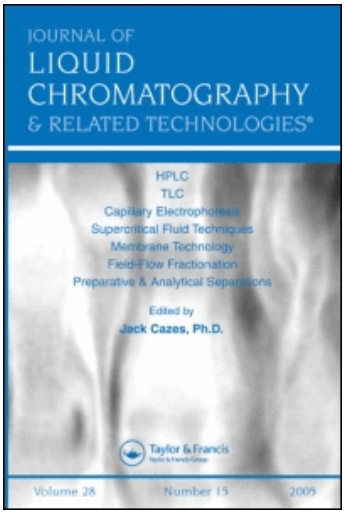

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SPECIAL REPORT

STANDARD PRACTICE OF LIQUID SIZE-EXCLUSION CHROMATOGRAPHY - SEC (GEL PERMEATION CHROMATOGRAPHY - GPC)

by Donald D. Bly, Chairman, ASTM D 20.70.04

Subcommittee D 20.70 of the American Society of Testing and Materials (ASTM) has been active for many years developing standard technology for use with the practice of liquid size exclusion chromatography (SEC), and for the use of specific SEC terms and relationships. This report discusses in an elementary way the ASTM organization and philosophy, the scope of the work of Section D 20.70.04 on liquid size exclusion chromatography, and the accomplishments of the section, its current activities, and its future plans.

The ASTM is a nonprofit organization formed for the development of standards on the characteristics and performance of materials, products, systems, and services and for the promotion of related knowledge. Standards include test methods, definitions, recommended practices, classifications, and specifications. There are more than 130 ASTM technical committees which cover prescribed areas of materials or technology, and committee members include producers, consumers, and generally interested personnel. Each committee is open to all interested people and elects its own officers whose activities are subject to Society regulations. One of the important phases of committee activity is to generate new standards which are adopted only after testing in the workplace and after surviving a multi-tiered balloting process. As in any domocratic organization, the voting privilege must be exercised responsibly for the Society to fullfill its mission. Copies of information on ASTM and the voluntary standardization system, the by-laws on technical committees, and information on regulations governing ASTM technical committees can be obtained from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pa. 19103.

Since about 1968 Section D 20.70.04 has been concerned with standardizing the practice of gel permeation chromatography and with standardizing the use of related terms and relationships. Historically, the technique to be discussed has been known as gel permeation chromatography (GPC), and much of the past and current literature use this nomenclature. However, the ASTM group now recommends liquid size-exclusion chromatography or size exclusion chromatography (SEC) as the preferred and more properly descriptive term. In fact, the name of Section D 20.70.04 is the Section on "Liquid Size-Exclusion Chromatography."

Several standard methods on SEC have been successfully balloted and are now in Part 35 of the Annual Book of ASTM Standards. This Annual Book of ASTM Standards is revised yearly to include all editorial or balloted technical updates to the existing methods.

Included in Part 35 are:

1. The Standard Practice for use of Liquid Exclusion Chromatography Terms and Relationships. D 3016-78.

2. Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by Liquid Exclusion Chromatography (Gel Permeation Chromatography - GPC). D 3536-76.

3. Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Certain Polymers by Liquid Exclusion Chromatography (Gel Permeation Chromatography - GPC) Using Universal Calibration. D 3593-77.

Section D 20.70.04 has also been responsible for the generation of two literature bibliographies, and a third is under development. These pamphlets can be purchased from ASTM under: Bibliography of Liquid Exclusion Chromatography (Gel Permeation Chromatography) AMD 40, and Bibliography of Liquid Exclusion Chromatography (Gel Permeation Chromatography), AMD 40-S1. Bibliography AMD 40, published in 1974, was intended to include all the GPC/SEC literature prior to 1972. The first supplement of about 800 references, AMD 40-S1, was published in 1977 and includes all of the literature 1972-1975 inclusive, while the similar second supplement will include all the literature 1975-1978 inclusively; it will be published in 1979-1980. Both the original bibliography and the supplement -S1 are divided into 8 subject categories, and both contain a permuted title index and an author index for easy search purposes. These bibliographies are very valuable to workers in gel permeation chromatography, but they do not include significant numbers of references to gel filtration chromatography work. Further description of these bibliographies and of the SEC technique including gel filtration are in a new book by Yau et al. (1)

Besides reviewing and updating the existing standard methods and bibliographies, Section D 20.70.04 currently is active in developing a standard high temperature SEC method for polyofefins. The committee is also working to develop a standard method of high-performance size exclusion chromatography and also has task groups working on measurement problems such as base-line definition, curve cutting, statistical significance of data, analysis of copolymers, the use of special detectors, and the use of bimodal columns. While not all of these studies will lead to separate standard methods, the participants in the task groups, and in the section, benefit from the exchange of technical information needed to solve these problems. When a consensus solution to a problem is obtained, it is balloted and ultimately incorporated into the appropriate standard method(s) during the annual revision process. Consequently, users should constantly refer to the latest edition of the Annual Book of ASTM Standards for a method of choice.

In 1968,the original ASTM section on "gel permeation chromatography" undertook to write one standard, general GPC method, but the approach was abandoned. Great difficulties arose in the treatment of polymers, solvents, and chromatography in general terms. Many polymers require specific solvents, hign or low temperature limits in handling, specific dissolution and filtration procedures, etc. for their subsequent analysis by size exclusion chromatography, and the list of options became too great for a general method to have meaning. Therefore, the section reorganized itself toward the development of specific standards, such as those listed above. The philosophy is that the user of SEC can adopt the principles illustrated by the method and use those principles for a polymer of specific interest.

