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HYDRODYNAMIC CHROMATOGRAPHY: PRACTICAL APPLICATIONS

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Introduction

Either in research, the control or the production of chemicals, or during general observations in biochemistry, characterization is a primary necessity. Depending on the product, the nature, structure, size, shape, and molecular weight are some of the important parameters to be measured. For instance, the molecular weight distribution of polymers and particle size of latex/colloids (MWD and PSD, respectively) have to be known so that they can be correlated with properties. The data may be obtained using many techniques. These techniques are governed according to the various properties of a material and depend on the size range of the investigated material. Hydrodynamic chromatography (HDC) is one of these techniques and has found applications for sizing soluble or dispersed solid components. This article will discuss the size distribution of organic latex particles from the theoretical and practical points of view. Progress in packing columns with fine materials or in the use of fine capillary tubes has allowed rapid separation of species with high resolution. A second field of interest is polymers in solution. The combined effects of hydrodynamic and exclusion chromatography have extended possibilities for the separation of high-molecular-weight materials.

Hydrodynamic chromatography is used for diameter determination in the micron range (some nm to some μm). It will work for both solid and soluble samples, which are eluted according to their decreasing size. This leads to a visual picture of the size distribution. The main interest of HDC lies in the rapid separation (fractionation, which is an alternative name for this method: HDF) of the liquid or solid components present in the sample. Often low peak capacity and poor resolution are its limitations and involve the necessity for peak dispersion correction. Moreover, a quantitative study requires a double calibration. The first relates to elution volume and diameter of the analysed particles; the second gives a correspondence between the signal intensity and size of particles. This intensity depends on the nature of the detector and the operating conditions, for instance the choice of wavelength in UV. As an example, **Figure 1** shows the different absorbance curves of polystyrene (PS) latexes of different sizes. **Figure 2** shows the change in absorbance and scattering with wavelength and illustrates different peak contributions of PS particles to the chromatogram.

HDC operates similarly to size exclusion chromatography (SEC) and field flow fractionation (FFF), but needs one (inert) mobile phase and one (hydrodynamic) field only. The interesting principle of particles separation is the difference in their transport rates in a capillary, related to their location in the eluent. Large particles are preferentially in the centre of the capillary, where the flow rate is max-

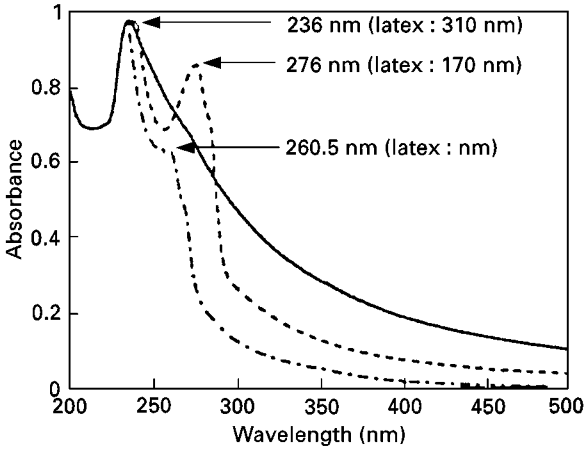

Figure 1 UV absorbance curves for polystyrene latex particles. (Reprinted from Nagasaki S, Tanaka S and Suzuki A (1993) Fast transport of colloidal particles through quartz-packed columns. *Journal of Nuclear Science and Technology* 30(11): 1136–1144.)

imum, so they are eluted faster than small ones, which are closer to the wall of the capillary, where the flow rate is zero. The ratio of the highest elution volume for a small molecule – called a marker – to that of a given particle is the separation factor (R_f). Besides the simplicity of the process, secondary advantages are the rapidity of measurement performed directly on the untreated medium and ease of operation of the equipment. Variation of operating parameters (flow rate, nature of eluent and additives, size of the capillary, etc.) allows a considerable range of possible applications. Chromatography is performed on two types of columns, open capillary or packed, where the interstitial space defines the channels. The use of very small particles (diameter 2 μm) or fine capillaries (diameter 4 μm) allows a high resolution. Relatively short capillary columns (3 m) lead to a rapid and efficient separation (5 min), as shown in **Figure 3** for monodisperse polystyrene latexes.

This article focuses on the main applications of HDC and which are under constant evaluation. There is no effect of density and no limitation on the nature of the sample, but most studies are related to the field of polymers. Since there is no solvent limitation (soluble samples) or no solubility condition (solid samples), all polymer families have been examined. Most of the applications are relative to synthetic organic colloid separation in latex production and diameter measurements for quality control. As mentioned above, interesting perspectives are apparent by combining HDC and SEC with porous packings.

