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GPC Streamliner

GPC/SEC Service Center

Analytical laboratories staff, inspectors and auditors know, that the most modern, precise, high quality systems and technical analysis instruments cannot guarantee the accuracy of analytical results. In order to get reasonable data, safe results and correct answers, it's mandatory to validate the systems into a specific and effective operational status. To ensure such a status is preserved, it is necessary to regularly schedule preventative actions such as system check and maintenance.

PSS offers experienced professional services to support GPC/SEC correct answers, system validation, and maintenance. This claim is backed by many years of GPC/SEC educational and practical experience and ability to obtain and maintain the DIN EN ISO 9001:2000 laboratory certification for sample analysis. PSS reliable GPC/SEC procedures and solutions can secure your investment and increase your productivity.

View some examples in this issue of the GPC Streamliner:

- PSS characterization of macromolecules with focus on additives: for all questions around sample analysis
- PSS solutions for users: detailed highly structured procedures for independent validation of GPC/SEC systems and to check your mode of operation.
- PSS GPC/SEC tips and tricks bring useful help to find the optimum sample concentration.

GPC/SEC Data Handling

Intelligent: WinGPC Unity Client Server with compliance pack

GPC/SEC is a powerful method for measuring molar mass averages and distributions of macromolecules in solution, separated according to their size. GPC/SEC fractions can be characterized using online or offline detection methods as viscosity, light scattering, FTIR, MALDI-TOF, or NMR detection. Simultaneous quantification of high or low molecular weight compounds or additives is possible. A hyphenated technique of two coupled separation techniques, (2-dimensional chromatography), is, used when separation according to size is not sufficient. It is a powerful tool for product de-formulation.

PSS contract analysis labs are fully equipped to perform all GPC/SEC separations as well as hyphenated techniques, to characterize macromolecules. Systems are dedicated to different products, applications, solvents, etc, serving our manufacturing efforts, and many industry and academia customers.

PSS specialists produce an ever increasing amount of data, which need to be handled, stored and retrieved

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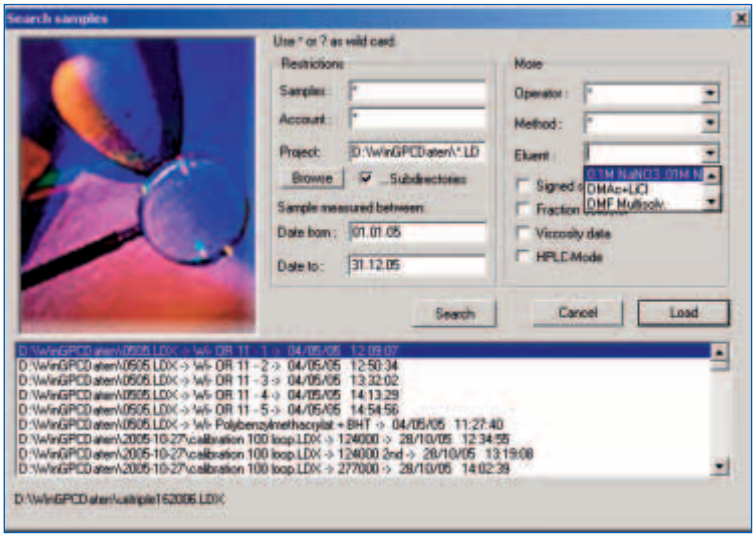
In This Issue

Feature

Catalog for Reference Polymers and GPC/SEC Columns available

GPC/SEC Data Handling



Statistic for all samples analyzed in 2005. The field „Eluent" shows all eluents that have been used during that period. If an eluent is selected, WinGPC shows the number of samples and the sample information of all samples measured in 2005 with this eluent.

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throughout the electronic record archiving period.

How can PSS multi-user, multi-instrument configuration be managed intelligently with convenient and secure, access to instruments, data, and results?

