

Quality Assurance with Inverse GPC



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Reproducible manufacturing of the pore system is indispensable to many technical applications using porous materials. An adequate system of monitoring production is required for quality assurance of the product. The type and structure of the pore system determine, for example, the accessibility of molecules to the pore system, the speed of the diffusion processes and the available surface area for the application. Classic examples of such applications are adsorbents for liquid chromatography and supports for catalysts and solid phase synthesis. Standard methods for the determination of physical parameters of porous materials (specific surface area, specific pore volume or average pore diameter) are nitrogen adsorption and mercury intrusion [1, 2]. These techniques can be used to measure pores from about 4Å (nitrogen ad-

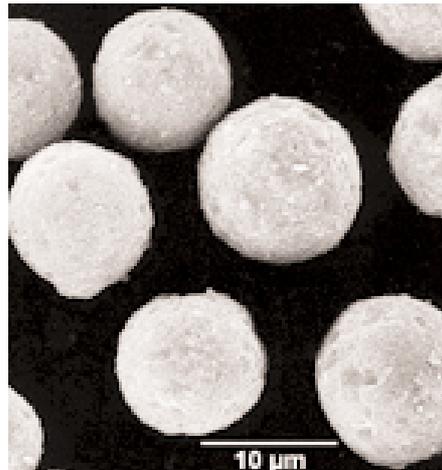


Fig. 1: SEM image of Sachtopore 5µm 100Å

sorption) or 35Å (mercury intrusion) upwards. However, it is generally not possible to draw conclusions on the accessibility of a pore system to larger molecules in day-to-day use, e.g. catalytic reactions on organic molecules or the chromatography of biopolymers. Furthermore, nitrogen-adsorption and mercury-intrusion tests provide hardly any information on the speed of transport processes for molecules dissolved in liquids. Pore ac-

cessibility and the kinetics of transport processes are, however, decisive criteria for the quality and economy of adsorptive separation processes, catalysis and synthesis on surfaces. An ideal complement to nitrogen adsorption and mercury intrusion is inverse gel permeation chromatography (GPC, also often called SEC) described in detail below [3, 4, 5] using Sachtopore (Fig. 1), a material for technical adsorption processes and for liquid chromatography, as an example [6, 7]. Since measurements using inverse GPC are also made in the liquid phase, the results provide information on the pore accessibility and the speed of exchange of substances for chromatographic applications. The method also determines standard properties, of course, such as pore volume, surface area, and average pore diameter.

Principle of inverse GPC

Inverse GPC is used to measure the pore structures in materials which permit rapid substance exchange with the medium. It is a 'dynamic method of measurement', whereby probe molecules of different sizes recognise the pore struc-