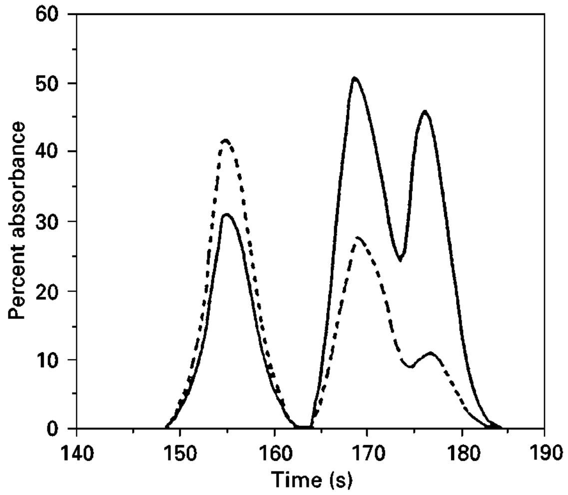

Figure 2 Effect of wavelength (——, 220 nm; - - - -, 254 nm) on the chromatogram of a trimodal mixture of polystyrene latexes (357, 176, 109 nm) on a capillary column 2 m × 4 μm, ionic strength 1 mM. (Reprinted from Dos Ramos JG and Silebi CA (1990) The determination of particle size distribution of submicrometer particles by capillary hydrodynamic fractionation. *Journal of Colloid and Interface Science* 135(1): 165–177.)

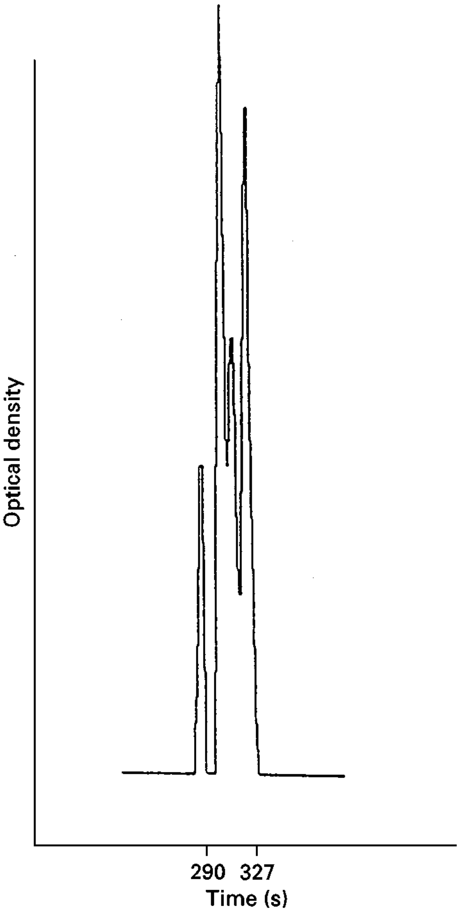

Figure 3 Fractogram of a mixture of four samples of Dow polystyrene latex of diameters 357, 234, 176 and 109 nm. 0.1 mM SLS, capillary 3 m × 4 μm. (Reprinted from Dos Ramos JG and Silebi CA (1989) An analysis of the separation of submicron particles by capillary hydrodynamic fractionation. *Journal of Colloid and Interface Science* 133(2): 302–320.)

Applications in Polymer Chemistry

Colloids/Latex

Some methods of polymer synthesis offer the possibility of preparing polymers with a defined average molecular weight with a narrow distribution (anionic initiation or modern controlled free-radical polymerization). This is important since some polymer properties are dependent on molecular weight and its distribution.

For certain applications it is the size which is the key parameter. For instance, it is the particle size which is important for rheological properties, film formation or protecting ability in relatively low-cost industrial coatings such as aqueous-phase paints and inks. Latexes of small particles have a lower viscosity than those of larger particles with the same percentage solids. They also have a better storage stability against sedimentation and further aggregation. In other applications, these 'water-borne' particles may also be high-value colloids for model compounds and reference materials. For instance, they are used as standards for calibration (membranes) or for packing chromatography columns. Surface modification allows many applications in biochemistry for diagnostic aids and purification. It is thus evident that accurate monitoring of diameter is important.

