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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 1159

PLASTICS

DETERMINATION OF VINYL ACETATE IN VINYL CHLORIDE-VINYL ACETATE COPOLYMERS

1st EDITION

January 1970

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BRIEF HISTORY

The ISO Recommendation R 1159, *Plastics – Determination of vinyl acetate in vinyl chloride-vinyl acetate copolymers,* was drawn up by Technical Committee ISO/TC 61, *Plastics,* the Secretariat of which is held by the American National Standards Institute (ANSI).

Work on this question led to the adoption of a Draft ISO Recommendation.

In April 1965, this Draft ISO Recommendation (No. 827) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

- Argentina
- Australia
- Austria
- Belgium
- Brazil
- Canada
- Chile
- Czechoslovakia
- Finland
- France
- Germany
- Greece
- Hungary
- India
- Ireland
- Italy
- Japan
- Netherlands
- New Zealand
- Poland
- Romania
- Sweden
- Switzerland
- Turkey
- U.A.R.
- United Kingdom
- U.S.A.
- U.S.S.R.
- Yugoslavia

No Member Body opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in January 1970, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 1159 January 1970

PLASTICS

DETERMINATION OF VINYL ACETATE IN VINYL CHLORIDE-VINYL ACETATE COPOLYMERS

1. SCOPE

This ISO Recommendation describes a method for determining the percentage of vinyl acetate in vinyl chloride-vinyl acetate copolymers.

2. PRINCIPLE

Dissolution of the sample in purified tetrahydrofuran, and hydrolysis of the acetate groups by potassium hydroxide in alcoholic solution.

Back titration of excess potassium hydroxide with sulphuric acid, using thymol blue as indicator.

Argentometric titration of hydrogen chloride liberated during hydrolysis.

3. REAGENTS

3.1 *Potassium hydroxide,* alcoholic solution approximately 0.5 N.

Dissolve 33 g of solid potassium hydroxide (KOH) in 500 ml of ethanol. Make up to 1000 ml, allow to stand overnight and decant the clear portion of the solution.

3.2 *Potassium hydroxide,* alcoholic solution approximately 0.2 N.

Prepare the solution in the same way as in clause 3.1, but using only 13.5 g of solid potassium hydroxide.

3.3 *Sulphuric acid,* 0.1 N standard volumetric solution.

3.4 *Sulphuric acid,* 0.05 N standard volumetric solution.

3.5 *Silver nitrate,* 0.1 N standard volumetric solution.

3.6 *Silver nitrate,* 0.05 N standard volumetric solution.

3.7 *Pure tetrahydrofuran,* further purified as in clause 7.2.

3.8 *Ethanol-water mixture* (1 : 1 by volume), neutralized to thymol blue, prepared from freshly boiled distilled water.

3.9 *Thymol blue* indicator solution. Dissolve 0.1 g of thymol blue in 100 ml of ethanol.

3.10 *Potassium hydroxide,* solid pellets.

3.11 *Potassium chromate,* 50 g/l solution.

4. APPARATUS

4.1 *Burette,* 25 ml, for acidimetry.

4.2 *Burette,* 10 ml, for argentometry.

4.3 *Electromagnetic stirrer.*

4.4 *Thermostated water bath,* to maintain a temperature of 30 ± 0.5 °C (see clause 7.1).

4.5 *Analytical balance,* to weigh to an accuracy of ± 0.0001 g.

4.6 *Volumetric flask,* 100 ml capacity, with ground glass stopper.

4.7 *Pipettes,* of 1, 5, 20 and 30 ml capacity.

5. TEST PROCEDURE

5.1 The time necessary for a quantitative saponification of vinyl acetate groups depends on the vinyl acetate content, the strength of the alcoholic potassium hydroxide solution used, the temperature and the amount of sample. Consequently, choose the appropriate procedure as indicated in the Table below, taking into account the assumed vinyl acetate content of the copolymer and the temperature at which saponification will take place.

TABLE – **Conditions for hydrolysis of vinyl chloride-vinyl acetate copolymers**

Assumed content of vinyl acetate	Mass of sample	Normality of alcoholic KOH solution	Normality of H_2SO_4 and $AgNO_3$ solutions	Time of hydrolysis (hours)		
				using a bath (4.4) at 30 ± 0.5 °C	at room temperature :	
%	g				20 to 25 °C	25 to 30 °C
0 to 5	0.4 to 0.5	0.2	0.05	2	3.5	2.5
5 to 10	0.18 to 0.2	0.2	0.05	2	3.5	2.5
10 to 30	0.18 to 0.2	0.5	0.1	1.5	2.5	2
30 to 60	0.18 to 0.2	0.5	0.1	2	3.5	2.5
60 and above	0.13 to 0.15	0.5	0.1	3	6	4

5.2 Accurately weigh out the quantity of dry copolymer indicated in the Table into the flask (4.6) (see clause 7.3) and add 20 ml of tetrahydrofuran (3.7) by means of a pipette. The dissolution of the copolymer is facilitated by magnetic stirring. After completed dissolution, immerse the flask in the thermostated bath at 30 °C and leave it for 10 minutes; add 5 ml of alcoholic potassium hydroxide solution of the strength indicated in the Table and thoroughly mix the contents of the flask by a gentle swirling motion. In case partial precipitation of the copolymer occurs at this stage, it must be redissolved by stirring. Allow hydrolysis to take place for the period of time prescribed in the Table.

