INTERNATIONAL
STANDARD

ISO
182-3

First edition
1993-04-01

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 à base d'homopolymères et 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
ISO 182-3:1993(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 182-3 was prepared by Technical Committee ISO/TC 61, *Plastics*, Sub-Committee SC 6, *Ageing, chemical and environmental resistance.*

Together with the three other parts of ISO 182, it cancels and replaces ISO Recommendation R 182:1970, of which the four parts of ISO 182 constitute a technical revision.

ISO 182 consists of the following parts, under the general title *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 1: Congo red method*

— *Part 2: pH method*

— *Part 3: Conductometric method*

— *Part 4: Potentiometric method*

Annexes A, B and C of this part of ISO 182 are for information only.

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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 part of ISO 182 may involve hazardous materials, operations and equipment. This part of ISO 182 does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this part of ISO 182 to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

1.1 This part of ISO 182 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 The method may be used as a quality control test during manufacture and conversion of PVC compounds. It may also be used for the characterization of PVC compounds and products, especially with regard to the effectiveness of their heat-stabilizing systems.

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

1.3 The method is recommended for compounded PVC materials and products only, although it can be used for polymers in powder form under appropriate conditions, to be agreed upon between the interested parties. The method is not recommended for PVC compounds in the form of dry blends, since such materials may not be sufficiently homogeneous.

1.4 PVC compounds and products may evolve other decomposition products, in addition to hydrogen chloride, at elevated temperatures. A limited number of these decomposition products may affect the conductivity of water when they are absorbed into it. Compensation for this effect is not within the scope of this part of ISO 182, and therefore care is necessary in attempting to compare results for dissimilar compounds and products. In this case a method suitable for the determination of chloride ion (Cl^-) in the absorbing solution shall be used (see ISO 182-4).

1.5 The method may 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 standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 182. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 182 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 182-4:1993, *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 4: Potentiometric method.*

ISO 565:1990, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings.*

ISO 4793:1980, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series.*

3 Definition

For the purposes of this part of ISO 182, the following definition applies.

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 part of ISO 182.

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 5.3) for 1 h at a rate of 7,2 l/h ± 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 Hydrochloric acid, aqueous solution, $c(\text{HCl}) = 0{,}1$ mol/l.

5.3 Demineralized water, with a pH of 4,0 ± 0,1 and a conductivity not greater than 40 µS/cm, adjusted by the addition of 0,1 mol/l hydrochloric acid.

6 Apparatus

The general arrangement of the apparatus is shown in figure 1. The figure shows a re-usable dehydrochlorination cell A. This cell may be replaced by a disposable cell B.

6.1 Dehydrochlorination cells.

6.1.1 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.

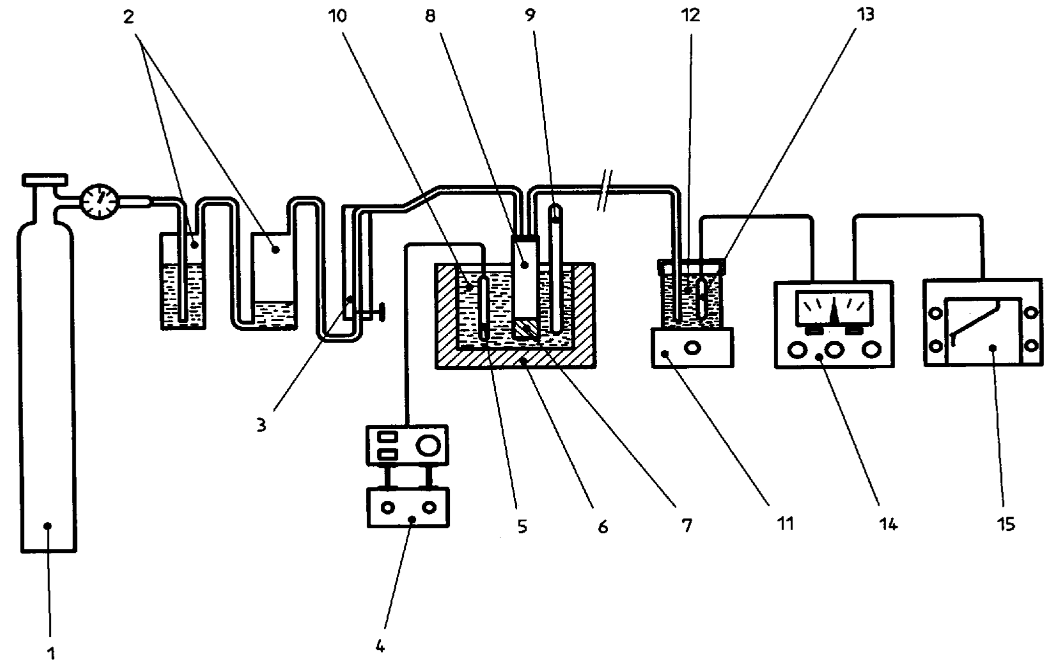
6.1.2 Cell B (disposable), with shape and dimensions as shown in figure 3.