These particles are obtained in the free-radical emulsion polymerization heterogeneous process. Their diameter is around 100 nm, which can be dealt with in HDC. This process tends to be substituted by bulk and organic solvents processes, in order to reduce the use of solvents in the production of polymers. General interest in these particles is 'triple' fold: their regular and spherical shape, and the possibility of obtaining a predetermined diameter of a given value. This diameter does not depend on mechanical treatment, such as milling and sieving, but depends on the chemical and thermodynamic values of the process: size measurement is a way to determine the polymerization mechanism in relation to these parameters.

Polymerization kinetics As has been mentioned, a major use of HDC is related to colloids obtained by emulsion polymerization, a process which allows simultaneous high-polymerization rates and high-molecular weights. The rapidity of the HDC measurement is compatible with kinetic studies and monitoring during the polymerization. Eluted fractions may be characterized further by transmission electron microscopy (TEM) and analytical centrifugation to verify the effective existence of detected particles and to obtain a calibration curve. Photon correlation spectroscopy (PCS) may be used for a simultaneous rapid analysis.

A normal emulsion system can be depicted as follows: a large fraction of the monomer is in large droplets (diameter around 1 μm); a small part of the monomer is dispersed in the aqueous phase either as an individual soluble molecule or as small aggregates stabilized by the surfactant, and called micelles (diameter around 5 nm). Various ionic and nonionic surfactants are used, besides steric ones, which are not as sensitive to electrolyte and pH effects. The initiator is in the aqueous phase: it is decomposed to active radicals by thermal activation or redox reaction. The primary radicals may add to soluble monomers molecules to form oligoradicals and/or enter into the micelle to give active particles. This is the first step of the polymerization up to a conversion of 5–10%: initiation or nucleation. The second step is the growth of these particles by consumption of the monomer contained in the large droplets. The number of particles remains constant up to 90% conversion, but their size increases. The rate of polymerization is constant during this second step. This rate (R_p) and number of particles (N) are governed by the concentration of monomer (M), initiator (I) and surfactant (S):

$$R_p = k_p\,[\mathrm{M}]\,N/2 \quad \text{and} \quad N[\mathrm{I}]^{0.4}[\mathrm{S}]^{0.6}$$

k_p is the propagation rate constant.

Measurement of conversion and of particle size allows determination of the number of particles. A constant number of particles and an increase in their size are observed. The values may be correlated to concentration. Exponents may differ to those expected in the classical scheme, where particles are spherical and uniform in size. Some deviations may occur, such as additional nucleation by coagulation of precursor particles generating new particles and a second size distribution. They are of lower stability and have a slower rate of polymerization. Large aggregates may be formed by association of particles, as a result of insufficient stabilization. This leads to a broad or multimodal size distribution.

When industrial processes are discontinuous, the particles size of successive batches may differ. In order to correct this and obtain a constant quality, several batches are blended to deliver a uniform size distribution, corresponding to specific properties. Instead of performing physico-chemical measurements (rheology, surface tension) and end use tests, HDC is a rapid means of diagnosis.

Most of the literature on HDC is related to the separation of latexes. Conditions of elution – particularly the ionic strength – affect the separation, but the surface charge density of the particles does not affect the separation factor. In contrast with polymers, the shear rate has little or no effect on particle size characterization. No deformation occurs when the particle is relatively rigid.

Modification of latexes To obtain large size latex, colloids obtained in a first step are polymerized further: successful results have been obtained with the method of Ugelstad.

Latexes are reactive to an extent depending on their stability. For instance, changes in size by the swelling of carboxylated styrene-butadiene latexes has been measured, according to changes in pH.

Flocculation of colloids in the presence of water-soluble ionic polymers or inorganic oxides has been observed by HDC in relation to other methods. Association of particulates under the effect of a thickener has been clearly demonstrated, though this association can be broken by intensive shear, and the same applies to aggregates.

Mini-emulsions

Mini-emulsions are oil droplets (50–500 nm) in water, stabilized by a surfactant (such as sodium lauryl sulfate) and a co-surfactant, which may be a long-chain alkane or a fatty alcohol with low water solubility. Their action is to reduce the oil diffusion from smaller to larger droplets. These mini-emulsions may also constitute an interesting polymerization system. Their stability depends on the relative concentration of components. An exponential decrease of droplet size has been observed when the concentration of cetyl alcohol is increased. The effect of the nature of the co-surfactant and ageing time has been studied. **Figure 4** shows chromatograms of a mini-emulsion at different times, corresponding to size differences: increase of diameter and decrease of dispersity occurs when cetyl alcohol is used. This is not observed when hexadecane is the co-surfactant.

