A.9. FLASH-POINT

1. METHOD

1.1. INTRODUCTION

It is useful to have preliminary information on the flammability of the substance before performing this test. The test procedure is applicable to liquid substances whose vapours can be ignited by ignition sources. The test methods listed in this text are only reliable for flash-point ranges which are specified in the individual methods.

The possibility of chemical reactions between the substance and the sample holder should be considered when selecting the method to be used.

1.2. DEFINITIONS AND UNITS

The flash-point is the lowest temperature, corrected to a pressure of 101,325 kPa, at which a liquid evolves vapours, under the conditions defined in the test method, in such an amount that a flammable vapour/air mixture is produced in the test vessel.

Units: Ct = T273,15(t in C and T in K)

1.3. REFERENCE SUBSTANCES

Reference substances do not need to be employed in all cases when investigating a new substance. They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

1.4. PRINCIPLE OF THE METHOD

The substance is placed in a test vessel and heated or cooled to the test temperature according to the procedure described in the individual test method. Ignition trials are carried out in order to ascertain whether or not the sample flashed at the test temperature.

1.5. QUALITY CRITERIA

1.5.1. Repeatability

The repeatability varies according to flash-point range and the test method used; maximum 2 C.

1.5.2. Sensitivity

The sensitivity depends on the test method used.

1.5.3. Specificity

The specificity of some test methods is limited to certain flash-point ranges and subject to substance-related data (e.g. high viscosity).

1.6. DESCRIPTION OF THE METHOD

1.6.1. Preparations

A sample of the test substance is placed in a test apparatus according to 1.6.3.1 and/or 1.6.3.2. For safety, it is recommended that a method utilizing a small sample size, circa 2 cm3, be used for energetic or toxic substances.

1.6.2. Test conditions

The apparatus should, as far as is consistent with safety, be placed in a draught-free position.

1.6.3. Performance of the test

1.6.3.1. Equilibrium method
See ISO 1516, ISO 3680, ISO 1523, ISO 3679.

1.6.3.2. Non-equilibrium method
Abel apparatus:
See BS 2000 part 170, NF M07-011, NF T66-009.
Abel-Pensky apparatus:
See EN 57, DIN 51755 part 1 (for temperatures from 5 to 65 C), DIN 51755 part 2 (for temperatures below 5 C), NF M07-036.
Tag apparatus:
See ASTM D 56.
Pensky-Martens apparatus:
See ISO 2719, EN 11, DIN 51758, ASTM D 93, BS 2000-34, NF M07-019.
Remarks:
When the flash-point, determined by a non-equilibrium method in 1.6.3.2., is found to be 0 ± 2 C, 21 ± 2 C or 55 ± 2 C, it should be confirmed by an equilibrium method using the same apparatus.
Only the methods which can give the temperature of the flash-point may be used for a notification.
To determine the flash-point of viscous liquids (paints, gums and similar) containing solvents, only apparatus and test methods suitable for determining the flash-point of viscous liquids may be used.
See ISO 3679, ISO 368O, ISO 1523, DIN 53213 part 1.

2. DATA

3. REPORTING
The test report shall, if possible, include the following information:
- the precise specification of the substance (identification and impurities),
- the method used should be stated as well as any possible deviations,
- the results and any additional remarks relevant for the interpretation of results.

4. REFERENCES
None.

A.11. FLAMMABILITY (GASES)

1. METHOD

1.1. INTRODUCTION
This method allows a determination of whether gases mixed with air at room temperature (circa 20 C) and atmospheric pressure are flammable and, if so, over what range of concentrations. Mixtures of increasing concentrations of the test gas with air are exposed to an electrical spark and it is observed whether ignition occurs.

1.2. DEFINITION AND UNITS
The range of flammability is the range of concentration between the lower and the upper explosion limits. The lower and the upper explosion limits are those limits of concentration of the flammable gas in admixture with air at which propagation of a flame does not occur.

1.3. REFERENCE SUBSTANCES
Not specified.

1.4. PRINCIPLE OF THE METHOD
The concentration of gas in air is increased step by step and the mixture is exposed at each stage to an electrical spark.

1.5. QUALITY CRITERIA
Not stated.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Apparatus
The test vessel is an upright glass cylinder having a minimum inner diameter of 50 mm and a minimum height of 300 mm. The ignition electrodes are separated by a distance of 3 to 5 mm and are placed 60 mm above the bottom of the cylinder. The cylinder is fitted with a pressure-release opening. The apparatus has to be shielded to restrict any explosion damage.
A standing induction spark of 0,5 sec. duration, which is generated from a high voltage transformer with an output voltage of 10 to 15 kV (maximum of power input 300 W), is used as the ignition source. An example of a suitable apparatus is described in reference (2).

1.6.2. Test conditions
The test must be performed at room temperature (circa 20 C).

1.6.3. Performance of the test
Using proportioning pumps, a known concentration of gas in air is introduced into the glass cylinder. A spark is passed through the mixture and it is observed whether or not a flame detaches itself from the ignition source and propagates independently. The gas concentration is varied in steps of 1 % vol. until ignition occurs as described above.
If the chemical structure of the gas indicates that it would be non-flammable and the composition of the stoichiometric mixture with air can be calculated, then only mixtures in the range from 10 % less than the stoichiometric composition to 10 % greater than this composition need be tested in 1 % steps.

2. DATA
The occurrence of flame propagation is the only relevant information data for the determination

of this property.

3. REPORTING

The test report shall, if possible, include the following information:

- the precise specification of the substance (identification and impurities),
- a description, with dimensions, of the apparatus used
- the temperature at which the test was performed,
- the tested concentrations and the results obtained,
- the result of the test: non-flammable gas or highly flammable gas,
- if it is concluded that the gas is non-flammable then the concentration range over which it was tested in 1 % steps should be stated,
- all information and remarks relevant to the interpretation of results have to be reported.

4. REFERENCES

(1) NF T 20-041 (SEPT 85). Chemical products for industrial use. Determination of the flammability of gases.

(2) W.Berthold, D.Conrad, T.Grewer, H.Grosse-Wortmann, T.Redeker und H.Schacke. 'Entwicklung einer Standard-Apparatur zur Messung von Explosionsgrenzen`. Chem.-Ing.-Tech. 1984, vol 56, 2, 126-127.

A.13. PYROPHORIC PROPERTIES OF SOLIDS AND LIQUIDS

1. METHOD

1.1. INTRODUCTION

The test procedure is applicable to solid or liquid substances, which, in small amounts, will ignite spontaneously a short time after coming into contact with air at room temperature (circa 20 C). Substances which need to be exposed to air for hours or days at room temperature or at elevated temperatures before ignition occurs are not covered by this test method.