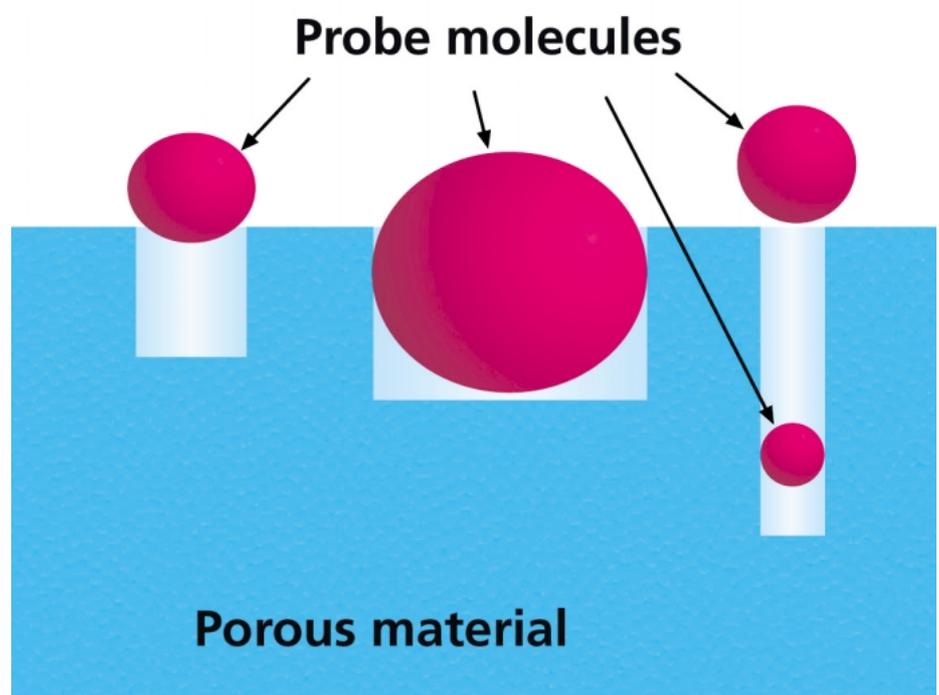


Fig. 2: GPC pore recognition using different-sized probe molecules

Keywords

Inverse GPC, pores, adsorbents, catalysis, chromatography

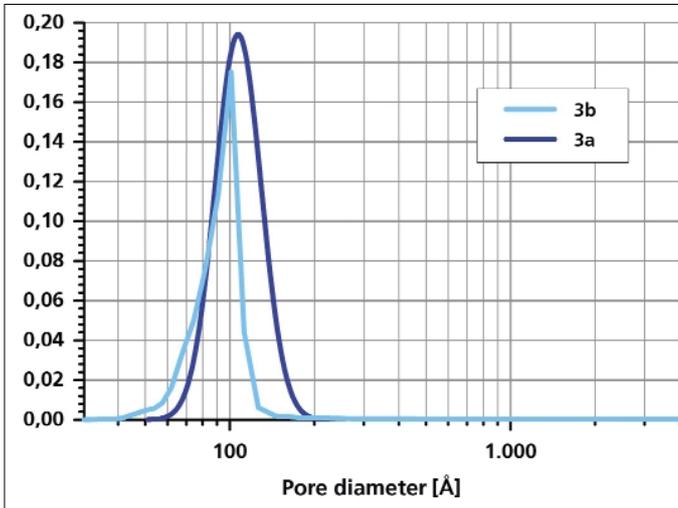


Fig. 3a: Pore size distribution of Sachtopore 5µm 100Å material determined by inverse GPC and calculated by PSS POROCheck. Fig. 3b: Pore size distribution of Sachtopore 5µm 100Å material determined by nitrogen adsorption - Pore diameter

Table 1: Relationship between elution volume and molar mass of the polystyrenes investigated

Molar mass of polystyrene (Dalton)	Elution volume (mL)
1,000,000	1.48
659,000	1.49
67,500	1.49
32,500	1.59
18,000	1.62
9,130	1.76
3,420	1.91
1,620	2.00
374	2.08

Table 2: PSS POROCheck analysis report with the physical parameters of the Sachtopore 5 µm 100Å material

Sample:	Sachtopore 5 µm, 100 Å
Polymer / Solvent System:	Polystyrene / THF
Comment:	Flow: 0.2 ml/min, Column dimension: 4x250 mm
Pore Model:	Slit-like pores
Pore volume and surface area:	
Pore volume fraction $V_p/(V_p+V_g)$:	0.295
Specific surface area:	163.6 ± 13.8 m ² /cm ³
Parameters of the pore size distribution (PSD) function:	
Average transverse pore dimension, $\langle R \rangle$:	12.2 ± 0.9 nm
Width of the PSD, σ :	4.0 ± 2.3 nm
Reduced PSD width, $\sigma/\langle R \rangle$:	0.33 ± 0.2 nm
SEC selectivity parameters:	
Optimal analyte radius:	3.8 nm
Optimal analyte molar mass:	14,300 D
Optimal K value:	0.341
Target size range:	0.85 size decades (1.0-7.4) nm

ture within a few seconds by penetrating to different depths. To make the measurements, the porous material is packed into a chromatography column which is fitted into an isocratic chromatography apparatus. The sample, consisting of probe molecules of different sizes dissolved in the eluent, is delivered to the column via the injection valve. The pump in the chromatography apparatus forces the sample to migrate through the packed chromatography column with the eluent.

The probe molecules of different sizes are transported through the porous material. The small probe molecules are able to recognise or fill the entire pore volume, including the smaller pores. The larger probe molecules recognise only the larger pores, but not the smaller pores. The eluent and the probe molecules are chosen to rule out the possibility of any interaction between the probe molecules and the porous material. The primary data obtained reflect only the dependence of the elution volume on the molecular mass and therefore the known molecular size of the probe molecules. Using appropriate software, these primary data are used to calculate the properties of the pores, which are displayed in graphic form.

When conducting measurements using inverse GPC, the porous materials are permanently saturated with solvent and are partially swollen (for example when using ion-exchange resins). The porous materials are also saturated with liquid when used for separation applications or catalysis. One advantage of determining the pore size with inverse GPC is therefore that it simulates the 'real' situation when investigating porous functional materials. Information on the accessibility of the pore system is obtained, which is an essential criterion in the properties of a product. The measuring range of inverse GPC covers pore sizes ranging

from 9Å to 6,000Å. Larger pores can also be investigated using larger polymer probe molecules. With this method therefore, the pore size range is similar to that covered by nitrogen adsorption and mercury intrusion. A frequently used measuring system consists of the eluent tetrahydrofuran (THF) and different sized polystyrenes as probe molecules. Some polymer-based porous materials swell markedly in THF. Similar aqueous systems are available for such materials, e.g. resins used for the chromatographic investigation of biopolymers. In such cases, polymers based on polysaccharides can be used as standards. The sample is not exposed to excess pressure which is in the range of only a few bar. This means that materials more sensitive to pressure can also be measured reliably and nondestructively. The pressure used for the mercury intrusion method can amount to several thousand bar and can result in destruction of the porous material during analysis. A typical inverse GPC assay involving the measurement of a set of differently sized polymers on a sample of porous material lasts 10 to 30 minutes. The time requirements depends on different factors, such as the flow rate and whether single substances or mixtures are being determined. For comparison: the measuring time for a sample using nitrogen adsorption can last up to 12 hours. With GPC, there is, of course, additional work involved in packing the chromatography column. Unlike analytical chromatography, however, an optimally packed column is not necessary. And, of course, a chromatography apparatus must be available, but these are now standard equipment in chemical companies.