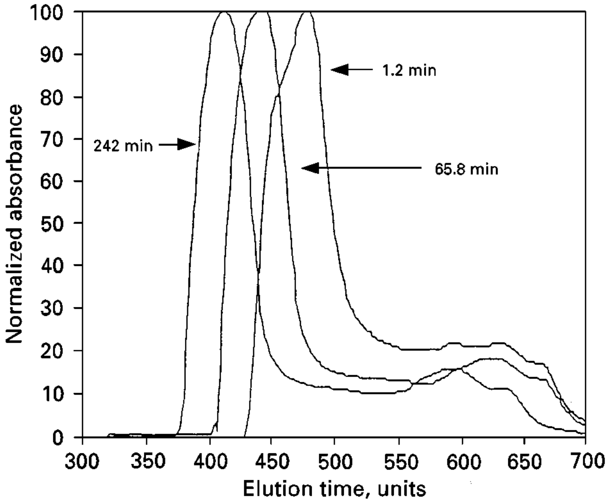

Figure 4 Fractograms at three different times for a toluene mini-emulsion prepared from a gel phase consisting of 10 mM SLS and 30 mM cetyl alcohol. (Reprinted from Miller CM, Venkatesan J, Silebi CA, Sudol ED and El-Aasser MS (1994) Characterisation of miniemulsion droplet size and stability using capillary hydrodynamic fractionation. *Journal of Colloid and Interface Science* 162: 11–18.)

Polymers

Dimensions of soluble polymers depend on molecular weight, nature of polymer, solvent type and temperature. A linear polymer is represented by an ideal random coil of a flexible chain, the radius of gyration being r_g. For actual polymers, requirements mean taking account of bond angles, hindered rotations and short-range intrachain interactions. Since polymer segments occupy space, this generates an 'exclusion volume', corresponding to an increase of dimensions; however 'unperturbed' dimensions, $\langle r_g^2 \rangle_0$, do not take solvent into account. Both interactions between the chains and between chain and solvent modify r_g. In a 'poor' solvent, these unperturbed dimensions mean that square of the radius of gyration $\langle r_g^2 \rangle_0$ is valid, since the polymer sphere is poor in the solvent. But in a 'good' solvent, it becomes $\langle r_g^2 \rangle = \alpha^2 \langle r_g^2 \rangle_0$, due to the expansion of the coil by the internal solvent molecules. For a given polymer, the unperturbed dimensions depend on solvent and temperature, corresponding to the θ conditions of Flory, with $\alpha = 1$. In these conditions, the a exponent of the Mark–Houwink viscosity law $[\eta] = KM^a$ is 0.5. Finally, applying classical theories of polymers in solution allows a relationship between size and molecular weight to be obtained. But the question is: what radius is to be considered in a chromatography experiment? In other words, is the apparent radius obtained in HDC a useful answer? Viscometric measurements show that polymer chains behave rather as non-free-draining (solvent immobilized in the interior of the chain) rather than a permeable coil. This means that the hard-sphere model is a reasonable approach. It may be represented by the hydrodynamic radius r_h, the value of which is about $0.7\, r_g$.

Polymer molecules which are in a laminar flow near the wall in a tube are in a high stress domain and can be elongated and oriented. Those in the centre of the tube are in a low stress region, so that they differ in entropy. The entropy gradient in the tube leads to a migration of the molecules away from the wall, called 'stress-induced diffusion'. This is favoured by a high flow rate, small tube diameter and high molecular weight. A second feature is a result of elongation: the cross-section of the chain is decreased and the molecule is eluted later. A third factor may affect the elution time: the fluid inertia induces a radial migration of the molecules towards an annular region of equilibrium, which is about at 0.6*R* (*R* is the capillary radius) of the centre of the tube (also called the 'tubular pinch effect'). This is more effective in capillary tubes than in packed columns.

Excellent results have been obtained for the separation of numerous polymers in solution, on columns packed with very small non-porous silica particles. As an example, a set of four polystyrenes (molecular weight differing by a ratio of 2) in THF was fully separated in less than 2 min (**Figure** 5). Two sets of polybutadienes (PB) and polyisoprenes (PIP) in THF at a lower flow rate were completely separated in 11 min. The maximum separation factor was about 1.3. An experimental calibration curve (molecular weight as a function of R_f) may be obtained for each polymer and fits theoretical predictions. A universal calibration curve is obtained when plotting relative size (chain radius r_p/R) as a function of $1/R_f$ (**Figure** 6). Alternatively, this means that different polymers of similar molecular weight may be separated, as shown in **Figure** 7. Other solvents of different thermodynamic properties are dioxane (PS, PB, PIP), toluene, methanol, ethyl methyl ketone and acetonitrile (PMMA), used in θ conditions (minimum interactions between chain and solvent, for a minimum coil size). The polymer size is effectively decreased, and the elution time is very sensitive to small changes in temperature around θ.