NOTE 1 Other types of cell may 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, 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.



1 N_2 cylinder
2 Purification train
3 Ball flowmeter
4 Electronic temperature controller (scale division 0,1 °C)
5 Temperature sensor
6 Heating bath
7 PVC test portion
8 Dehydrochlorination cell
9 Thermometer (scale division 0,1 °C)
10 Silicone oil
11 Magnetic stirrer
12 Absorbing solution
13 Measuring electrode(s)
14 Conductance meter
15 Recorder

Figure 1 — General arrangement of apparatus

Dimensions in millimetres

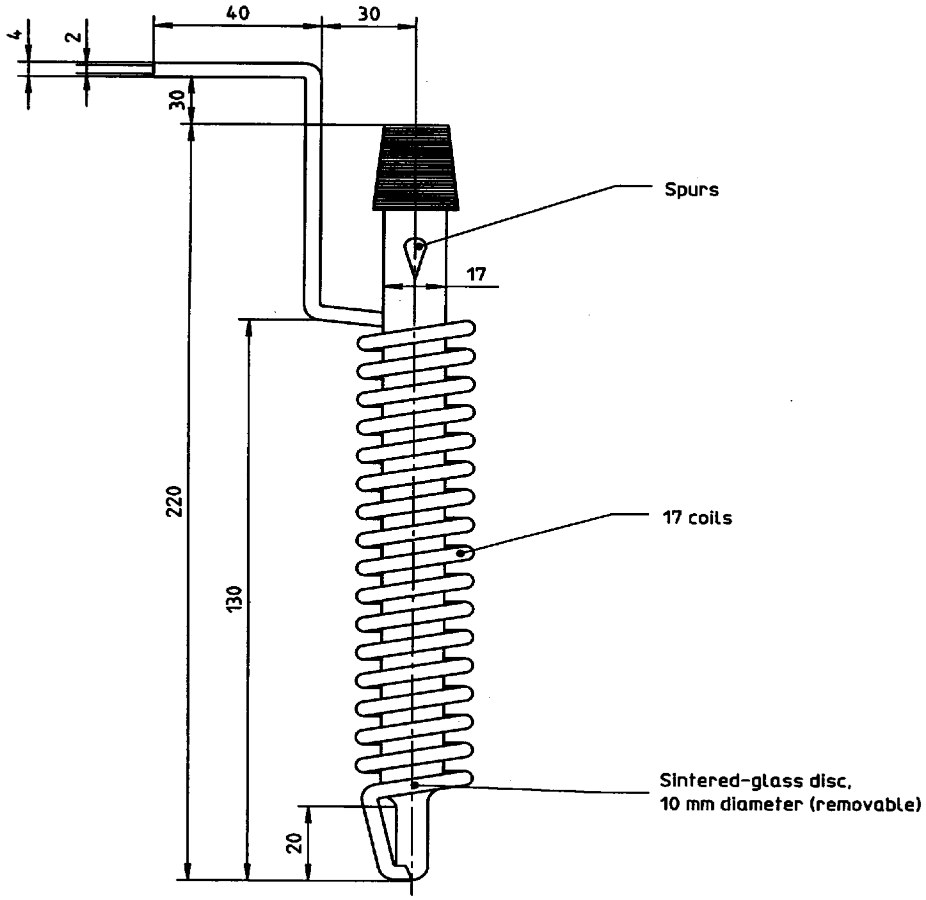


Figure 2 — Cell A (re-usable) for dehydrochlorination of PVC samples

Dimensions in millimetres

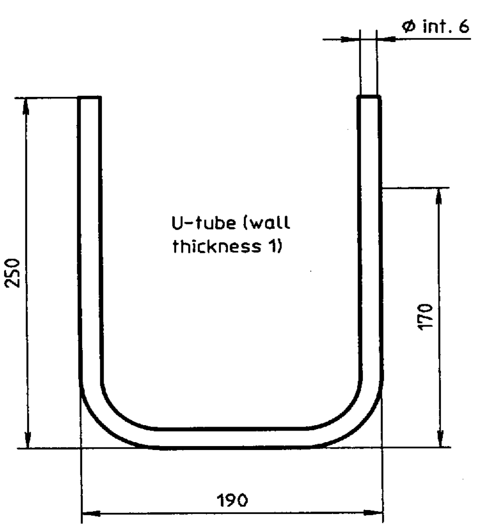


Figure 3 — Cell B (disposable) for dehydrochlorination of PVC samples

6.3 Glass connection tube, for use with cell A, 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.

6.4 Expansion joints and cell connections, for use with cell B. Cell B is connected to the apparatus through flexible polytetrafluoroethylene (PTFE) and silicone rubber tubes. Special joints allow for thermal expansion. The complete joint arrangement is shown in figure 5.

6.5 Oil bath, with a capacity of at least 10 l. The bath 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 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.