1.2 DEFINITIONS AND UNITS

Substances are considered to have pyrophoric properties if they ignite or cause charring under the conditions described in 1.6.
The auto-flammability of liquids may also need to be tested using method A.15 Auto-ignition temperature (liquids and gases).

1.3. REFERENCE SUBSTANCES

Not specified.

1.4. PRINCIPLE OF THE METHOD

The substance, whether solid or liquid, is added to an inert carrier and brought into contact with air at ambient temperature for a period of five minutes. If liquid substances do not ignite then they are absorbed onto filter paper and exposed to air at ambient temperature (circa 20 C) for five minutes. If a solid or liquid ignites, or a liquid ignites or chars a filter paper, then the substance is considered to be pyrophoric.

1.5. QUALITY CRITERIA

Repeatability: because of the importance in relation to safety, a single positive result is sufficient for the substance to be considered pyrophoric.

1.6. DESCRIPTION OF THE TEST METHOD

1.6.1. Apparatus

A porcelain cup of circa 10 cm diameter is filled with diatomaceous earth to a height of about 5 mm at room temperature (circa 20 C).
Note:
Diatomaceous earth or any other comparable inert substance which is generally obtainable shall be taken as representative of soil onto which the test substance might be spilt in the event of an accident.
Dry filter paper is required for testing liquids which do not ignite on contact with air when in contact with an inert carrier.

1.6.2. Performance of the Test

a) Powdery Solids
1 to 2 cm3 of the powdery substance to be tested is poured from circa 1 m height onto a non-combustible surface and it is observed whether the substance ignites during dropping or within five minutes of settling.
The test is performed six times unless ignition occurs.

b) Liquids
Circa 5 cm3 of the liquid to be tested is poured into the prepared porcelain cup and it is observed

whether the substance ignites within five minutes.
If no ignition occurs in the six tests, perform the following tests:
A 0,5 ml test sample is delivered from a syringe to an indented filter paper and it is observed whether ignition or charring of the filter paper occurs within five minutes of the liquid being added. The test is performed three times unless ignition or charring occurs.

2. DATA

2.1. TREATMENT OF RESULTS

Testing can be discontinued as soon as a positive result occurs in any of the tests.

2.2. EVALUATION

If the substance ignites within five minutes when added to an inert carrier and exposed to air, or a liquid substance chars or ignites a filter paper within five minutes when added and exposed to air, it is considered to be pyrophoric.

3. REPORTING

The test report shall, if possible, include the following information :
- the precise specification of the substance (identification and impurities),
- the results of the tests,
- any additional remark relevant to the interpretation of the results.

4. REFERENCES

(1) NF T 20-039 (SEPT 85). Chemical products for industrial use. Determination of the spontaneous flammability of solids and liquids.
(2) Recommendations on the Transport of Dangerous

A.15. AUTO-IGNITION TEMPERATURE (LIQUIDS AND GASES)

1. METHOD

1.1. INTRODUCTION

Explosive substances and substances which ignite spontaneously in contact with air at ambient temperature should not be submitted to this test. The test procedure is applicable to gases, liquids and vapours which, in the presence of air, can be ignited by a hot surface.

The auto-ignition temperature can be considerably reduced by the presence of catalytic impurities, by the surface material or by a higher volume of the test vessel.

1.2. DEFINITIONS AND UNITS

The degree of auto-ignitability is expressed in terms of the auto-ignition temperature. The auto-ignition temperature is the lowest temperature at which the test substance will ignite when mixed with air under the conditions defined in the test method.

1.3. REFERENCE SUBSTANCES

Reference substances are cited in the standards (see 1.6.3). They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

1.4. PRINCIPLE OF THE METHOD

The method determines the minimum temperature of the inner surface of an enclosure that will result in ignition of a gas, vapour or liquid injected into the enclosure.

1.5. QUALITY CRITERIA

The repeatability varies according to the range of auto-ignition temperatures and the test method used.

The sensitivity and specificity depend on the test method used.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Apparatus

The apparatus is described in the method referred to in 1.6.3.

1.6.2. Test conditions

A sample of the test substance is tested according to the method referred to in 1.6.3.

1.6.3. Performance of the test

See IEC 79-4, DIN 51794, ASTM-E 659-78, BS 4056, NF T 20-037.

2. DATA

Record the test-temperature, atmospheric pressure, quantity of sample used and time-lag until ignition occurs.

3. REPORTING

The test report shall, if possible, include the following information:

- the precise specification of the substance (identification and impurities),
- the quantity of sample used, atmospheric pressure,
- the apparatus used,
- the results of measurements (test temperatures, results concerning ignition, corresponding time-

lags),
- all additional remarks relevant to the interpretation of results.

4. REFERENCES

None.

A.18. NUMBER - AVERAGE MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS

1. METHOD

This Gel Permeation Chromatographic method is a replicate of the OECD TG 118 (1996). The fundamental principles and further technical information are given in reference (1).

1.1 INTRODUCTION

Since the properties of polymers are so varied, it is impossible to describe one single method setting out precisely the conditions for separation and evaluation which cover all eventualities and specificities occurring in the separation of polymers. In particular complex polymer systems are often not amenable to gel permeation chromatography (GPC). When GPC is not practicable, the molecular weight may be determined by means of other methods (see Annex). In such cases, full details and justification should be given for the method used.

The method described is based on DIN Standard 55672 (1). Detailed information about how to carry out the experiments and how to evaluate the data can be found in this DIN Standard. In case modifications of the experimental conditions are necessary, these changes must be justified. Other standards may be used, if fully referenced. The method described uses polystyrene samples of known polydispersity for calibration and it may have to be modified to be suitable for certain polymers, e.g. water soluble and long-chain branched polymers.

1.2 DEFINITIONS AND UNITS

The number-average molecular weight M_n and the weight average molecular weight M_w are determined using the following equations:

$$M_n = \frac{\sum_{i=1}^{n} H_i}{\sum_{i=1}^{n} H_i / M_i} \qquad M_w = \frac{\sum_{i=1}^{n} H_i x M_i}{\sum_{i=1}^{n} H_i}$$

where,

H_i is the level of the detector signal from the baseline for the retention volume V_i,
M_i is the molecular weight of the polymer fraction at the retention volume V_i, and
n is the number of data points.

The breadth of the molecular weight distribution, which is a measure of the dispersity of the system, is given by the ratio M_w/M_n.

1.3 REFERENCE SUBSTANCES

Since GPC is a relative method, calibration must be undertaken. Narrowly distributed, linearly constructed polystyrene standards with known average molecular weights M_n and M_w and a known molecular weight distribution are normally used for this. The calibration curve can only be used in the determination of the molecular weight of the unknown sample if the conditions for the separation of the sample and the standards have been selected in an identical manner.