Combined HDC and SEC fractionation has been shown to expand the elution scale and allow complete separation of a wide range of polystyrenes, using porous silica (**Figure** 8) and polymeric packings. This offers interesting possibilities for elution of very high-molecular-weight materials. The

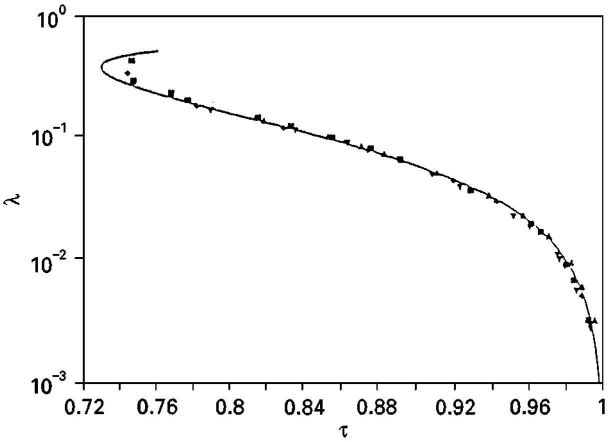

Figure 6 Universal calibration curve: $\lambda = r_p/R$ and $\tau = 1/R_f$. (Reprinted from Stegeman G, Kraak JC, Poppe, H and Tijssen R (1993) Hydrodynamic chromatography of polymers in packed columns. *Journal of Chromatography A* 657: 283–303.)

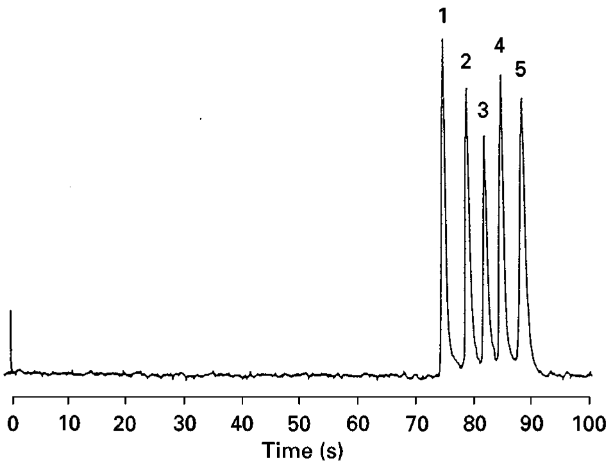

Figure 5 High-speed HDC of polystyrenes (1: 775 000; 2; 336 000; 3: 127 000; 4: 43 900; 5: toluene as marker) dissolved in THF on a column 150 × 4.6 mm, packed with 1.50-μm nonporous silica particles. UV detection. (Reprinted from Stegeman G, Kraak JC, Poppe H and Tijssen R (1993) Hydrodynamic chromatography of polymers in packed columns. *Journal of Chromatography A* 657: 283–303.)

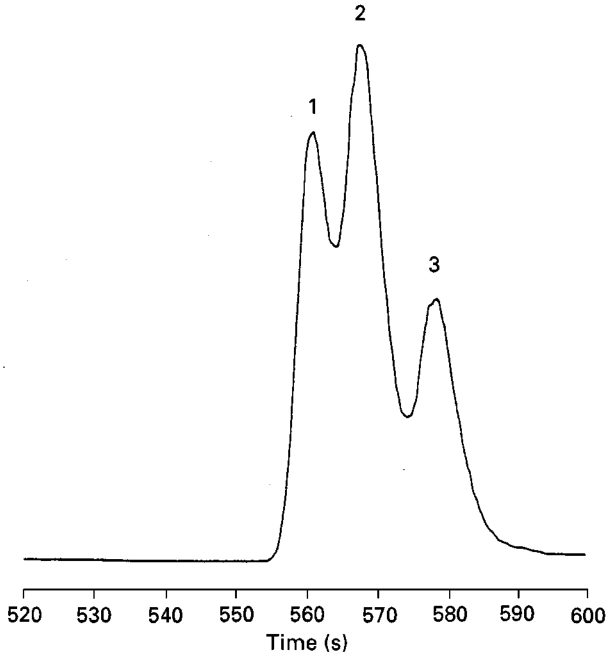

Figure 7 Three different polymers of similar molecular weight in THF. 1: PB 330 000; 2: PIP 295 000; 3: PS 336 000. (Reprinted from Stegeman G, Kraak JC, Poppe H and Tijssen RJ (1993) Hydrodynamic chromatography of polymers in packed columns. *Journal of Chromatography A*, 657: 283–303.)