PSS uses a Client/Server installation of WinGPC Unity. All detectors and instruments (resources) are connected to the network and are accessed and administered using the WinGPC Server. Users login on their PC (client PC) with their username and password. Resources in use are marked, while free resources can be reserved to leave time to prepare the samples and the instrument. The documentation is done automatically; WinGPC Unity registers the login and fills the session audit trail with time, date, user, userlevel, and action. The audit trails can be reviewed in WinGPC if users have the corresponding user right, but not edited or changed.

The sample information, raw data, and meta data are saved within a sample database. This database provides fast access to sample information via the convenient search routine and guarantees for exceptional data security. Samples can be directly loaded from the search sample window, to review, re-evaluate or to (re-) print results. The comprehensive sample audit trail logs automatically every access with time stamp, user, userlevel, and performed action as well as changed parameters and reason for change (if required). Electronic signatures protect the electronic record against changes. While temporary changes are possible, e.g. to check baseline influence or calibration influence, they can not be saved, printed, or exported in any way. This approach combines the highest security with enough flexibility for the users. Their workflow is supported and followed while documentation is done automatically in the background.

We also use the WinGPC sample database to evaluate instrument runtime and to perform statistics. By setting the search criteria, WinGPC Unity delivers information about the number of samples per period, per instrument, per solvent, per method, and any combination.

Beside the lab users, the system administrators profit from the Client/Server solution. Updates need only to be installed once. Installation qualification (IQ) and software verification are also requested only on the server, where WinGPC Unity is installed. Backup of the measured data and the methods is also restricted to the server saving time and money. The client PCs must fulfill only minimum requirements regarding the hardware.

A client/server solution therefore allows efficient and effective management of resources, increases data security and integrity and can help to provide timely, secure and correct results with increased traceability.

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Announcement

2005 Instrument Innovation Award for MALLS Detector

PSS proudly presented the 2005 Instrument Innovation Award to Brookhaven Instruments Corporation (BIC) for their molecular weight analyzer. The award ceremony was held at ACHEMA 2006 in Frankfurt. Dr. Daniela Held, PSS marketing manager, presented the PSS 2005 Instrument Innovation Award to Dr. Walther Tscharnuter, BIC R&D director, during a well attended celebration session.

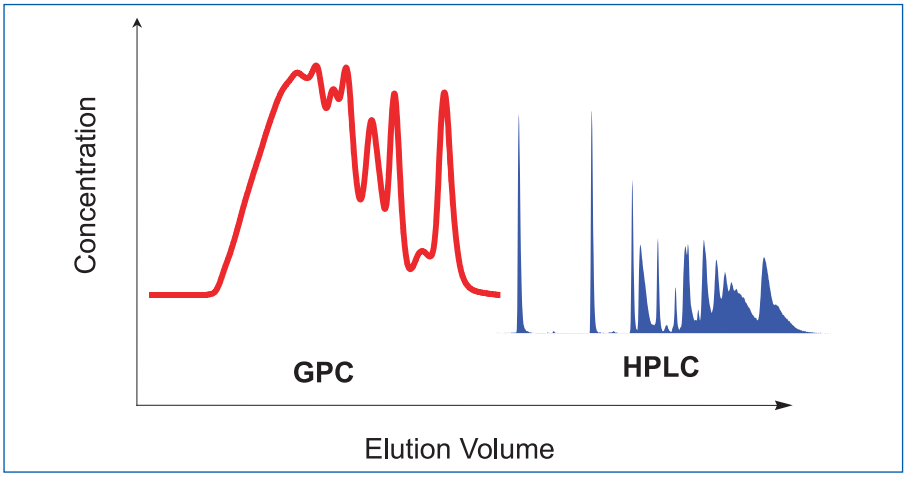
The PSS Instrument Innovation Award was initiated in celebration of the 20th anniversary of the founding of PSS Polymer Standards Service GmbH. The award will be presented to manufacturers of scientific instruments that provide innovation and technical significance in the field of macromolecular characterization.