A determined relationship between the molecular weight and elution volume is only valid under the specific conditions of the particular experiment. The conditions include, above all, the temperature, the solvent (or solvent mixture), the chromatography conditions and the separation column or system of columns.

The molecular weights of the sample determined in this way are relative values and are described as ‘polystyrene equivalent molecular weights’. This means that dependent on the structural and chemical differences between the sample and the standards, the molecular weights can deviate from the absolute values to a greater or a lesser degree. If other standards are used, e.g. polyethylene glycol, polyethylene oxide, polymethyl methacrylate, polyacrylic acid, the reason should be stated.

1.4 PRINCIPLE OF THE TEST METHOD

Both the molecular weight distribution of the sample and the average molecular weights (M_n, M_w) can be determined using GPC. GPC is a special type of liquid chromatography in which the sample is separated according to the hydrodynamic volumes of the individual constituents (2).

Separation is effected as the sample passes through a column which is filled with a porous material, typically an organic gel. Small molecules can penetrate the pores whereas large molecules are excluded. The path of the large molecules is thereby shorter and these are eluted first. The medium-sized molecules penetrate some of the pores and are eluted later. The smallest molecules, with a mean hydrodynamic radius smaller than the pores of the gel, can penetrate all of the pores. These are eluted last.

In an ideal situation, the separation is governed entirely by the size of the molecular species, but in practice it is difficult to avoid at least some absorption effects interfering. Uneven column packing and dead volumes can worsen the situation (2).

Detection is effected by e.g. refractive index or UV-absorption and yields a simple distribution curve. However, to attribute actual molecular weight values to the curve, it is necessary to calibrate the column by passing down polymers of known molecular weight and, ideally, of broadly similar structure e.g. various polystyrene standards. Typically a Gaussian curve results, sometimes distorted by a small tail to the low molecular weight side, the vertical axis indicating the quantity, by weight, of the various molecular weight species eluted, and the horizontal axis the log molecular weight.

1.5 QUALITY CRITERIA

The repeatability (Relative Standard Deviation : RSD) of the elution volume should be better than 0.3 %. The required repeatability of the analysis has to be ensured by correction via an internal standard if a chromatogram is evaluated time-dependently and does not correspond to the above mentioned criterion (1). The polydispersities are dependent on the molecular weights of the standards. In the case of polystyrene standards typical values are:

$M_p < 2000$	$M_w/M_n < 1.20$
$2000 \leq M_p \leq 10^6$	$M_w/M_n < 1.05$
$M_p > 10^6$	$M_w/M_n < 1.20$

(M_p is the molecular weight of the standard at the peak maximum)

1.6 DESCRIPTION OF THE TEST METHOD

1.6.1 Preparation of the standard polystyrene solutions

The polystyrene standards are dissolved by careful mixing in the chosen eluent. The recommendations of the manufacturer must be taken into account in the preparation of the solutions.

The concentrations of the standards chosen are dependent on various factors, e.g. injection volume, viscosity of the solution and sensitivity of the analytical detector. The maximum injection volume must be adapted to the length of the column, in order to avoid overloading. Typical injection volumes for analytical separations using GPC with a column of 30 cm x 7.8 mm are normally between 40 and 100 µl. Higher volumes are possible, but they should not exceed 250 µl. The optimal ratio between the injection volume and the concentration must be determined prior to the actual calibration of the column.

1.6.2 Preparation of the sample solution

In principle, the same requirements apply to the preparation of the sample solutions. The sample is dissolved in a suitable solvent, e.g. tetrahydrofuran (THF), by shaking carefully. Under no circumstances should it be dissolved using an ultrasonic bath. When necessary, the sample solution is purified via a membrane filter with a pore size of between 0.2 and 2 µm.

The presence of undissolved particles must be recorded in the final report as these may be due to high molecular weight species. An appropriate method should be used to determine the percentage by weight of the undissolved particles. The solutions should be used within 24 hours.

1.6.3 Apparatus

- solvent reservoir
- degasser (where appropriate)
- pump
- pulse dampener (where appropriate)
- injection system
- chromatography columns

- detector
- flowmeter (where appropriate)
- data recorder-processor
- waste vessel

It must be ensured that the GPC system is inert with regard to the utilised solvents (e.g. by the use of steel capillaries for THF solvent).

1.6.4 Injection and solvent delivery system

A defined volume of the sample solution is loaded onto the column either using an auto-sampler or manually in a sharply defined zone. Withdrawing or depressing the plunger of the syringe too quickly, if done manually, can cause changes in the observed molecular weight distribution. The solvent-delivery system should, as far as possible, be pulsation-free ideally incorporating a pulse dampener. The flow rate is of the order of 1 ml/min.

1.6.5 Column

Depending on the sample, the polymer is characterised using either a simple column or several columns connected in sequence. A number of porous column materials with defined properties (e.g. pore size, exclusion limits) are commercially available. Selection of the separation gel or the length of the column is dependent on both the properties of the sample (hydrodynamic volumes, molecular weight distribution) and the specific conditions for separation such as solvent, temperature and flow rate (1)(2)(3).

1.6.6 Theoretical plates

The column or the combination of columns used for separation must be characterised by the number of theoretical plates. This involves, in the case of THF as elution solvent, loading a solution of ethyl benzene or other suitable non-polar solute onto a column of known length. The number of theoretical plates is given by the following equation:

$$N = 5.54\left(\frac{V_e}{W_{1/2}}\right)^2 \qquad \text{or} \qquad N = 16\left(\frac{V_e}{W}\right)^2$$

where,

N is the number of theoretical plates

V_e is the elution volume at the peak maximum

W is the baseline peak width

$W_{1/2}$ is the peak width at half height

1.6.7 **Separation efficiency**

In addition to the number of theoretical plates, which is a quantity determining the bandwidth, a part is also played by the separation efficiency, this being determined by the steepness of the calibration curve. The separation efficiency of a column is obtained from the following relationship:

$$\frac{V_{e,Mx} - V_{e,(10Mx)}}{\text{cross sectional area of the column}} \geq 6.0 \left[\frac{cm^3}{cm^2}\right]$$

where,

$V_{e,Mx}$ is the elution volume for polystyrene with the molecular weight M_x

$V_{e,(10.Mx)}$ is the elution volume for polystyrene with a ten times greater molecular weight.