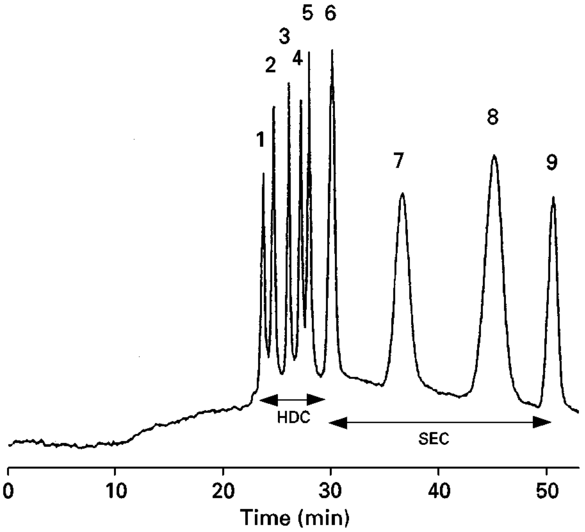

Figure 8 HDC–SEC separation of polystyrenes (10^{-3} molecular weight 1: 4000; 2: 2200; 3: 775; 4: 336; 5: 127; 6: 43.9; 7: 12.5; 8: 2.2; 9: toluene as marker) on three columns of 15 cm each, packed with Hypersil 3-μm porous particles. (Reprinted from Stegeman G, Kraak JC, and Poppe H (1991) Hydrodynamic and size-exclusion chromatography of polymers of porous particles. *Journal of Chromatography* 550: 721–739.)

calibration curve on silica (**Figure 9**) clearly shows HDC and SEC domains (higher molecular weight and steeper slope for HDC). With narrow-pore cross-linked polystyrene, only one classical sigmoidal SEC curve is obtained.

Some authors have attempted to determine molecular weight or size for very large polymers, for instance water-soluble ones, which are used as viscosifiers in oil-recovery wells. The porous structure induces converging and diverging flow channels, where polymer solutions have non-Newtonian behaviour. At high flow rate, under pressure and passing through small pores, polymer coils may undergo chain extension and orientation which modify their size and viscosity.

Flow and dynamic behaviour of flexible and rigid macromolecules in a packed bed has been studied comparatively. Partially hydrolysed (10%) polyacrylamide (molecular weight higher than 12 million) was a flexible model of a random coil, xanthan polysaccharide (molecular weight over 2 million) a model for a rigid backbone and tobacco mosaic virus as a rodlike structure (length 0.7 μm, diameter 15 nm). They have been eluted on a column packed with an ion exchange resin (diameter 11 μm). Deformation of the initial flexible linear polymers occurs, since their apparent size changes with flow rate, at a value corresponding to unity for De, the Deborah number, defined as the ratio of hydrodynamic forces to Brownian forces. The polymers which have been strongly sheared or sonicated before the chromatographic analysis do not show this change in size, since the chain has been extensively broken. The effective size of rodike polymers decreases when the flow rate increases: this is accounted for by orientation. For xanthans, two domains are observed when the flow rate increases: constant size, then a decrease after a flow value corresponding to the chain elongation (**Figure 10**). The slope (−0.5) of the high flow rate region fits that of the dumbbell model. Xanthan

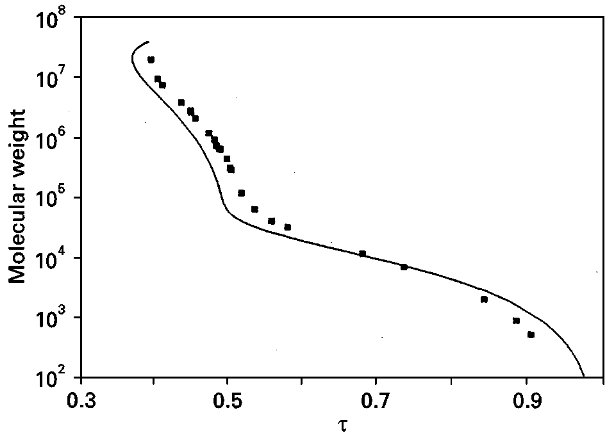

Figure 9 HDC–SEC calibration graph (molecular weight as a function of the ratio of the solvent to polymer migration velocity) with polystyrene on three columns of 15-cm each, packed with Hypersil 3-μm porous particles. (Reprinted from Stegeman G, Kraak JC and Poppe H (1991) Hydrodynamic and size-exclusion chromatography of polymers on porous particles. *Journal of Chromatography* 550: 721–739.)