High Throughput Workshop

The 5th DPI Workshop "Combinatorial and high-throughput approaches in polymer science" took place at Eindhoven, the Netherlands, June 26th and 27th, 2006. Around 150 scientists attended the event. The program consisted of lectures and extensive presentation of experiments in the laboratories of the High Throughput Experimentation Centre of the TU Eindhoven. PSS started a scientific cooperation with the Schubert-Group, organizers of this successful event, in 2005.

For further information contact:
http://www.combimat.org/workshop2006.htm

Additive Tracing



2 dimensional separation of a complexe HALS additive

Very often application problems result from the additives to polymers, not from the polymers themselves. Therefore it's very important to identify and quantify these additives with fast and reliable analyses.

Sample preparation

If the concentration of the additives is in percent (%), it is possible to run a GPC/SEC-FTIR coupling to identify and quantify the polymers and additives directly. However, when the amount of additive is not sufficient for a direct analysis, an extraction of the additives is necessary. To shorten the extraction time the sample has to be pulverized. Previous analyses have shown that the polymer chains will not undergo degradation upon pulverization.

Sample separation, identification and quantification

The extract mixtures have to be separated into individual additives, preferably by GPC/SEC in THF. The GPC/SEC technique has a two fold advantage:

- first the option to use a refractive index detector which allows to detect all the additives, rather than just the UV active additives, and
- second that all additives elute quantitatively from the column (which must not be true for HPLC or GC/MS).

Additionally, unlike Headspace Gas Chromatography (GC), GPC/SEC is a gentle nondestructive LC method. PSS produces GPC/SEC separation columns specially designed for additives.
The identification of the additives, even in traces is done with LC-FTIR coupling according to a patented technique with evaporation of the eluent and separation of the samples on a germanium target.

Search in the PSS additive data base

Many known additive samples are in stock at PSS to be used as reference material during analysis. Their analytical data are collected in a data base, which contains additionally the following parameters: a FTIR spectrum, the GPC/SEC related retention volume and the HPLC retention times with a total of 4 detectors.

5 parameters assure a close identification of additives:

- FTIR spectrum
- Retention volume GPC/SEC
- UV/RI ratio GPC/SEC
- Retention time HPLC
- UV/ELSD ratio HPLC

Identification of complex additives

GPC/SEC, HPLC or GC by themselves cannot separate many additives from complex additive mixtures like the polymeric steric hindered amines (HALS). In this case the online 2-dimensional chromatography (combining GPC/SEC and HPLC) is very helpful.
GPC/SEC in the first dimension separates the molecules according to size and HPLC in the second dimension, according to their chemical behavior. Once the complex mixture is separated, quantification is possible. For unknown substances, the identification is possible when FTIR is coupled to the 2D system's second dimension.

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Innovations

Software and Standards for Membrane Characterization

GPC/SEC is a fast, robust and significant method for the characterization of membranes, especially in their native environment (swelled state). PSS offers now the ability to perform an automated, fast and simple membrane characterization including cut-off and pore size distribution determination. The PSS software, WinGPC Unity with Sieve Curve option comes with a custom-made solution of especially characterized membrane standards. These new PSS membrane standards are featured by a broad molar mass distribution, the molar mass average M_w and M_n as well as the integral molar mass information M_{min}, M_{max} and the corresponding radii of gyration Rg_{min} and Rg_{max}.
The GPC/SEC membrane characterization is accomplished by filtering the sample through the membrane. Depending on the membrane type and quality some smaller molecules can pass the pores of the membrane while others will be retained. The filtered and the unfiltered stock solution are then measured on a GPC/SEC system. The average pore size distribution and the cut-off the membrane is determined automatically by comparing the elution profiles of the unfiltered sample to the filtered fraction.