Despite these advantages of inverse GPC in investigating porosity and despite the fact that the method has been known for a long time, not a great deal of use has been made of it. In particular, this can be attributed to the fact

that until recently, there were no user-friendly computer programs for analysis, so it could not be used efficiently. In collaboration with Professor Gorbunov, an expert with impressive credentials in the determination of porosity in the field of liquid chromatography, user-friendly and powerful software has now been developed for the familiar inverse GPC procedure. The Windows-based PSS POROCheck program can be used for direct analysis and provides appealing graphic displays of porosity measurement using inverse GPC. In addition to the pore size, distribution of pore sizes, and the accessible surface area of materials investigated, it is also possible to easily display a wide range of other variables.

Measurement of Sachtopore

Sachtopore, a material based on crystalline titanium dioxide for technical adsorption procedures and liquid chromatography, is a classic example of a porous material with a large surface area. Primary crystals grow together to form a three-dimensional network which gives the material the necessary large surface area and porosity needed for its applications. A standard HPLC column packed with Sachtopore 5µm 100Å was fitted into an isocratic chromatography apparatus (HP 1100). Different sized PSS polystyrene standards with defined molecular masses between 162 and 2,180,000 Da dissolved in THF were then used for measurement.

Further chromatographic conditions were: eluent: THF; flow-rate: 0.2 mL/min; amount injected: 5 µL; sample concentration: 2 mg/mL eluent; detection: UV 254 nm; temperature: 20°C. The data acquisition was done with PSS WinGPC software, Version 6.2. Table 1 shows the relationship between the molar mass of the polystyrenes investigated and the elution volume. Data processing was performed with the PSS POROCheck software

to determine the pore related properties. Table 1 shows that there is a clear relationship between the molar mass of smaller polystyrenes of up to 67,500 Da and their elution volume. Pore recognition occurs here in the manner shown in Fig. 2. The data in Table 1 were entered into the PSS POROCheck software. The pore size, pore distribution, surface determination, confidence interval for the method, and many other variables were directly determined. The resulting pore size distribution curve is shown in Fig. 3a. Fig. 3b shows the pore size distribution curve determined by nitrogen adsorption. The results with the two methods agree very well. The average pore diameter calculated from the nitrogen sorption method was 117Å (calculated from the results of nitrogen adsorption). The average pore diameter based on the layer model determined using inverse GPC was 122Å. The precision of the results, numerically and graphically, was good based on the confidence intervals calculated (Fig. 4, Table 2). The symmetrical error scatter shows that the method was systematically used correctly. The evaluation and the results are therefore plausible. The analysis report produced by PSS POROCheck presents all the results in tabular form (Tab. 2).

Summary

Inverse GPC is suitable for the analysis of both small and wide-pore systems. The measuring range covered of 9–6,000Å is very wide. A significant advantage of inverse GPC analysis is that the measurement takes place under conditions very close to the application. The analysis also provides information on the effective accessibility of the pores to different-sized molecules. The results of GPC analyses can make a significant contribution to the clarification of many so far not completely understood properties of porous materials for cataly-

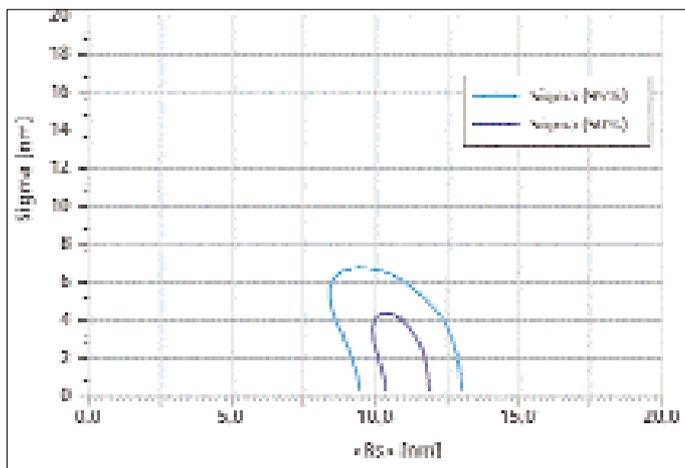


Fig. 4: Confidence interval for the pore size distribution of Sachtopore 5µm 100Å material determined by inverse GPC and calculated by the PSS POROCheck software

sis, separation and solid phase systems. This method is therefore an ideal complement to nitrogen adsorption and mercury intrusion. Further advantages are that the assays are run under low pressure, which means that systems sensitive to pressure can also be tested, as well as the comparatively short duration of the assays. Inverse GPC therefore repre-

sents a rapid method for routine product monitoring and quality assurance in the manufacture of porous materials, especially those for use in chromatography applications.

The software and a suitable set of polymer standards are available in the form of a complete kit. For a small numbers of samples or if a

suitable HPLC apparatus is not available, we can, of course, also conduct measurements under contract.

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