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

6.7 Balance, with a scale division of 1 mg.

6.8 Measurement cell.

A suitable measurement cell is shown in figure 6. 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.

6.9 Magnetic stirrer, capable of providing gentle agitation within the measurement cell.

6.10 Conductance meter, with a conductivity probe constant of 1 cm^{-1}, giving direct readings in µS/cm, and preferably equipped with an automatic temperature compensating device and an output for a chart recorder.

NOTE 2 Graphite electrodes have been shown to operate in a more trouble-free manner than platinized platinum electrodes.

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

6.12 Flowmeter, for example a rotameter, or other suitable device capable of measuring a gas flow-rate within the range 120 cm^3/min ± 4 cm^3/min.

7 Preparation of test samples

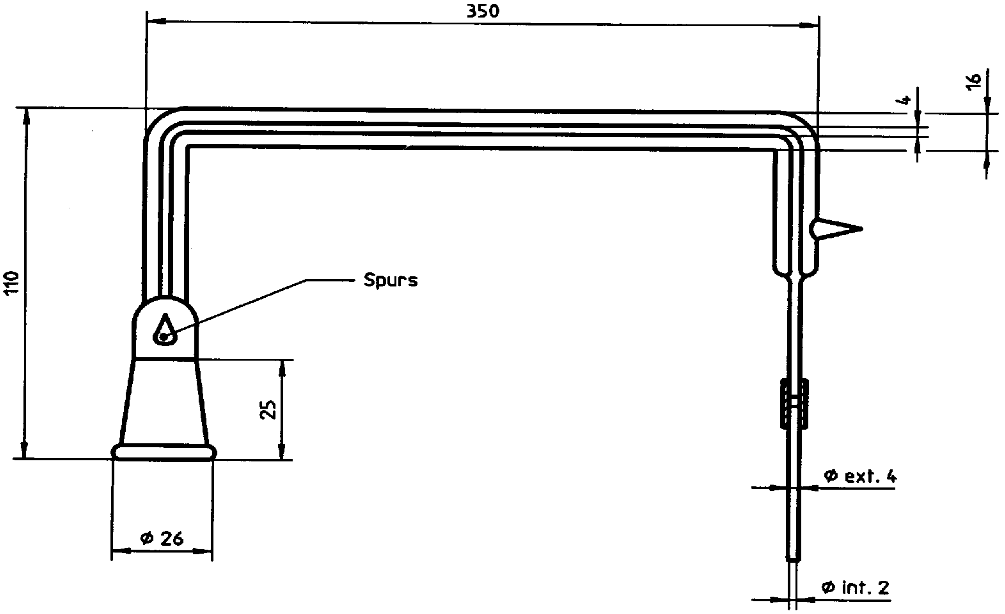
The measured stability times t_s depend to some extent on the surface area of the prepared test portions as well as on their thermal history. Any cutting or grinding of a material necessary to produce the test portions shall be conducted in a uniform manner, avoiding heating of the material.