PSS new Biodegradable High molar mass Poly(L-lactide) Standards

PSS offers an extended Poly(L-lactide) Reference Kit from 150D up to 1.000.000 D. This enables the analysis of most industrial or scientific Poly(L-lactide) samples with one single calibration curve, eliminating the possibility of > 50% error from a calibration with polystyrene molar mass standards. No longer there is a need for universal calibration or additional light scattering measurements to determine the molar mass information for unknown Poly(L-lactide) samples. Polylactides can be measured in Trifluoroethanol with Potassiumtrifluoroacetate on PSS PFG columns.

Evaporative Light Scattering Detector ELS4000

PSS offers a new highly sensitive evaporative light scattering (ELS) detector ELS4000 which provides very low detection limits and an enhanced dynamic range without baseline shifts, even under extreme gradients. Due to a new technology the detector can be operated at low temperatures with different flow rates in organic as well as in aqueous mobile phases. A large touch screen enables the easy control of this powerful detector. It is recommended for separations which require higher sensitivity like 2D chromatography and additive analysis.

System Suitability Test with PSS EasyValid

PSS EasyValid Validation Kit for GPC/SEC System Suitability Test

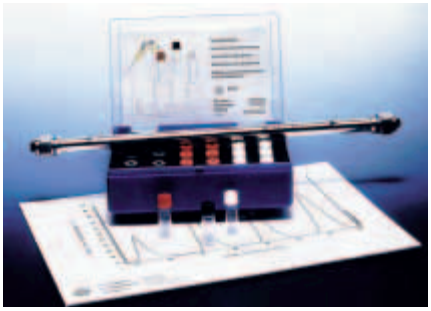
When new GPC/SEC instruments are installed or when single components are replaced, a system suitability test must be performed, to test the reliability and performance of the complete system. This ensures that the system will yield „true“ GPC/SEC results. PSS has therefore developed a dedicated GPC/SEC system suitability test that evaluates the integral system: equipment, electronics, and analytical operations, using the PSS EasyValid Validation Kit. This Kit is designed for the validation of GPC/SEC instrumentation with concentration detectors independently of brand. Wile molar mass sensitive detectors, like light scattering detectors or viscometers, can be left in the system during validation, an additional PSS Visco/LS validation kit is required for their complete validation.

Now available is the EasyValid for THF, while the aqueous system validation kit will be ready in December 2006. The validation can be performed using any GPC/SEC software that supports independent baseline and integration limits and calibration curves with a 5th order polynomial fit. For PSS WinGPC Unity users with Report Designer option PSS offers free report layouts for the automatic result comparison with pass/fail flags directly on the report. In addition, WinGPC Unity import files with the detailed and complete sample information are delivered with the Validation Kit.

The validation itself follows the typical procedures and steps performed for any measurement:

1. Using the kit's validation column attached to the system, a system test is performed and a calibration curve will be established.
2. Certified reference materials, characterized in extensive round robin test, are injected and analyzed.
3. The obtained results are compared with the reference values given, either automatically or interactively.

The validation is successful when the obtained



results for the molar mass averages are within thea allowed range. Besides the GPC/SEC average test, the detailed user documentation offers additional tests to check the raw data quality and the overall performance of the system. Predefined documents for all results help during the validation and allow consistent documentation and tracking.

The PSS EasyValid Validation Kit consists of:

- One PSS Validation column
- Calibration standards and certified reference materials in 1,5ml color coded glass vials
- WinGPC Unity report layouts and import files
- Comprehensive user documentation with detailed examples to support experts or beginners alike

The Validation Kit EasyValid is ideal:

- for checking the system performance after installation
- as part of the OQ/PV (Operational Qualification/Performance Verification)
- for performance review after maintenance
- for review after changing system components
- for verifying the own operations
- for inter laboratory consistence checks
- for identifying systematic errors
- for training new employees

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Knowledge Bank

I have a GPC question ...

Every GPC user knows a situation where somebody has a question on a particular topic and is not sure about the optimum solution. PSS Knowledge Bank offers comprehensive information to registered users of the PSS homepage www.polymer.de:

... for questions about an application: See the application data base.