The resolution of the system is commonly defined as follows:

$$R_{1,2} = 2x \frac{V_{e1} - V_{e2}}{W_1 + W_2} x \frac{1}{\log_{10}(M_2 / M_1)}$$

where,

V_{e1}, V_{e2} are the elution volumes of the two polystyrene standards at the peak maximum

W_1, W_2 are the peak widths at the base line

M_1, M_2 are the molecular weights at the peak maximum (should differ by a factor of 10)

The R-value for the column system should be greater than 1.7 (4).

1.6.8 **Solvents**

All solvents must be of high purity (for THF purity of 99.5 % is used). The solvent reservoir (if necessary in an inert gas atmosphere) must be sufficiently large for the calibration of the column and several sample analyses. The solvent must be degassed before it is transported to the column via the pump.

1.6.9 Temperature control

The temperature of the critical internal components (injection loop, columns, detector and tubing) should be constant and consistent with the choice of solvent.

1.6.10 Detector

The purpose of the detector is to record quantitatively the concentration of sample eluted from the column. In order to avoid unnecessary broadening of peaks the cuvette volume of the detector cell must be kept as small as possible. It should not be larger than 10 µl except for light scattering and viscosity detectors. Differential refractometry is usually used for detection. However, if required by the specific properties of the sample or the elution solvent, other types of detectors can be used, e.g. UV/VIS, IR, viscosity detectors, etc.

2. DATA AND REPORTING

2.1 DATA

The DIN Standard (1) should be referred to for the detailed evaluation criteria as well as for the requirements relating to the collecting and processing of data.

For each sample, two independent experiments must be carried out. They have to be analysed individually.

M_n, M_w, M_w/M_n and M_p must be provided for every measurement. It is necessary to indicate explicitly that the measured values are relative values equivalent to the molecular weights of the standard used.

After determination of the retention volumes or the retention times (possibly corrected using an internal standard), log M_p values (M_p being the peak maxima of the calibration standard) are plotted against one of those quantities. At least two calibration points are necessary per molecular weight decade, and at least five measurement points are required for the total curve, which should cover the estimated molecular weight of the sample. The low molecular weight end-point of the calibration curve is defined by n-hexyl benzene or another suitable non-polar solute. The number average and the weight-average molecular weights are generally determined by means of electronic data processing, based on the formulas of section 1.2. In case manual digitisation is used, ASTM D 3536-91 can be consulted (3).

The distribution curve must be provided in the form of a table or as figure (differential frequency or sum percentages against log M). In the graphic representation, one molecular weight decade should be normally about 4 cm in width and the peak maximum should be about 8 cm in height. In the case of integral distribution curves the difference in the ordinate between 0 and 100 % should be about 10 cm.

2.2 TEST REPORT

The test report must include the following information:

2.2.1 **Test substance:**

-available information about test substance (identity, additives, impurities);

- description of the treatment of the sample, observations, problems.

2.2.2 **Instrumentation:**

- reservoir of eluent, inert gas, degassing of the eluent, composition of the eluent, impurities;

- pump, pulse dampener, injection system;

- separation columns (manufacturer, all information about the characteristics of the columns, such as pore size, kind of separation material etc., number, length and order of the columns used);

- number of the theoretical plates of the column (or combination), separation efficiency (resolution of the system);

- information on symmetry of the peaks;

- column temperature, kind of temperature control;

- detector (measurement principle, type, cuvette volume);

- flowmeter if used (manufacturer, measurement principle);

- system to record and process data (hardware and software).

2.2.3 **Calibration of the system:**

- detailed description of the method used to construct the calibration curve;

- information about quality criteria for this method (e.g. correlation coefficient, error sum of squares, etc.);

- information about all extrapolations, assumptions and approximations made during the experimental procedure and the evaluation and processing of data;

- all measurements used for constructing the calibration curve have to be documented in a table which includes the following information for each calibration point:

- name of the sample

- manufacturer of the sample

- characteristic values of the standards M_p, M_n, M_w, M_w/M_n, as provided by the manufacturer or derived by subsequent measurements, together with details about the method of determination

- injection volume and injection concentration

- M_p value used for calibration

- elution volume or corrected retention time measured at the peak maxima

- M_p calculated at the peak maximum

- percentage error of the calculated M_p and the calibration value.

2.2.4 **Evaluation:**

- evaluation on a time basis: methods used to ensure the required reproducibility (method of correction, internal standard etc.);

- information about whether the evaluation was effected on the basis of the elution volume or the retention time;

- information about the limits of the evaluation if a peak is not completely analysed;

- description of smoothing methods, if used;

- preparation and pre-treatment procedures of the sample;

- the presence of undissolved particles, if any;

- injection volume (µl) and injection concentration (mg/ml);

- observations indicating effects which lead to deviations from the ideal GPC profile;

- detailed description of all modifications in the testing procedures;

- details of the error ranges;

- any other information and observations relevant for the interpretation of the results.

3. REFERENCES

(1) DIN 55672 (1995) Gelpermeationschromatographie (GPC) mit Tetrahydrofuran (THF) als Elutionsmittel, Teil 1.

(2) Yau, W.W., Kirkland, J.J., and Bly, D.D. eds, (1979). Modern Size Exclusion Liquid Chromatography, J. Wiley and Sons.

(3) ASTM D 3536-91, (1991). Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution by Liquid Exclusion

Chromatography (Gel Permeation Chromatography-GPC). American Society for Testing and Materials, Philadelphia, Pennsylvania.

(4) ASTM D 5296-92, (1992). Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography. American Society for Testing and Materials, Philadelphia, Pennsylvania.

ANNEX

EXAMPLES OF OTHER METHODS FOR DETERMINATION OF NUMBER AVERAGE MOLECULAR WEIGHT (M_n) FOR POLYMERS

Gel permeation chromatography (GPC) is the preferred method for determination of M_n, especially when a set of standards are available, whose structure are comparable with the polymer structure. However, where there are practical difficulties in using GPC or there is already an expectation that the substance will fail a regulatory M_n criterion (and which needs confirming), alternative methods are available, such as:

1. **Use of Colligative Properties**

1.1 **Ebullioscopy / Cryoscopy**: involves measurement of boiling point elevation (ebullioscopy) or freezing point depression (cryoscopy) of a solvent, when the polymer is added. The method relies on the fact that the effect of the dissolved polymer on the boiling/freezing point of the liquid is dependent on the molecular weight of the polymer (1) (2).

Applicability, $M_n < 20{,}000$.

1.2 **Lowering of Vapour Pressure**: involves the measurement of the vapour pressure of a chosen reference liquid before and after the addition of known quantities of polymer (1) (2).

Applicability, $M_n < 20{,}000$ (theoretically; in practice however of limited value).