NOTE 3 Cryogenic grinding is recommended.

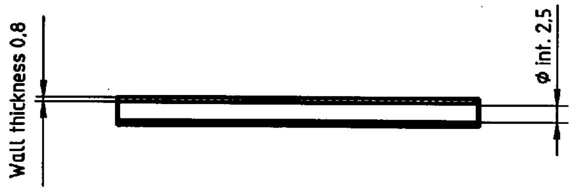
7.1 PVC plastisols

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.

Dimensions in millimetres



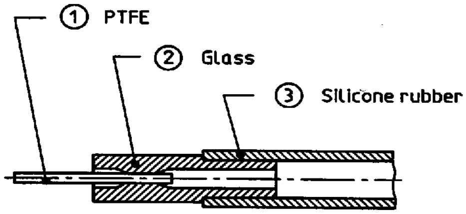
a) Glass tube for use with cell A



b) PTFE tubing for use with cell B

Figure 4 — Tubes for connecting the dehydrochlorination cell to the measurement cell

Dimensions in millimetres



1 PTFE tube: Φ ext. 4,1
Φ int. 2,5
2 Glass tube: Φ ext. 8
Φ int. 6
3 Silicone rubber tube: Φ ext. 12
Φ int. 6

Figure 5 — Expansion joint for connection on each side of cell B

Dimensions in millimetres

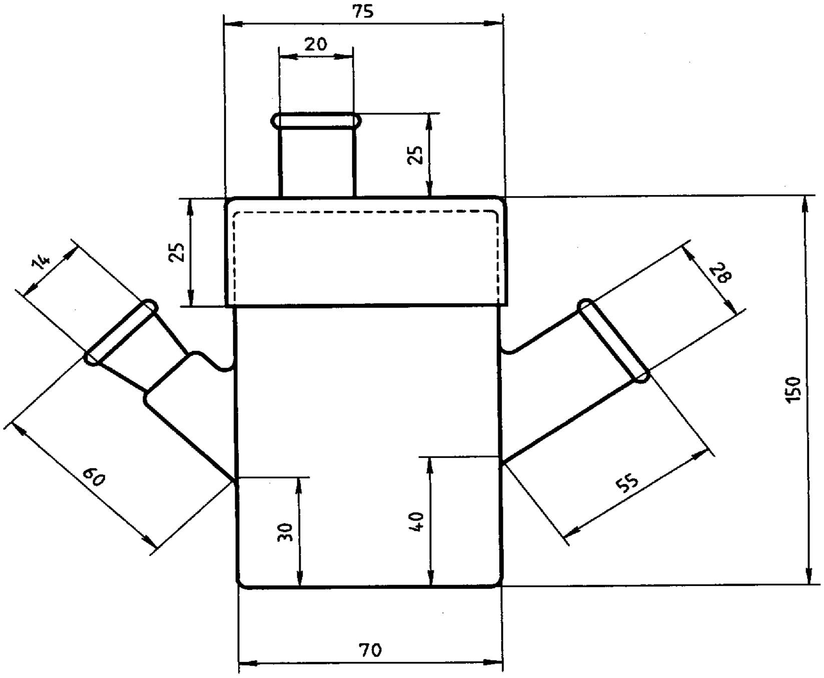


Figure 6 — Example of a suitable measurement cell

7.2 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 (ISO 565, R 20/3 series) and an amount adequate to prepare the test portions is retained on a 1,4 mm sieve.

7.3 PVC film and sheet

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

7.4 PVC coatings

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

7.5 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

Weigh, to the nearest 0,01 g, 2 g of the test sample, prepared in accordance with the appropriate part of clause 7.

Introduce this test portion into the chosen dehydrochlorination cell (6.1) and connect the cell to the remainder of the apparatus (6.3 or 6.4), 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 oil bath (6.5) to the agreed test temperature. Start the flow of nitrogen through the dehydrochlorination cell, adjust to a flow-rate of 120 cm^3/min ± 4 cm^3/min and flush the cell for about 5 min to eliminate air. During this period, the dehydrochlorination cell shall not be heated. The nitrogen flowing through the cell shall be allowed to escape to the atmosphere without passing through the absorbing liquid contained in the measurement cell (6.8).

