Hexafluoroisopropanol (HFIP) and gel permeation chromatography of polyesters and polyamides

Gel permeation chromatography (GPC, also known as size exclusion chromatography, SEC) is a liquid chromatography method that analyzes the molecular weight distribution of polymers. For regulatory submissions on polymers under various legislations around the world, authorities insist on GPC data. Like other liquid chromatography methods, GPC requires that the sample to be analyzed be dissolved in a solvent.

For semi-crystalline polyesters such has PET and PBT and polyamides such as PA6 or PA66, finding a suitable solvent was a challenge. Originally, attempts were made to use phenolic solvents, such as m-cresol, but the high temperatures needed to dissolve the polymers in these solvents leads to degradation of the polymer [1] [2], reducing the molecular weight, creating new oligomers and thus changing the property that GPC is intended to measure.

There are very few solvents that can dissolve these polyesters or polyamides without heating and hydrolytic degradation, namely dichloroacetic acid, hexafluoroisopropanol (HFIP) and trifluoroethanol. [1] [2] [3] [4] Dichloroacetic acid is highly corrosive and thus not compatible with the metals used in GPC equipment. [2] [4] HFIP is preferred over trifluoroethanol because it dissolves a larger variety of polymers. [3]

HFIP is extremely expensive [5], so polymer analysts have striven to minimize its consumption. There have been two approaches to this:

1. **HFIP mixtures with chloroform as eluent**

In this approach, the polymer is first dissolved in a small amount of HFIP and then diluted with chloroform. In one method, the PET solution in HFIP is then diluted with chloroform to 98:2 vol-% chloroform/HFIP and uses the same chloroform/HFIP ratio for the eluent. [1] Other authors first dissolve the polymer in HFIP, then dilute the dissolved sample with chloroform to 94:6 vol. % chloroform/HFIP and use chloroform without HFIP as the eluent. [6] The use of chloroform/HFIP mixtures allows PS calibration standards, but has raised questions about the constancy of conditions during the chromatographic run, as well as making HFIP re-use more difficult. [4]

2. **HFIP as sole eluent**

Since the mid-1990s, most analysts have chosen to use HFIP as the sole eluent. [2] [3] [4] [7] [8] [9] [10] [11] Despite the high cost of HFIP, using HFIP as eluent became affordable because laboratories can re-distill and reuse the HFIP [12] [13] [14][1] and GPC equipment manufacturers developed special columns for HFIP that use small volumes. [15] [16] [17]. The availability of better detectors and PMMA standards also facilitated the shift away from mixed eluents.[2] Most authors using HFIP as eluent add ca. 0.1% of trifluoroacetate salts[3] to the eluent to suppress aggregation of the polymer.

[1] Note that the spinning band columns used for the distillation of HFIP have spinning bands made of PTFE to ensure their chemical and mechanical stability. Please refer to consultation input by equipment suppliers about the importance of the continued availability of PTFE and other fluoropolymers for laboratory and chemical equipment in the EU.

[2] The older PS standards cannot be used in pure HFIP but can be used in the chloroform mixtures with HFIP.

[3] These salts are also PFASs. When the HFIP is redistilled for reuse, they will remain in the sump, which must be collected and incinerated as hazardous waste, “07 01 03* organic halogenated solvents, washing liquids and mother liquors”.

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