1.3 **Membrane Osmometry**: relies on the principle of osmosis, i.e. the natural tendency of solvent molecules to pass through a semi-permeable membrane from a dilute to a concentrated solution to achieve equilibrium. In the test, the dilute solution is at zero concentration, whereas the concentrated solution contains the polymer. The effect of drawing solvent through the membrane causes a pressure differential that is dependent on the concentration and the molecular weight of the polymer (1) (3) (4).

Applicability, M_n between 20,000 - 200,000.

1.4 **Vapour Phase Osmometry**: involves comparison of the rate of evaporation of a pure solvent aerosol to at least three aerosols containing the polymer at different concentrations (1) (5) (6).

Applicability, $M_n < 20{,}000$.

2. End-Group Analysis

To use this method, knowledge of both the overall structure of the polymer and the nature of the chain terminating end groups is needed (which must be distinguishable from the main skeleton by e.g. NMR or titration/derivatisation). The determination of the molecular concentration of the end groups present on the polymer can lead to a value for the molecular weight (7) (8) (9).

Applicability, M_n up to 50,000 (with decreasing reliability).

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(1) Billmeyer, F.W. Jr., (1984). Textbook of Polymer Science, 3rd Edn., John Wiley, New York.

(2) Glover, C.A., (1975). Absolute Colligative Property Methods. Chapter 4. In: Polymer Molecular Weights, Part I P.E. Slade, Jr. ed., Marcel Dekker, New York.

(3) ASTM D 3750-79, (1979). Standard Practice for Determination of Number-Average Molecular Weight of Polymers by Membrane Osmometry. American Society for Testing and Materials, Philadelphia, Pennsylvania.

(4) Coll, H. (1989). membrane Osmometry. In: Determination of Molecular Weight, A.R. Cooper ed., J. Wiley and Sons, pp. 25-52.

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(6) Morris, C.E.M., (1989). Vapour Pressure osmometry. In: Determinationn of Molecular Weight, A.R. Cooper ed., John Wiley and Sons.

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A.19. LOW MOLECULAR WEIGHT CONTENT OF POLYMERS

1. METHOD

This Gel Permeation Chromatographic method is a replicate of the OECD TG 119 (1996). The fundamental principles and further technical information are given in the references.

1.1 INTRODUCTION

Since the properties of polymers are so varied, it is impossible to describe one single method setting out precisely the conditions for separation and evaluation which cover all eventualities and specificities occurring in the separation of polymers. In particular complex polymer systems are often not amenable to gel permeation chromatography (GPC). When GPC is not practicable, the molecular weight may be determined by means of other methods (see Annex). In such cases, full details and justification should be given for the method used.

The method described is based on DIN Standard 55672 (1). Detailed information about how to carry out the experiments and how to evaluate the data can be found in this DIN Standard. In case modifications of the experimental conditions are necessary, these changes must be justified. Other standards may be used, if fully referenced. The method described uses polystyrene samples of known polydispersity for calibration and it may have to be modified to be suitable for certain polymers, e.g. water soluble and long-chain branched polymers.

1.2 DEFINITIONS AND UNITS

Low molecular weight is arbitrarily defined as a molecular weight below 1000 dalton.

The number-average molecular weight M_n and the weight average molecular weight M_w are determined using the following equations:

$$M_n = \frac{\sum_{i=1}^{n} H_i}{\sum_{i=1}^{n} H_i / M_i} \qquad M_w = \frac{\sum_{i=1}^{n} H_i x M_i}{\sum_{i=1}^{n} H_i}$$

where,

H_i is the level of the detector signal from the baseline for the retention volume V_i,
M_i is the molecular weight of the polymer fraction at the retention volume V_i, and
n is the number of data points.

The breadth of the molecular weight distribution, which is a measure of the dispersity of the system, is given by the ratio M_w/M_n.

1.3 REFERENCE SUBSTANCES

Since GPC is a relative method, calibration must be undertaken. Narrowly distributed, linearly constructed polystyrene standards with known average molecular weights M_n and M_w and a known molecular weight distribution are normally used for this. The calibration curve can only be used in the determination of the molecular weight of the unknown sample if the conditions for the separation of the sample and the standards have been selected in an identical manner.

A determined relationship between the molecular weight and elution volume is only valid under the specific conditions of the particular experiment. The conditions include, above all, the temperature, the solvent (or solvent mixture), the chromatography conditions and the separation column or system of columns.

The molecular weights of the sample determined in this way are relative values and are described as ‘polystyrene equivalent molecular weights’. This means that dependent on the structural and chemical differences between the sample and the standards, the molecular weights can deviate from the absolute values to a greater or a lesser degree. If other standards are used, e.g. polyethylene glycol, polyethylene oxide, polymethyl methacrylate, polyacrylic acid, the reason should be stated.

1.4 PRINCIPLE OF THE TEST METHOD

Both the molecular weight distribution of the sample and the average molecular weights (M_n, M_w) can be determined using GPC. GPC is a special type of liquid chromatography in which the sample is separated according to the hydrodynamic volumes of the individual constituents (2).

Separation is effected as the sample passes through a column which is filled with a porous material, typically an organic gel. Small molecules can penetrate the pores whereas large molecules are excluded. The path of the large molecules is thereby shorter and these are eluted first. The medium-sized molecules penetrate some of the pores and are eluted later. The smallest molecules, with a mean hydrodynamic radius smaller than the pores of the gel, can penetrate all of the pores. These are eluted last.

In an ideal situation, the separation is governed entirely by the size of the molecular species, but in practice it is difficult to avoid at least some absorption effects interfering. Uneven column packing and dead volumes can worsen the situation (2).

Detection is effected by e.g. refractive index or UV-absorption and yields a simple distribution curve. However, to attribute actual molecular weight values to the curve, it is necessary to calibrate the column by passing down polymers of known molecular weight and, ideally, of broadly similar structure e.g. various polystyrene standards. Typically a Gaussian curve results, sometimes distorted by a small tail to the low molecular weight side, the vertical axis indicating the quantity, by weight, of the various molecular weight species eluted, and the horizontal axis the log molecular weight.

The low molecular weight content is derived from this curve. The calculation can only be accurate if the low molecular weight species respond equivalently on a per mass basis to the polymer as a whole.

