticized PVC	compound for cable sheathing;
3	VC/VAC (copolymer of vinyl chloride and vinyl acetate)	compound for phonograph of records.

The tests were conducted by three laboratories (one laboratory twice, in different years):

A	Italy I	(1989);
A'	Italy I	(1990);
B	Italy II	(1989);
C	Belgium	(1989);
D	France	(1990).

All samples were supplied by laboratory A (Italy I). All tests were conducted with dehydrochlorination cell A at 200 °C. The data shown in Table 1 were obtained.

The results of an interlaboratory test using a metal block heating bath are shown in Annex C.

13.2 Repeatability

By application of the statistical method according to ISO 5725-2[3] to the data obtained for sample 1, the following value of the repeatability r was obtained (see Annex B):

$$r = 6{,}64$$

The calculation was not made for samples 2 and 3, owing to insufficient data. However, by comparison of the standard deviations, the repeatability appears to be of the same order of magnitude.

13.3 Reproducibility

From the same table of results, by the appropriate calculation, the following values for the reproducibility R and the overall mean stability time m were obtained (see Annex B):

$$R = r = 6{,}64$$

$$m = 78{,}12\ \text{min}$$

13.4 Comparison with the pH-meter method (ISO 182-2)

From the data shown in the right-hand columns of Table 1, the results of the statistical calculation are:

$$m = 78{,}46\ \text{min}$$

$$r = 3{,}77$$

$$R = 4{,}15$$

which is comparable to those values obtained by the conductometric method.

13.5 Factors affecting the stability time

13.5.1 From tests conducted by laboratory C (Belgium), the principal factors affecting the stability time t_s appear to be those described in 13.5.2 and 13.5.3.

13.5.2 The size of the cut or ground particles of the test portion, as pointed out in 7.2.

On test portions of the same sample of unplasticized PVC having different particle sizes, the values shown in Table 2 were obtained.

13.5.3 The decomposition temperature.

On two samples each of two different compounds of unplasticized PVC, values shown in Table 3 were obtained.

Table 1 — Repeat determinations of stability time for three PVC products over a two-year period

Year	Sample	Type[a]	Laboratory	Test temperature	Stability time *t* min									
					Conductometric method (ISO 182-3)					pH-meter method (ISO 182-2)				
				°C	Number of tests	Range min	Mean min	Standard deviation *s* min	Overall mean min	Number of tests	Range min	Mean min	Standard deviation *s* min	Overall mean min
1989	1	PVC-U	A	200	2	76 to 77	76,5	0,5	78,125	2	78 to 81	79,5	1,5	78,46
1989	1	PVC-U	B	200	2	76 to 82	79	3,0		2	77 to 77	77	0	
1989	1	PVC-U	C	200	2	79 to 81	80	1,0						
1990	1	PVC-U	A'	200	2	76 to 78	77	1,0						
1990	1	PVC-U	D	200	—	—	—	—	—	5	77,4 to 80,4	78,9	2,5	
1989	2	PVC-P	A	200	—	—	—	—	—	2	185 to 208	196	11,5	
1989	2	PVC-P	B	200	2	185 to 189	187	2,0						
1989	2	PVC-P	C	200	2		183							
1990	3	VC/VAC	A'	200	2	17 to 17	17	0						
1990	3	VC/VAC	D	200						5	17,34 to 19,54			

[a] PVC-U = unplasticized PVC, PVC-P = plasticized PVC, VC/VAC = copolymer of vinyl chloride and vinyl acetate.

Table 2 — Unplasticized PVC, θ = 200 °C

Sieve aperture mm	t_s mm
1,05	105
1,45 to 1,05	106
2,01 to 1,45	112
2,92 to 2,01	122 to 131

Table 3 — Unplasticized PVC

Sample	θ °C	t_s min
1	200	108
	199,2	117
2	200	75
	199,2	84

Results show a Δt_s of about 10 min for a $\Delta\theta$ of 0,8 °C.

It is very important, therefore, to maintain the temperature of the heating bath/heating block with an accuracy of at least ±0,1 °C as specified in 6.5.

13.6 Conclusions

Under the same conditions of decomposition of the test portion, the measurements obtained by the pH-meter and the conductance meter, if properly calibrated, are equivalent.

Annex A
(informative)

Cleaning of the apparatus

A.1 Dehydrochlorination cell A

After removing the residual charred PVC, soak the cell in a bath of tetrahydrofuran for several hours; then remove the cell, dry it and immerse it in a chromic acid mixture (solution of 5 g of potassium dichromate in 1 l of concentrated sulfuric acid). Finally, rinse the cell in double-distilled water.

At the end of the treatment, check the cell to ensure that all traces of decomposed PVC have been removed.

The use of chromic acid/sulfuric acid mixtures is not permitted in certain laboratories. In such circumstances, an appropriate alternative should be used.

A.2 Sintered glass discs

Soak the used sintered glass discs (see 6.2) in a bath of tetrahydrofuran for six days. Dry them and then immerse them in chromic acid mixture (see A.1) for an additional three days. Rinse with double-distilled water and dry in an oven.

Discs which remain dirty after this treatment should be discarded.

A.3 Glass connecting tube

Wash the tube with acetone, ethanol or diethyl ether and dry in air.

A.4 Measurement cell

Wash the measurement cell with chromic acid mixture (see A.1) and rinse it in double-distilled water.

Annex B
(informative)

Calculation of repeatability and reproducibility — Conductometric and pH-meter methods

B.1 Calculation of *r* and *R* for unplasticized PVC — Conductometric method

The calculation of *r* and *R* was made according to ISO 5725-2, with one sample and two tests by each participating laboratory. The results obtained are given in Table B.1.

Table B.1 — Precision of the conductometric method for unplasticized PVC

Laboratory	Unplasticized PVC sample parameters					
	$\bar{y}_i$ min	s_i	n_i	w_i	$\bar{y}_i^2$	w_i^2
A	76,5	0,5	2	1	5 852	1
A'	77	1,0	2	2	5 929	4
B	79	3,0	2	6	6 241	36
C	80	1,0	2	2	6 400	4
$p = 4$	$\sum \bar{y}_i = 312{,}5$				$\sum \bar{y}_i^2 = 24\,422$	$\sum w_i^2 = 45$

$\bar{y}_i$ = mean value of t_s, in minutes

s_i = *standard deviation*

$w_i = y_1 - y_2$

n_i = *number of tests*

p = number of participating laboratories

$T_1 = \sum y_i = 312{,}5$

$T_2 = \sum \bar{y}_i^2 = 24\,422$

$T_3 = \sum w_i = 45$

$$s_r^2 = \frac{T_3}{2p} = \frac{45}{8} = 5{,}625$$

$$s_L^2 = \frac{pT_2 - T_1^2}{p(p-1)} - \frac{s_r^2}{2}$$

$$s_L^2 = 2{,}666 - 2{,}812 < 0$$

$$r = 2{,}8\sqrt{s_r^2} = 6{,}64$$

$$R = r = 6{,}64$$

$$m = 78{,}125 \text{ min}$$

B.2 Calculation of r and R for unplasticized PVC — pH-meter method

The calculation of *r* and *R* was made according to ISO 5725-2, with one sample and different numbers of tests ($n > 2$) by each participating laboratory. The results obtained are given in Table B.2.