... if you need help for WinGPC: See many tips in the WinGPC software data base.

... and for an article or GPC Tips and Tricks: See the publication data base.

Upcoming Events

GPC/SEC Training Course

22.03. – 23.03.2007: This training course provides GPC/SEC theory lectures and practical sessions for modern analysis of macromolecules using gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC). It covers the theoretical background of the separation technique, gives practical advice for reproducible and accurate analysis, and shows the application advantages as well as the limitations of GPC/SEC and GPC/SEC hyphenation with light scattering, viscometry and other techniques. In the praxis sessions small workgroups (maximum 5 people) verify a GPC/SEC system, check the performance of the separation column, calibrate, and evaluate samples using different techniques. Each group has its own tutor, an experienced polymer chemist, to discuss also special applications and questions.
Official Language: English

Professional Meetings

16.10. – 18.10.2006: International Conference on Polyolefin Characterization, Houston, TX, USA.

Talk: High Temperature Gel Permeation Chromatography (GPC) Coupling Methods for Complex Polyolefin Applications

Shows and Exhibits

19.09. – 21.09.2006: Analytica China; Shanghai/China
Booth: W2.2562

27.09. – 29.09.2006: Polymeric Materials; Halle/Germany
Poster: The influence of the stationary phase polarity on GPC/SEC separations

16.11. – 18.11.2006: Analytica-Anacon; Bangalore, India

31.01. – 02.02.2007:
SCM3: Third International Symposium on the Separation and Characterization of Natural and Synthetic Macromolecules; Amsterdam, The Netherlands

Talk: Relationship between physical treatment of different starches and their molecular structure determined by GPC/SEC-MALLS

25.09. – 28.09.2007
Ilmac; Basel/Switzerland

Impressum

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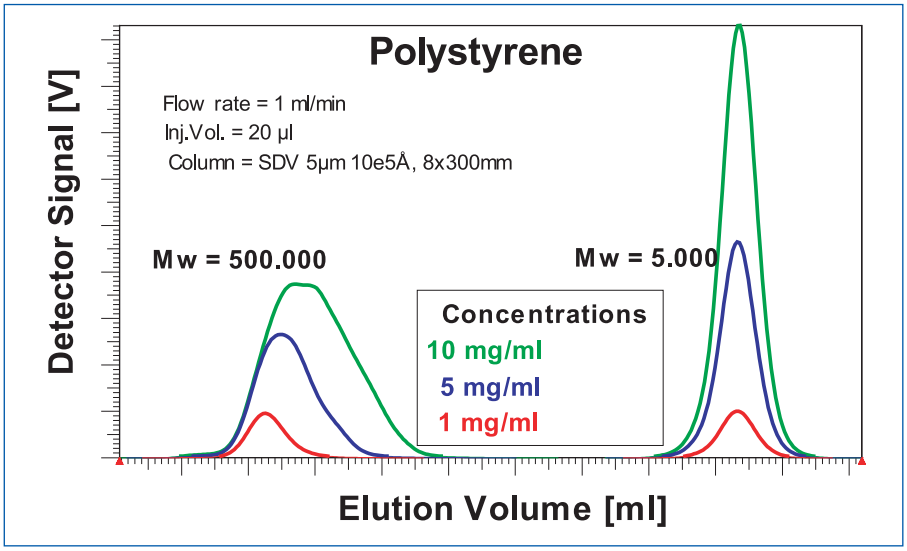
GPC Tips and Tricks



Elution volume as a function of the sample concentration for various molar masses

Sample concentration – an essential analysis part

Larger signals and improved signal-to-noise ratios can be achieved by increasing the sample concentration or the injection volume. However, a large signal is not always the best answer and does not guarantee accurate molar mass determination (as shown in Figure 1).

How do I find the optimum sample concentration and injection volume for my GPC/SEC measurements?

