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Plastics — Homopolymer and copolymer resins of vinyl chloride — Determination of residual vinyl chloride monomer by gas-chromatographic analysis of dry powder

Plastiques — Résines d'homopolymères et de copolymères de chlorure de vinyle — Dosage du chlorure de vinyle résiduel par chromatographie en phase gazeuse sur poudre sèche

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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 24538 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

Plastics — Homopolymer and copolymer resins of vinyl chloride — Determination of residual vinyl chloride monomer by gas-chromatographic analysis of dry powder

SAFETY STATEMENT — Persons using this document should be familiar with normal laboratory practice, if applicable. This document does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any regulatory requirements.

1 Scope

This International Standard specifies a method for the determination of residual vinyl chloride monomer in homopolymer and copolymer resins of vinyl chloride.

The method is based on a static headspace gas-chromatographic technique (i.e. the analysis of the vapour phase in equilibrium with the solid phase at constant temperature) and is suitable for all kinds of homopolymer and copolymer resin. It is done directly on the resin in powder form.

For compounded material, granulate, extrudate, films, etc., use ISO 6401.

NOTE In the case of compounded material, it is necessary to dissolve the sample in a suitable solvent in order to reach complete headspace equilibrium.

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 472, *Plastics — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 apply.

4 Principle

A weighed amount of the sample is sealed into a glass vial. After thermal conditioning for a certain period of time to permit the vinyl chloride monomer (VCM) to equilibrate between the powder and the vapour phase, a gas sample is taken from the headspace, e.g. by automatic injection, into the gas chromatograph. The components are separated on a column and detected using a flame-ionization detector.

5 Apparatus and materials

5.1 Gas chromatograph, fitted either with an automatic static headspace sampler or with facilities for manual sample injection. Chromatographic columns and conditions shall be chosen in such a way that VCM and impurities are separated reliably.

NOTE Examples of suitable columns are described in Annex A.

5.2 Flame-ionization detector (FID).

5.3 Glass vials, for most purposes of capacity 22 ml and 10 ml, with PTFE-faced silicone or butyl rubber septa and aluminium caps. No peaks which could interfere with the VCM determination shall come from the septa.

5.4 Crimping and decapping tools, for sealing and reopening the vials.

5.5 Gastight syringes, of capacity up to 5 ml, depending on the VCM concentration. Syringes are chosen in accordance with the volume analysed.

5.6 Analytical balance, capable of reading to 0,1 mg.

5.7 Data system, or equivalent system (recording potentiometer or integrator), for the acquisition and evaluation of gas-chromatographic data.

5.8 Vinyl chloride gas standards, prepared by consecutive dilution of pure VCM (purity greater than 99,5 % by volume), for calibration purposes.

The use of a commercially available standard in helium, nitrogen or air in a gas cylinder fitted with a capillary outlet or a syringe adapter is recommended.

SAFETY PRECAUTIONS — Vinyl chloride is a flammable gas at ambient temperature. The preparation of calibration samples must therefore be carried out under a well-ventilated hood.

5.9 FID gases and carrier gas.

For low limits of quantification, so-called “zero air” (dry, contaminant-free air) shall be used for the FID and the other gases used shall be of similarly high purity.

6 Sampling

During storage, a concentration gradient may have formed in the PVC being sampled, since the upper layers release residual VCM faster. Cooling of the sample is advisable, but condensation of humidity shall be avoided. To minimize losses of residual monomer, carry out sample preparation as quickly as possible. When exchanging samples between laboratories or when storage is necessary, seal samples in completely filled glass vials.

7 Procedure

Two different procedures are described.

Procedure A is suitable for determining the residual VCM content of homopolymers and copolymers of vinyl chloride down to a level of 0,01 mg/kg. Calibration is performed by adding known amounts of VCM to samples of completely VCM-free PVC.

Procedure B is similar to procedure A except that a smaller amount of test sample is used and calibration is performed using external VCM standards rather than VCM added to PVC.

In procedure A, it is important to perform the calibration using the same type of PVC as that being analysed and using the same mass of PVC as that taken as the test sample. It is also important that equilibrium between the solid and gaseous phases be established under the same conditions during calibration and during actual analysis and that the reduction in the headspace volume caused by the presence of the PVC in the vial be allowed for.

8 Procedure A

8.1 Preparation of test sample and analysis

Before taking the test sample, it is recommended that the vial into which the test sample will be placed be purged with nitrogen in order to remove any possible traces of VCM.

Weigh between 2 g and 4 g of the PVC resin to be analysed (the same amount as used for calibration), to the nearest 0,001 g, into a clean 22 ml vial and seal the vial immediately with a septum and an aluminium cap. Place it in the headspace sampler of the gas chromatograph for 15 min at 120 °C to allow it to come to temperature equilibrium and then start the analysis run. Perform two determinations on each sample.

8.2 Calibration

Calibration is performed by adding known amounts of VCM to samples of totally degassed (i.e. VCM-free) PVC in vials.

In order to ensure that the same equilibrium is established between the solid and gaseous phases during calibration as during the actual analysis and in order to allow for the reduction in headspace volume caused by the presence of the PVC in the vial, use the same mass (for example 2 g) and the same type of PVC for the calibration as for the actual analysis.

NOTE The mass of PVC taken to prepare the calibration standards and the test sample will affect the sensitivity of the method.

To obtain VCM-free PVC, heat the PVC in an oven at 100 °C until the VCM peak given by the degassed PVC is no longer detectable by the chromatograph.

The calibration can be performed using diluted or pure VCM gas.