Methods D 3536-76 and D 3593-77 are similar in format. The more general universal calibration method was created after theory and technology were sufficiently developed to justify the approach. The method is divided into sixteen sections or parts, the first five of which are concerned with the Scope, other Applicable Documents, a Summary of the Method, the Significance and Use of such a method,and Units and Symbols used in the method. The Scope begins, for example, by stating that the method ".. covers the determination of molecular weight (MW) averages and the distribution of molecular weights for linear, tetrahydrofuran-soluble macromolecules by liquid exclusion chromatography (GPC) using the principles of Universal Calibration..". The other sections which follow make up the rest of the method,and their titles generally are self explanatory:

Apparatus Used
Column Specifications

Preparation of Apparatus
Preparation of Sample
Procedure (Chromatographic)
Calibration
Data Acquisition
Calculation of Molecular Weight Averages and Distributions
Evaluation of Axial Dispersion (Curve Broadening Errors)
Report
Precision and Accuracy

The method is written as far as possible in general terms and no one manufacturer's columns or chromatographic equipment is specified. However, performance requirements are specified. The general approach is based on traditional GPC methodology, 4 ft. Styragel columns and the Waters Associates Model 200 Gel Permeation Chromatograph. This approach was taken because at the time the method was under development only Waters equipment was readily available commercially. However, it was anticipated that alternative columns and equipment would become available. As described below, Section D 20.70.04 is now working on a new high-performance method to exploit recent technological developments and to provide additional alternatives to column and equipment selection.

While the reader is referred to D 3593-77 for details concerning the above sections of the method, a comment about Precision and Accuracy is in order. In the method (1977 version), it is stated that while the precision of the method could be established, the accuracy could not be proved since literature data (k & a values of the Mark Houwink equation) must be used for calibration. It was later realized that the accuracy of the method could be established by comparing SEC-computed intrinsic viscosities and measured viscosities for a series of different polymers. This approach has now been demonstrated. By round robin testing seven different polymer types in 8 different laboratories, it was established that using this method and appropriate k and a values, the SEC-computed intrinsic viscosities agree in all cases with the measured values within experimental error. These results indicate the method to be applicable and accurate for: polycarbonate, poly(methyl methacrylate), poly(octadecyl methacrylate), poly(vinyl acetate), poly(vinyl chloride), polychloroprene, and polystyrene. This information will be incorporated into method D 3593-77 when approved via the ASTM balloting process.

As technology has progressed, it has become possible to perform more accurate molecular weight analyses by size exclusion chroma-

tography in shorter and shorter time periods. (See Reference 1.) Equipment has been developed to use higher pressures, lower dead-volume components, and shorter, small-particle columns. Because of these developments, the standard methods (listed early in this report) will gradually become outdated. Thus, Section D 20.70.04 is currently working to define the scope of a high performance method.

During a recent meeting of one of the D 20.70.04 Task Groups, a rough draft of a working scope was developed for use in setting up a high performance SEC method. Since this development is a current activity of the group, the reader should be aware that the final method may contain alterations to this scope. Nevertheless, the preliminary scope is cited here so that the reader can learn of the current activities of the group.

Preliminary scope: the section will develop a high performance method for poly(methyl methacrylate) using universal calibration with polystyrene standards. Using this approach there will be no specifications on calibration curve shape,and the single broad standard calibration concept can be introduced and used; this approach has not been employed in previous methods. The specific resolution (Ref. 2) expressed as Rs_{10} is to be greater than 1.8 for polystyrene throughout the range 5×10^3-2×10^6 molecular weight, and it is to be obtained in less than 30 minutes, i.e., for anywhere in this MW range, for a pair of polystyrene standards one decade apart in MW, the resolution, Rs_{10}, generated in 30 minutes or less should be 1.8. Secondly, a performance specification will be made as follows: the calibration curve should be defined with polystyrene standards; then, the chromatograms for those standards should be integrated and the $\bar{M}_w$ calculated. The respective $\bar{M}_w$ for each standard should deviate by $\leq$ 5% from the reported value. In those molecular weight regions of the polystyrene calibration curve where the deviations do consistently exceed 5%, the calibration curve should not be used for unknown samples (e.g. even for calculating the PMMA calibration curve).

In the future,the scope will also include automated data handling procedures, but how these will be specified has not yet been determined. The general format of the high performance method will follow the format of D 3593-77, but several new sections will be added to account for new technology and procedural sophistication. The final draft of the method will be round-robin tested by task group members using standard ASTM procedures, and a precision and accuracy statement for the method will be included in its final form.

It is hoped this report brings to focus some aspects of ASTM procedures and the attendant democratic process used for developing

consensus standards. It is further hoped that the report will encourage the use of specific, standardized SEC procedures in the laboratory.

References

(1) Modern Size-Exclusion Chromatography (Practice of Gel Permeation and Gel Filtration), W. W. Yau, J. J. Kirkland, and D. D. Bly, John Wiley and Sons, New York, 1979.

(2) W. W. Yau, J. J. Kirkland, D. D. Bly and H. J. Stoklosa, "Effect of Column Performance on the Accuracy of Molecular Weights Obtained from Size Exclusion Chromatography (Gel Permeation Chromatography)," J. Chromatogr. 125, 219-230 (1976), Equations 6 and 7.