The optimum concentration and injection volume depends on the sample itself. The first find out if the samples are generally high- or low- molecular weight. Since high molar masses lead to high solution viscosities, a high concentration can produce a very viscous injection band, so that the diffusion process on the column can be hindered. When this happens, higher elution volumes are measured, yielding lower molar masses for the samples when they are evaluated with a conventional calibration curve. Even when absolute methods are used (e.g. light scattering) the distribution information gets lost. This problem is less pronounced for low molecular weights.

Usually the recommended GPC/SEC sample concentration for broadly-distributed technical samples lies within the range of 0,1 to 10 g/l, with injection volumes from 2 to 100 µl. In practice, 2-3 g/ sample concentration is sufficient and a good value to start with for broad distributed samples (PDI>1,5) and 1g/l is recommended for small distributed samples like polymer reference materials, i.e., PDI<1,15.

Because of a viscosity effect, the injected mass (injection volume x concentration) affects both the peak position (retention volume) and the peak shape. For a given injection volume, lower the sample concentration until the peak position and shape stay constant. Only the peak area should change as a function of the injected mass or concentration (see illustration).

Alternatively, increase the injection volume if the detector signal becomes too small due to low concentration. This guarantees, that the signal-to-noise ratio is large enough. In cases of extremely high molar masses (e.g. several millions) inject up to 250 µl of sample, at a concentration of 0,1 g/l.

With broadly-distributed samples or small molecules the concentration range can be increased up to 10 g/l without running into the peak shape or peak position trouble. Here the viscosity effect does not play a substantial role.

Result:

- with large molecules use smaller sample concentration and increase injection volume
- with small molecules work with high concentrations and small injection volumes
- choose a large porous column at the beginning of the column combination in order to reduce the viscosity of highly viscous samples at the beginning

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Application

Characterization of Polylactide

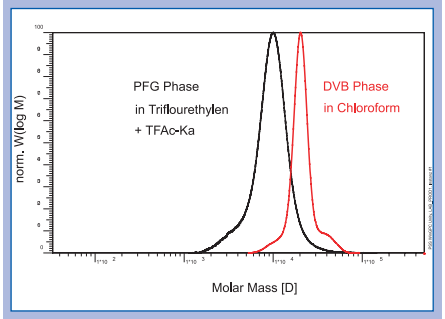
Polylactides are important biodegradable thermoplastic polymers widely used by the biotechnology industry. Polylactides can be processed into films and fibers. Some biomedical applications are sutures, dialysis and drug delivery devices. Polylactides are also used for compost bags, diapers and packaging. For those applications mainly broadly distributed Polylactides are used in molar masses > 100.000g/mol.

Sample Preparation:

The sample was dissolved completely in the solvent, sat for about 24 hours and was filtered through a 0,45µm membrane.

Analytical Conditions:

Eluent: Trifluoroethanal (TFE) with 10g/l Potassiumtrifluoroacetate (KTFAc)
Columns: PSS PFG, 7 _m, 100Å +1000Å, each 8 x 300 mm, + guard column
Calibrants: PSS Poly(L-lactide)-Standards
Data acquisition: PSS WinGPC Unity
Detectors: RI and UV (230nm)
Flow rate: 1 ml/min
Concentration: 1,0 - 3,0 g/l
Inject volume: 20 - 100 µl
Temperature: 25 - 35°C



Results:

The Poly(L-lactide) results depend strongly on the method. The new method, based on PFG columns using TFE with KTFAc added, leads to very robust and interaction free chromatography yielding reproducible chromatograms, a good signal to noise ratio, real molar masses and reasonable distribution information. Under less polar conditions, such as in chloroform on styrene-divinylbenzene based material (an older method recommended when better matching materials were not available) the chromatograms show multimodal distributions or artificial shoulders. Further, Poly(L-lactide) shows interaction with the stationary phase.

Conclusion:

The best suitable GPC/SEC method for the analysis of Poly(L-lactide) is the interaction-free chromatography with PSS PFG gel columns in TFE and KTFAc.