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 oil 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

Introduce 180 ml of demineralized water as specified in 5.3 into the measurement cell and start the stirrer. Allow the measurement cell to reach thermal equilibrium in the range 23 °C ± 2 °C and maintain it at that temperature.

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

NOTE 4 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 °C ± 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 oil bath and immediately place the end of the connecting tube into the demineralized water contained in the measurement cell.

Start the stopclock and/or the recorder 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 Precision

In a two-year period (1989 and 1990), international round-robin tests were carried out to evaluate the precision of the method described in this part of ISO 182, in comparison with the pH-meter method (ISO 182-2[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 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.

12.1 Repeatability

By application of the statistical method according to ISO 5725[2] 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.

12.2 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):

$R = r = 6,64$
$m = 78,12$ min

12.3 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:

$m = 78,46$ min
$r = 3,77$
$R = 4,15$

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

12.4 Factors affecting the stability time

From tests conducted by laboratory C (Belgium), the principal factors affecting the stability time t_s appear to be those described in 12.4.1 and 12.4.2.

12.4.1 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.

12.4.2 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	Type1)	Laboratory	Test temperature °C	Stability time, t_s, min									
					Conductometric method (ISO 182-3)					pH-meter method (ISO 182-2)				
					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			

1) PVC-U = unplasticized PVC, PVC-P = plasticized PVC, VC/VAC = copolymer of vinyl chloride and vinyl acetate.

Table 2 — Unplasticized PVC, $\theta = 200$ °C

Sieve aperture mm	t_s min
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 oil bath with an accuracy of at least ± 0,1 °C as specified in 6.5.

12.5 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.

13 Test report

The test report shall include the following information:

a) reference to this part of ISO 182;

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 part of ISO 182;

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

i) the date of the test.

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.

NOTE 5 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, 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
$p = 4$	$\Sigma\bar{y}_i = 312{,}5$				$\Sigma\bar{y}_i^2 = 24\ 422$	$\Sigma w_i^2 = 45$

$\bar{y}_i$ = 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

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

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

$T_3 = \Sigma w_i = 45$

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

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

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

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

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

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

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, with one sample and different numbers of tests ($n > 2$) by each participating laboratory. The results obtained are given in table B.2.

Table B.2 — Precision of the pH-meter method for unplasticized PVC

Laboratory	**Unplasticized PVC sample parameters**							
	$\bar{y}_i$ min	Range min	s_i min	n_i	$\bar{y}_i n_i$	$\bar{y}_i^2$	$\bar{y}_i^2 n_i$	s_i^2
A	79,5	78 to 81	1,5	2	159,0	6 320	12 640	2,25
B	77	77 to 77	0	2	154,0	5 929	11 840	0
C	78,5	77,4 to 80,4	1,4	5	394,5	6 225	31 125	1,96
$p = 3$				$\sum n_i^2 = 33$	$\sum \bar{y}_i n_i = 707{,}5$		$\sum \bar{y}_i^2 n_i = 55\ 623$	

$T_1 = \sum \bar{y}_i n_i = 707{,}5$

$T_2 = \sum \bar{y}_i^2 n_i = 55\ 623$

$T_3 = \sum n_i = 9$

$T_4 = \sum n_i^2 = 33$

$T_5 = \sum (n_i - 1)\, s_i^2 = 2{,}25 + 0 + 4(1{,}96) = 10{,}9$

$s_r^2 = \frac{T_5}{T_3 - p} = \frac{10{,}9}{9 - 3} = 1{,}816\ 6$

$r = 2{,}8 \sqrt{s_r^2} = 3{,}773\ 9$

$m = \frac{T_1}{T_3} = \frac{707{,}5}{9} = 78{,}61$ min

$s_L^2 = \left[\frac{T_2 T_3 - T_1^2}{T_3 (p - 1)} - s_r^2 \right] \left[\frac{T_3 (p - 1)}{T_3^2 - T_4} \right]$

$s_R^2 = s_L^2 + s_r^2 = 2{,}197\ 8$

$r = 2{,}8 \sqrt{2{,}197\ 8} = 4{,}15$

$R = 4{,}15$

$m = 78{,}61$ min

$r = 3{,}77$

Annex C
(informative)

Bibliography

[1] ISO 182-2:1990, *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 2: pH method.*

[2] ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

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