1.5 QUALITY CRITERIA

The repeatability (Relative Standard Deviation : RSD) of the elution volume should be better than 0.3 %. The required repeatability of the analysis has to be ensured by correction via an internal standard if a chromatogram is evaluated time-dependently and does not correspond to the above mentioned criterion (1). The polydispersities are dependent on the molecular weights of the standards. In the case of polystyrene standards typical values are:

$M_p < 2000$	$M_w/M_n < 1.20$
$2000 \leq M_p \leq 10^6$	$M_w/M_n < 1.05$
$M_p > 10^6$	$M_w/M_n < 1.20$

(M_p is the molecular weight of the standard at the peak maximum)

1.6 DESCRIPTION OF THE TEST METHOD

1.6.1 **Preparation of the standard polystyrene solutions**

The polystyrene standards are dissolved by careful mixing in the chosen eluent. The recommendations of the manufacturer must be taken into account in the preparation of the solutions.

The concentrations of the standards chosen are dependent on various factors e.g. injection volume, viscosity of the solution and sensitivity of the analytical detector. The maximum injection volume must be adapted to the length of the column, in order to avoid overloading.

Typical injection volumes for analytical separations using GPC with a column of 30 cm x 7.8 mm are normally between 40 and 100 µl. Higher volumes are possible, but they should not exceed 250 µl. The optimal ratio between the injection volume and the concentration must be determined prior to the actual calibration of the column.

1.6.2 Preparation of the sample solution

In principle, the same requirements apply to the preparation of the sample solutions. The sample is dissolved in a suitable solvent, e.g. tetrahydrofuran (THF), by shaking carefully. Under no circumstances should it be dissolved using an ultrasonic bath. When necessary, the sample solution is purified via a membrane filter with a pore size of between 0.2 and 2 µm.

The presence of undissolved particles must be recorded in the final report as these may be due to high molecular weight species. An appropriate method should be used to determine the percentage by weight of the undissolved particles. The solutions should be used within 24 hours.

1.6.3 Correction for content of impurities and additives

Correction of the content of species of $M < 1000$ for the contribution from non-polymer specific components present (e.g. impurities and/or additives) is usually necessary, unless the measured content is already < 1 %. This is achieved by direct analysis of the polymer solution or the GPC eluate.

In cases where the eluate, after passage through the column, is too dilute for a further analysis it must be concentrated. It may be necessary to evaporate the eluate to dryness and dissolve it again. Concentration of the eluate must be effected under conditions which ensure that no changes occur in the eluate. The treatment of the eluate after the GPC step is dependent on the analytical method used for the quantitative determination.

1.6.4 Apparatus

GPC apparatus comprises the following components:

- solvent reservoir
- degasser (where appropriate)
- pump
- pulse dampener (where appropriate)
- injection system
- chromatography columns
- detector
- flowmeter (where appropriate)
- data recorder-processor

-.waste vessel

It must be ensured that the GPC system is inert with regard to the utilised solvents (e.g. by the use of steel capillaries for THF solvent).

1.6.5 Injection and solvent delivery system

A defined volume of the sample solution is loaded onto the column either using an auto-sampler or manually in a sharply defined zone. Withdrawing or depressing the plunger of the syringe too quickly, if done manually, can cause changes in the observed molecular weight distribution. The solvent-delivery system should, as far as possible, be pulsation-free ideally incorporating a pulse dampener. The flow rate is of the order of 1 ml/min.

1.6.6 Column

Depending on the sample, the polymer is characterised using either a simple column or several columns connected in sequence. A number of porous column materials with defined properties (e.g. pore size, exclusion limits) are commercially available. Selection of the separation gel or the length of the column is dependent on both the properties of the sample (hydrodynamic volumes, molecular weight distribution) and the specific conditions for separation such as solvent, temperature and flow rate (1) (2) (3).

1.6.7 Theoretical plates

The column or the combination of columns used for separation must be characterised by the number of theoretical plates. This involves, in the case of THF as elution solvent, loading a solution of ethyl benzene or other suitable non-polar solute onto a column of known length. The number of theoretical plates is given by the following equation:

$$N = 5.54\left(\frac{V_e}{W_{1/2}}\right)^2 \qquad \textbf{or} \qquad N = 16\left(\frac{V_e}{W}\right)^2$$

where,

N is the number of theoretical plates

V_e is the elution volume at the peak maximum

W is the baseline peak width

$W_{1/2}$ is the peak width at half height

1.6.8 Separation efficiency

In addition to the number of theoretical plates, which is a quantity determining the bandwidth, a part is also played by the separation efficiency, this being determined by the steepness of the calibration curve. The separation efficiency of a column is obtained from the following relationship:

$$\frac{V_{e,Mx} - V_{e,(10Mx)}}{\textit{cross sectional area of the column}} \geq 6.0\left[\frac{cm^3}{cm^2}\right]$$

where,

$V_{e,Mx}$ is the elution volume for polystyrene with the molecular weight M_x

$V_{e,(10.Mx)}$ is the elution volume for polystyrene with a ten times greater molecular weight.

The resolution of the system is commonly defined as follows:

$$R_{1,2} = 2x\frac{V_{e1} - V_{e2}}{W_1 + W_2} x \frac{1}{\log_{10}(M_2/M_1)}$$

where,

V_{e1}, V_{e2} are the elution volumes of the two polystyrene standards at the peak maximum

W_1, W_2 are the peak widths at the base line

M_1, M_2 are the molecular weights at the peak maximum (should differ by a factor of 10)

The R-value for the column system should be greater than 1.7 (4).

1.6.9 Solvents

All solvents must be of high purity (for THF purity of 99.5 % is used). The solvent reservoir (if necessary in an inert gas atmosphere) must be sufficiently large for the calibration of the column and several sample analyses. The solvent must be degassed before it is transported to the column via the pump.

1.6.10 Temperature control

The temperature of the critical internal components (injection loop, columns, detector and tubing) should be constant and consistent with the choice of solvent.

1.6.11 Detector

The purpose of the detector is to record quantitatively the concentration of sample eluted from the column. In order to avoid unnecessary broadening of peaks the cuvette volume of the detector cell must be kept as small as possible. It should not be larger than 10 µl except for light scattering and viscosity detectors. Differential refractometry is usually used for detection. However, if required by the specific properties of the sample or the elution solvent, other types of detectors can be used, e.g. UV/VIS, IR, viscosity detectors, etc.

2. DATA AND REPORTING

2.1 DATA

The DIN Standard (1) should be referred to for the detailed evaluation criteria as well as for the requirements relating to the collecting and processing of data.

For each sample, two independent experiments must be carried out. They have to be analysed individually. In all cases it is essential to determine also data from blanks, treated under the same conditions as the sample.

It is necessary to indicate explicitly that the measured values are relative values equivalent to the molecular weights of the standard used.