5.3 After hydrolysis, add 30 ml of ethanol-water mixture (3.8) dropwise, while stirring. This addition causes the copolymer to precipitate with a fine grain. Add 1 ml of thymol blue solution (3.9). While stirring, titrate the excess potassium hydroxide with sulphuric acid solution of the strength indicated in the Table until the deep green colour changes to orange. Under the same test conditions, carry out a blank test in the absence of copolymer, titrating from blue to yellow.

5.4 After completed acidimetric titration, add 1 ml of sulphuric acid solution (3.3) and titrate the mixture potentiometrically with silver nitrate solution of the strength indicated in the Table, stirring continuously. The volume of silver nitrate solution used is equivalent to the hydrogen chloride split off during hydrolysis of the copolymer.(See clause 7.4.)

6. CALCULATION AND EXPRESSION OF RESULTS

6.1 When using 0.1 N sulphuric acid and silver nitrate solutions, the percentage vinyl acetate content is calculated as follows :

$$\text{percentage vinyl acetate} = \frac{0.8609\,(V_1 - V_2 - V_3)}{m}$$

6.2 When using 0.05 N sulphuric acid and silver nitrate solutions, the percentage vinyl acetate content is calculated as follows :

$$\text{percentage vinyl acetate} = \frac{0.4304\,(V_1 - V_2 - V_3)}{m}$$

where

V_1 is the volume, in millilitres, of sulphuric acid used in the blank test;

V_2 is the volume, in millilitres, of sulphuric acid used in the determination;

V_3 is the volume, in millilitres, of silver nitrate solution used;

m is the mass, in grammes, of copolymer sample.

6.3 Carry out two determinations. If they differ by more than 0.4 % of the vinyl acetate content the test should be repeated. Report the average of two acceptable determinations.

7. NOTES ON PROCEDURE

7.1 If no thermostat is available it is permissible to proceed at room temperature. The appropriate conditions are given in the Table, page 4.

7.2 *Purification of tetrahydrofuran*

Tetrahydrofuran often contains matter reacting with potassium hydroxide. Using solvent containing such impurities leads to results higher than theoretical.

Purification is carried out as follows : introduce 1 litre of tetrahydrofuran and 50 g of solid potassium hydroxide into a two-neck 2 litre distillation flask (see Figure, page 7). Through one of the necks introduce nitrogen to the bottom of the flask. (Nitrogen produces an inert atmosphere and stirs the contents of the flask.) Connect the second neck to the reflux condenser (b) and liquid seal (c and d). Pass nitrogen at a rate of 5 litres per hour for an initial period of 15 minutes, then adjust to a slow rate (one bubble per second). Now heat the flask in a water bath and reflux for approximately 5 hours. After this time, remove the condenser and distil off the tetrahydrofuran over the potassium hydroxide, still in a slow stream (one bubble per second) of nitrogen. Discard the first 50 ml of distillate, then collect the solvent and store in a brown bottle with a ground glass stopper.

The solvent may be checked for purity as follows : pipette 10 ml of the tetrahydrofuran into a 100 ml glass-stoppered flask and 10 ml of boiled distilled water into a second flask. Add 5 ml of 0.5 N alcoholic potassium hydroxide solution (3.1) to each of the two flasks, stopper them and allow to stand for 1 hour. Then dilute the contents with about 30 ml of ethanol-water mixture (3.8), add 1 ml of thymol blue solution (3.9) and titrate the mixture with 0.1 N sulphuric acid solution until a yellow colour appears. The two volumes of 0.1 N sulphuric acid solution used must not differ by more than 0.1 ml.

It is not advisable to store purified tetrahydrofuran for more than a week. If possible freshly distilled solvent should be used. Tetrahydrofuran purified as above but stored for more than a week needs to be purified only by distillation over solid potassium hydroxide in a slow stream of nitrogen.

Nitrogen used in this work should not contain more than 0.1 % (V/V) of oxygen.

7.3 When analysing an unknown sample, carry out a preliminary test under conditions valid for a copolymer containing 10 to 30 % of vinyl acetate.

7.4 The potentiometric titration may be replaced by a slightly less accurate visual titration by Mohr's method. In this case the solution, without being acidified, is filtered on a sintered glass filter. The precipitate and filter are washed until the reaction with silver nitrate is negative. If the solution to be titrated (which is yellow) turns green on the addition of 1 ml of the potassium chromate (3.11) used as indicator, this coloration is removed by adding a few drops of 0.1 N sulphuric acid solution until the yellow colour is restored.

When visual titration is employed, the times allowed for hydrolysis are to be maintained carefully, since increased times give rise to dark-coloured solutions presenting difficulties for visual titration. Such dark-coloured solutions, however, can conveniently be titrated potentiometrically.

8. TEST REPORT

The test report should include the following information :

(*a*) the reference of the method used;

(*b*) full identification of the test sample;

(*c*) the results expressed as a percentage of vinyl acetate in the sample;

(*d*) the date of the test.