

OECD GUIDELINE FOR TESTING OF CHEMICALS

Solution/Extraction Behaviour of Polymers in Water

INTRODUCTION

1. The original proposal for this guideline was contained in a working document on methods for polymer characterisation from the European Commission (EC). It was submitted to an OECD meeting of experts hosted by Japan in April 1993 in Tokyo, which recommended that the proposal serve as a basis for the development of an OECD Guideline. During 1994 the Secretariat circulated in the Member countries the EC text formatted as an OECD Guideline. Subsequently, a Joint OECD/EC meeting of experts discussed and modified the guideline proposal in May 1994. A revised text was circulated for further comments in Member countries. Following two commenting rounds, the draft guideline was finalised in its present form.

INITIAL CONSIDERATIONS

2. For certain polymers, such as emulsion polymers, initial preparatory work may be necessary before the method set out in this guideline can be used. The method is not applicable to liquid polymers and to polymers that react with water under the test conditions.
3. 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.

PRINCIPLE OF THE METHOD

4. The solution/extraction behaviour of polymers in an aqueous medium is determined using the flask method (see Guideline 105) with the modifications described below.

DESCRIPTION OF THE METHOD

Equipment

5. The following equipment is required for the method:
- crushing device, e.g., grinder for the production of particles of known size (1)
 - apparatus for shaking with possibility of temperature control
 - membrane filter system
 - analytical equipment
 - standardised sieves

Preparation of the samples

6. 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).
7. 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.

PROCEDURE

Conducting the experiment

8. 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 of 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.
9. 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.
10. The solution/extraction behaviour of polymers in water at 20°C at pH 2 and pH 9 and at 37°C at-pH 7 may be determined in the same way as described for the conduct of the experiment at 20°C (see paragraph 8). 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, potassium hydroxide or NH₃.
11. 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 (paragraph 8).

Analysis

Test conducted with one sample size

12. 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.

13. 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 CO₂ 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; etc.) or by vacuum evaporation to dryness of the aqueous extract and spectroscopic (IR, UV, etc.) or AAS/ICP analysis of the residue.

14. 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, e.g., by IR, UV, AAS/ICP, for the notified polymer content. Any components in this residue which are identified as being impurities or additives are to be discounted for the purposes 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.

Test conducted with two different sample sizes

15. All aqueous extracts are analysed for TOC.

16. 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. Next, the filtrate is again centrifuged or filtered. The residues remaining on the filter, or in the centrifuge tube, are dried at 40°C under vacuum and weighed. Drying is continued until a constant weight is reached.

DATA AND REPORTING

Test conducted with one sample size

17. 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 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).

Test conducted with two different sample sizes

18. The individual TOC values of the aqueous extracts of the two triplicate experiments and the average value per 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).

19. 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.

20. 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 soluble and extractable material in the original sample.

TEST REPORT

21. The test report must include the following information:

Test substance:

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

Experimental conditions:

- description of the procedures used and experimental conditions;
- description of the analytical and detection methods.

Results:

- results of solubility/extractivity in mg/l: individual values and mean value for the extraction tests in the various solutions, broken down in polymer parts 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.

LITERATURE

(1) DIN 53733 (1976). Zerkleinerung von Kunststoffergezeugnissen für Prüfzwecke.