After determination of the retention volumes or the retention times (possibly corrected using an internal standard), log M_p values (M_p being the peak maxima of the calibration standard) are plotted against one of those quantities. At least two calibration points are necessary per molecular weight decade, and at least five measurement points are required for the total curve, which should cover the estimated molecular weight of the sample. The low molecular weight end-point of the calibration curve is defined by n-hexyl benzene or another suitable non-polar solute. The portion of the curve corresponding to molecular weights below 1000 is determined and corrected as necessary for impurities and additives. The elution curves are generally evaluated by means of electronic data processing. In case manual digitisation is used, ASTM D 3536-91 can be consulted (3).

If any insoluble polymer is retained on the column, its molecular weight is likely to be higher than that of the soluble fraction, and if not considered would result in an overestimation of the low molecular weight content. Guidance for correcting the low molecular weight content for insoluble polymer is provided in the Annex.

The distribution curve must be provided in the form of a table or as figure (differential frequency or sum percentages against log M). In the graphic representation, one molecular weight decade should be normally about 4 cm in width and the peak maximum should be about 8 cm in height. In the case of integral distribution curves the difference in the ordinate between 0 and 100 % should be about 10 cm.

2.2 TEST REPORT

The test report must include the following information:

2.2.1 **Test substance:**

- available information about test substance (identity, additives, impurities);

- description of the treatment of the sample, observations, problems.

2.2.2 **Instrumentation:**

- reservoir of eluent, inert gas, degassing of the eluent, composition of the eluent, impurities;

- pump, pulse dampener, injection system;

- separation columns (manufacturer, all information about the characteristics of the columns, such as pore size, kind of separation material etc., number, length and order of the columns used);

- number of the theoretical plates of the column (or combination), separation efficiency (resolution of the system);

- information on symmetry of the peaks;

- column temperature, kind of temperature control;

- detector (measurement principle, type, cuvette volume);

- flowmeter if used (manufacturer, measurement principle);

- system to record and process data (hardware and software).

2.2.3 **Calibration of the system:**

- detailed description of the method used to construct the calibration curve;

- information about quality criteria for this method (e.g. correlation coefficient, error sum of squares, etc.);

- information about all extrapolations, assumptions and approximations made during the experimental procedure and the evaluation and processing of data;

- all measurements used for constructing the calibration curve have to be documented in a table which includes the following information for each calibration point:

  - name of the sample

  - manufacturer of the sample

  - characteristic values of the standards M_p, M_n, M_w, M_w/M_n, as provided by the manufacturer or derived by subsequent measurements, together with details about the method of determination

  - injection volume and injection concentration

  - M_p value used for calibration

- elution volume or corrected retention time measured at the peak maxima

- M_p calculated at the peak maximum

- percentage error of the calculated M_p and the calibration value.

2.2.4 Information on the low molecular weight polymer content:

- description of the methods used in the analysis and the way in which the experiments were conducted;

- information about the percentage of the low molecular weight species content (w/w) related to the total sample;

- information about impurities, additives and other non-polymer species in percentage by weight related to the total sample;

2.2.5 **Evaluation:**

- evaluation on a time basis: all methods to ensure the required reproducibility (method of correction, internal standard etc.);

- information about whether the evaluation was effected on the basis of the elution volume or the retention time;

- information about the limits of the evaluation if a peak is not completely analysed;

- description of smoothing methods, if used;

- preparation and pre-treatment procedures of the sample;

- the presence of undissolved particles, if any;

- injection volume (µl) and injection concentration (mg/ml);

- observations indicating effects which lead to deviations from the ideal GPC profile;

- detailed description of all modifications in the testing procedures;

- details of the error ranges;

- any other information and observations relevant for the interpretation of the results.

3. REFERENCES

(1) DIN 55672 (1995) Gelpermeationschromatographie (GPC) mit Tetrahydrofuran (THF) als Elutionsmittel, Teil 1.

(2) Yau, W.W., Kirkland, J.J., and Bly, D.D. eds. (1979). Modern Size Exclusion Liquid Chromatography, J. Wiley and Sons.

(3) ASTM D 3536-91, (1991). Standard Test method for Molecular Weight Averages and Molecular Weight Distribution by Liquid Exclusion Chromatography (Gel Permeation Chromatography-GPC). American Society for Testing and Materials, Philadelphia, Pennsylvania.

(4) ASTM D 5296-92, (1992). Standard Test method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography. American Society for Testing and Materials, Philadelphia, Pennsylvania.

ANNEX

GUIDANCE FOR CORRECTING LOW MOLECULAR CONTENT FOR THE PRESENCE OF INSOLUBLE POLYMER

When insoluble polymer is present in a sample, it results in mass loss during the GPC analysis. The insoluble polymer is irreversibly retained on the column or sample filter while the soluble portion of the sample passes through the column. In the case where the refractive index increment (dn/dc) of the polymer can be estimated or measured, one can estimate the sample mass lost on the column. In that case, one makes a correction using an external calibration with standard materials of known concentration and dn/dc to calibrate the response of the refractometer. In the example hereafter a poly(methyl methacrylate) (pMMA) standard is used.

In the external calibration for analysis of acrylic polymers, a pMMA standard of known concentration in tetrahydrofuran, is analysed by GPC and the resulting data are used to find the refractometer constant according to the equation:

$$\mathbf{K = R / (C \times V \times dn/dc)}$$

where :

K is the refractometer constant (in microvolt·second/ml),

R is the response of the pMMA standard (in microvolt·second),

C is the concentration of the pMMA standard (in mg/ml),

V is the injection volume (in ml) and

dn/dc is the refractive index increment for pMMA in tetrahydrofuran (in ml/mg).

The following data are typical for a pMMA standard:

R = 2937891

C = 1.07 mg/ml

V = 0.1 ml

dn/dc = 9×10^{-5} ml/mg

The resulting K value, 3.05×10^{11} is then used to calculate the theoretical detector response if 100 % of the polymer injected had eluted through the detector.

A.20. SOLUTION / EXTRACTION BEHAVIOUR OF POLYMERS IN WATER

1. METHOD

The method described is a replicate of the revised version of OECD TG 120 (1997). Further technical information is given in reference (1).

1.1 INTRODUCTION

For certain polymers, such as emulsion polymers, initial preparatory work may be necessary before the method set out hereafter can be used. The method is not applicable to liquid polymers and to polymers that react with water under the test conditions.

When the method is not practical or not possible, the solution/extraction behaviour may be investigated by means of other methods. In such cases, full details and justification should be given for the method used.

1.2 REFERENCE SUBSTANCES

None

1.3 PRINCIPLE OF THE TEST METHOD

The solution/extraction behaviour of polymers in an aqueous medium is determined using the flask method (see A.6 Water Solubility, Flask method) with the modifications described below.

1.4 QUALITY CRITERIA

None.