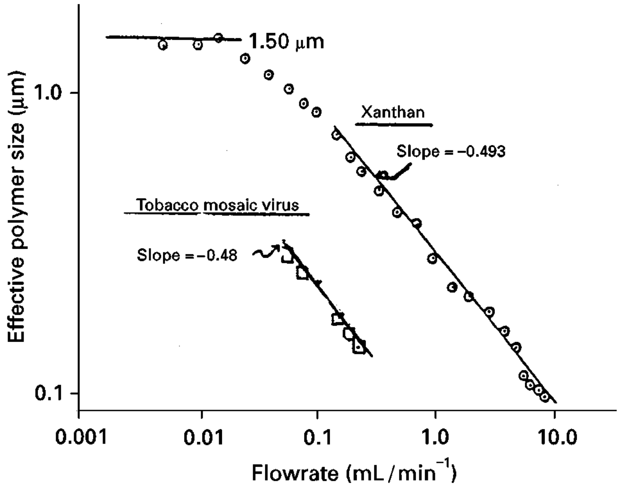

Figure 10 Effective size of xanthan and tobacco mosaic virus as the flow rate is varied in a column 248 × 10 mm packed with 11-μm ion exchange particles; eluent with 2 g L^{-1} nonionic surfactant and 2 mM NaN_3. (Reprinted from Hoagland DA and Prud'homme RK (1989) Hydrodynamic chromatography as a probe of polymer dynamics during flow through porous media. *Macromolecules* 22: 775–781.)

polysaccharide behaviour has also been studied on nonporous SiC particles.

Biomaterials

Biomembranes are efficient separating materials. They are found in cells and are an excellent model for synthetic chemistry. They have many applications such as the separation of enantiomers, isotope enrichment, photosynthesis, and catalysis. Liposomes are used as drug-delivery systems and membranes, so their size and the amount of the transported material are important factors. Elution of liposomes from egg yolk lecithin has been performed on a column packed with porous inert glass, at different ionic strengths. An equivalent capillary radius R is given by the formula $R = d/[2 - 2(2 - R_f)^{1/2}]$, where d is the diameter of a colloidal particle, known from calibration with polystyrene standards. Recycling of the sample improves the separation (**Figure 11**).

Separation of natural products such as milk or globular proteins is also of interest. Preliminary results have been obtained for very large proteins on small nonporous glass spheres (**Figure 12**). Decreasing the ionic strength improves the separation. For common proteins, which require smaller particle sizes, the difficulty lies in the affinity of silica to proteins. The alternatives are to modify chemically the OH groups by grafting an inert moiety, or using an aqueous buffer, to repel proteins from the surface.

Inorganic Compounds

Silica or carbon black are widely used in various industries as fillers, the effect of which depends on the size. A variety of other compounds has been examined: paper fibres, cement, clay, metals and metal oxides of Fe, Ti, Al, silver halides. It has been found that a difference in density does not alter the elution order. The calibration based on polystyrene latexes remains valid for carbon black particles of density 1.86, and the results agree with those obtained by photon correlation spectroscopy.

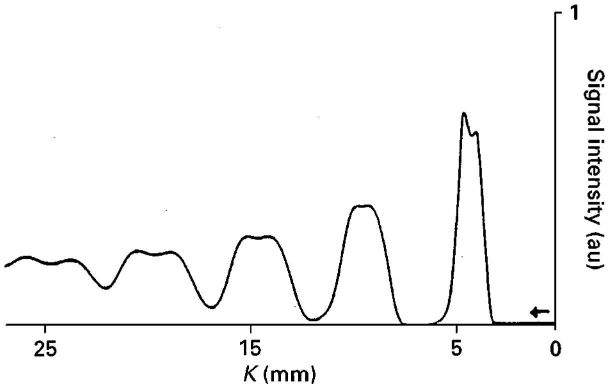

Figure 11 HDC of liposomes from egg yolk lecithin on inert glass particles (125–180 μm) in a 300 × 15-mm column, eluent with 0.02 mM NaCl; filtration on 0.3-μm pore size, four recycles. (Reprinted from Molina FJ, Vila AO, Martos MJ and Figueruelo JE (1991) Estimation of the size of liposomes by modified HDC. *Journal of High Resolution Chromatography* 14: 590–592.)