Take five 22 ml headspace vials, each containing between 2 g and 4 g of VCM-free PVC resin weighed to the nearest 0,001 g. If diluted (for example 0,4 %) VCM gas is used to prepare these calibration standards, transfer, for instance, 0 ml, 0,2 ml, 0,5 ml, 1 ml and 2 ml of the VCM gas to the individual vials using gastight syringes. If pure VCM gas is used, transfer, for instance, 0 µl, 2,5 µl, 5 µl, 10 µl and 20 µl of the VCM gas to the individual vials, again using gastight syringes.

Allow the vials to stand at room temperature for at least half an hour to allow the VCM to equilibrate between the headspace and the PVC. Then place the vials containing the calibration standards in the static headspace sampler (or in a thermostatic bath) and allow to come to temperature equilibrium at 120 °C for 15 min before analysis.

Keep all parameters (time allowed for the vial and contents to come to temperature equilibrium, the equilibrium temperature, the injection parameters, etc.) constant for calibration and sample analysis.

8.3 Calculation

8.3.1 General

Carry out the calculations below to one decimal place.

8.3.2 Evaluation of the calibration run

The calculation of the results can be done by evaluation of the peak area.

8.3.3 Calculation of the mass of VCM calibration standard in each vial

When commercially available diluted VCM gas in a gas cylinder is used for calibration, the concentration of the VCM gas may be given in millilitres per cubic metre. If so, it is first necessary to convert this to milligrams per cubic metre, as follows:

$$c_{w/v} = \frac{c_{v/v} \times M_{\mathrm{VCM}}}{V}$$

where

$c_{w/v}$ is the concentration of the VCM gas in the gas cylinder in milligrams per cubic metre (mg/m^3);

$c_{v/v}$ is the concentration of the VCM gas in the gas cylinder in millilitres per cubic metre (ml/m^3);

M_{VCM} is the molar mass of VCM (= 62,5 g);

V is the molar volume at 20 °C and 1 013 mbar (= 24,1 l).

Then calculate the mass of VCM in each vial using the following equation:

$$c_{\mathrm{St}} = \frac{c_{w/v} \times V_{\mathrm{D}}}{1\,000}$$

where

c_{St} is the mass of VCM in the vial, in milligrams (mg);

$c_{w/v}$ is the concentration of the VCM gas in the gas cylinder in milligrams per cubic metre (mg/m^3);

V_{D} is the volume of VCM gas introduced into the vial, in litres (l).

If the calibration is performed using pure VCM, c_{St} is calculated using the same equations, but using a value for $c_{v/v}$ of 1.

In order to take into account the (non-negligible) added volume of VCM calibration standard, it is necessary to correct the value of c_{St} calculated above, using the following equation:

$$c_{\mathrm{St\,corr}} = c_{\mathrm{St}} \times (V_{\mathrm{v}} - m/\rho)/(V_{\mathrm{v}} + V_{\mathrm{D}} - m/\rho)$$

where

$c_{\mathrm{St\,corr}}$ is the value of c_{St}, in milligrams (mg), corrected for the added volume of VCM calibration standard;

V_{v} is the volume of the vial (= 22 ml);

m is the mass of PVC resin in the vial, in grams (g);

V_{D} is the volume of VCM gas introduced into the vial, in litres (l);

ρ is the density of the PVC resin, in grams per millilitre (g/ml) (generally 1,4 g/ml).

8.3.4 Determination of the response factor

For each calibration standard, calculate the detector response factor, RF, from the following equation:

$$\mathrm{RF} = \frac{c_{\mathrm{St\,corr}}}{A_{\mathrm{St}}}$$

where

$c_{\mathrm{St\,corr}}$ is the value of c_{St}, in milligrams (mg), corrected for the added volume of VCM calibration standard;

A_{St} is the area of the VCM peak obtained in the calibration run.

Calculate the arithmetic mean of the values of RF obtained for each calibration standard.

8.3.5 Calculation of the VCM content in the sample

Calculate the VCM content in the sample from the following equation:

$$c_{\mathrm{sample}} = (A_{\mathrm{s}} \times \mathrm{RF_m}) / m$$

where

c_{sample} is the VCM content in the sample, in milligrams per kilogram of sample (mg/kg PVC);

A_{s} is the area of the VCM peak obtained in the sample run;

$\mathrm{RF_m}$ is the mean response factor calculated in 8.3.4;

m is the mass of the test sample, in kilograms (kg).

9 Procedure B

9.1 Preparation of test sample and analysis

Weigh 0,20 g ± 0,001 g of the resin to be analysed into a clean, preferably 10 ml, vial (if a different size of vial is used, adjust the size of the test sample so that the ratio of the test sample volume to the headspace volume is approximately the same as with a 0,20 g test sample and a 10 ml vial). Seal the vial immediately with a septum and an aluminium cap. Place it in the headspace sampler of the gas chromatograph for 15 min at 120 °C to allow it to come to temperature equilibrium and then start the analysis run. Perform two determinations on each sample.

9.2 Calibration

The determination is based on external-standard calibration using at least two calibrant concentrations. From each calibration run, the detector response factor is determined. The mean response factor is then used to calculate the VCM content of the sample from the sample analysis run.

Flush a gastight syringe with VCM gas from a gas cylinder (a few strokes of the plunger are sufficient to replace all the air in the syringe). Then take e.g. 1 ml of VCM gas smoothly (i.e. in one uninterrupted movement) from an unrestricted laminar flow of gas coming from the capillary outlet of the VCM gas cylinder and transfer it to an empty sealed headspace vial. Repeat with at least one more vial, introducing a different volume of VCM into each vial.