1.5 DESCRIPTION OF THE TEST METHOD

1.5.1 Equipment

The following equipment is required for the method:

- crushing device, e.g. grinder for the production of particles of known size
- apparatus for shaking with possibility of temperature control
- membrane filter system
- appropriate analytical equipment
- standardised sieves

1.5.2 Sample Preparation

A representative sample has first to be reduced to a particle size between 0.125 and 0.25 mm using appropriate sieves. Cooling may be required for the stability of the sample or for the grinding process. Materials of a rubbery nature can be crushed at liquid nitrogen temperature (1).

If the required particle size fraction is not attainable, action should be taken to reduce the particle size as much as possible, and the result reported. In the report, it is necessary to indicate the way in which the crushed sample was stored prior to the test.

1.5.3 Procedure

Three samples of 10 g of the test substance are weighed into each of three vessels fitted with glass stoppers and 1000 ml of water is added to each vessel. If handling an amount of 10 g polymer proves impracticable, the next highest amount which can be handled should be used and the volume of water adjusted accordingly.

The vessels are tightly stoppered and then agitated at 20 °C. A shaking or stirring device capable of operating at constant temperature should be used. After a period of 24 hours, the content of each vessel is centrifuged or filtered and the concentration of polymer in the clear aqueous phase is determined by a suitable analytical method. If suitable analytical methods for the aqueous phase are not available, the total solubility/extractivity can be estimated from the dry weight of the filter residue or centrifuged precipitate.

It is usually necessary to differentiate quantitatively between the impurities and additives on the one hand and the low molecular weight species on the other hand. In the case of gravimetric determination, it is also important to perform a blank run using no test substance in order to account for residues arising from the experimental procedure.

The solution/extraction behaviour of polymers in water at 37 °C at pH 2 and pH 9 may be determined in the same way as described for the conduct of the experiment at 20 °C. The pH values can be achieved by the addition of either suitable buffers or appropriate acids or bases such as hydrochloric acid, acetic acid, analytical grade sodium or potassium hydroxide or NH_3.

Depending on the method of analysis used, one or two tests should be performed. When sufficiently specific methods are available for direct analysis of the aqueous phase for the polymer component, one test as described above should suffice. However, when such methods are not available and determination of the solution/extraction behaviour of the polymer is limited to indirect analysis by determining only the total organic carbon content (TOC) of the aqueous extract, an additional test should be conducted. This additional test should also be done in triplicate, using ten times smaller polymer samples and the same amounts of water as those used in the first test.

1.5.4 Analysis

1.5.4.1 Test conducted with one sample size

Methods may be available for direct analysis of polymer components in the aqueous phase. Alternatively, indirect analysis of dissolved/extracted polymer components, by determining the total content of soluble parts and correcting for non polymer-specific components, could also be considered.

Analysis of the aqueous phase for the total polymeric species is possible:

either by a sufficiently sensitive method e.g.

- TOC using persulphate or dichromate digestion to yield CO_2 followed by estimation by IR or chemical analysis;

- Atomic Absorption Spectrometry (AAS) or its Inductively Coupled Plasma (ICP) emission equivalent for silicon or metal containing polymers;

- UV absorption or spectrofluorimetry for aryl polymers;

- LC-MS for low molecular weight samples;

or by vacuum evaporation to dryness of the aqueous extract and spectroscopic (IR, UV, etc.) or AAS/ICP analysis of the residue.

If analysis of the aqueous phase as such is not practicable, the aqueous extract should be extracted with a water-immiscible organic solvent e.g. a chlorinated hydrocarbon. The solvent is then evaporated and the residue analysed as above for the notified polymer content. Any components in this residue which are identified as being impurities or additives are to be subtracted for the purpose of determining the degree of solution/extraction of the polymer itself.

When relatively large quantities of such materials are present, it may be necessary to subject the residue to e.g. HPLC or GC analysis to differentiate the impurities from the monomer and monomer-derived species present so that the true content of the latter can be determined.

In some cases, simple evaporation of the organic solvent to dryness and weighing the dry residue may be sufficient.

1.5.4.2 Test conducted with two different sample sizes

All aqueous extracts are analysed for TOC.

A gravimetric determination is performed on the undissolved/not extracted part of the sample. If, after centrifugation or filtering of the content of each vessel, polymer residues remain attached to the wall of the vessel, the vessel should be rinsed with the filtrate until the vessel is cleared from all visible residues. Following, the filtrate is again centrifuged or filtered. The residues remaining on the filter or in the centrifuge tube are dried at 40^0C under vacuum and weighed. Drying is continued until a constant weight is reached.

2. DATA

2.1 TEST CONDUCTED WITH ONE SAMPLE SIZE

The individual results for each of the three flasks and the average values should be given and expressed in units of mass per volume of the solution (typically mg/l) or mass per mass of polymer sample (typically mg/g). Additionally, the weight loss of the sample (calculated as the weight of the solute divided by the weight of the initial sample) should also be given. The relative standard deviations (RSD) should be calculated. Individual figures should be given for the total substance (polymer+essential additives etc.) and for the polymer only (i.e. after subtracting the contribution from such additives).

2.2 TEST CONDUCTED WITH TWO DIFFERENT SAMPLE SIZES

The individual TOC values of the aqueous extracts of the two triplicate experiments and the average value for each experiment should be given expressed as units of mass per volume of solution (typically mgC/l), as well as in units of mass per weight of the initial sample (typically mgC/g).

If there is no difference between the results at the high and the low sample/water ratios, this may indicate that all extractable components were indeed extracted. In such a case, direct analysis would normally not be necessary.

The individual weights of the residues should be given and expressed in percentage of the initial weights of the samples. Averages should be calculated per experiment. The differences between 100 and the percentages found represent the percentages of soluble and extractable material in the original sample.

3. REPORTING

3.1 TEST REPORT

The test report must include the following information :

3.1.1 Test substance:

-available information about test substance (identity, additives, impurities, content of low molecular weight species).

3.1.2 Experimental conditions:

-description of the procedures used and experimental conditions;

-description of the analytical and detection methods.

3.1.3 Results:

-results of solubility/extractivity in mg/l; individual and mean values for the extraction tests in the various solutions, broken down in polymer content and impurities, additives, etc.

-results of solubility/extractivity in mg/g of polymer

-TOC values of aqueous extracts, weight of the solute and calculated percentages, if measured

-the pH of each sample

-information about the blank values

-where necessary, references to the chemical instability of the test substance, during both the testing

process and the analytical process

-all information which is important for the interpretation of the results.

4. REFERENCES

(1) DIN 53733 (1976) Zerkleinerung von Kunststofferzeugnissen fur Prufzwecke.