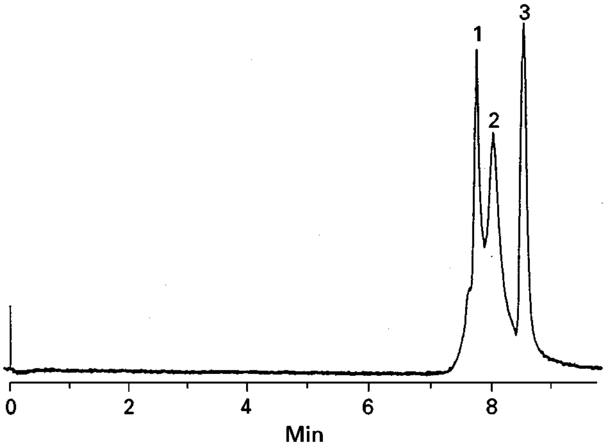

Figure 12 Separation of proteins on nonporous silica gel 2.1 μm particles, column 250 × 4.6 mm, sodium borate 5 mM, pH = 9. 1: thyroglobulin; 2: γ-globulin; 3: glycine. (Reprinted from Kraak JC, Oostervink R, Poppe H, Esser U and Unger KK (1989) Hydrodynamic chromatography of macromolecules on 2 μm nonporous spherical silica gel packings. *Chromatographia* 27(11/12): 585–590.)

Applications are also found in geology.

Conclusion

Despite its ability to provide useful results in size separations and determination, HDC is still only infrequently used. However, efforts are being made to improve its resolution and ease of use. Progress in synthesizing small size particles for packings and in narrow capillaries effectively allows rapid and excellent separation. Combined HDC and SEC offers new possibilities for determination of size and molecular weight of polymers in solution. HDC is also of interest in fundamental studies of flow behaviour in tubing or pores which are encountered in 'transport technology of materials': various fluids, solid particles, waste in rocks and soils, as well as in factories or pipes. In such work silica has the interesting advantage of being a hard spherical model for HDC mechanism studies.

See also: **II/Chromatography: Liquid:** Mechanisms: Size Exclusion Chromatography. **Particle Size Separation:** Theory and Instrumentation of Field Flow Fractionation.

Further Reading

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HYDROGEN RECOVERY USING INORGANIC MEMBRANES

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Introduction

Global annual production and utilization of hydrogen now total some 6×10^{11} Nm^3. Of this amount, approximately 50% is produced by steam reforming or partial oxidation of natural gas. Other sources include electrolysis of water and recovery from refinery off-gases. The main use of bulk hydrogen includes synthesis of ammonia, hydrotreating of heavy petroleum feedstocks, hydrogenation of vegetable oils and manufacture of transformer steels and other metallurgical heat treatment operations. More recent applications where high purity hydrogen is required include semiconductor processing and fuel cells. To obtain high purity several methods may be adopted, such as pressure swing adsorption and cryogenic technology. However, both these methods have disadvantages, including cost and degree of purity obtained; the cryogenic method gives purities ranging from 90 to 98% only.

Membranes can provide an efficient low cost means of separation and purification for hydrogen. Although polymeric membranes are well proven for gas separation, they are limited to temperatures not much greater than 250°C whereas, in many applications, high temperature processing is required. Inorganic membranes have shown considerable development in recent years and, apart from their high temperature stability, they have in general much higher fluxes than polymeric membranes.

Inorganic membranes suitable for the recovery and purification of hydrogen may be divided into two classes, namely, porous and dense membranes. The former includes materials such as alumina, silica, zirconia and porous metals, for example, stainless steel. The dense membranes include palladium and its alloys, in which the unique permeation properties of palladium to hydrogen are utilized.

Porous Membranes

To achieve appropriate separations with this type of membrane, the pore size needs to be small. However, to achieve a suitable gas permeation rate through the membrane, the membrane should be as thin as possible. To meet this requirement, a composite structure is usually adopted in which a thin finely microporous separation layer is supported on a thicker more open microporous material. Such structures have now been developed by a number of procedures.

The various possible gas permeation mechanisms applicable to porous membranes are illustrated in **Figure 1**.

In this figure, the progression from Knudsen diffusion to molecular sieving is in parallel with increasing permselectivities (it should be noted that viscous flow gives no separation). The separation factor for all the processes depends strongly on the pore size and its distribution, the temperature, pressure and the