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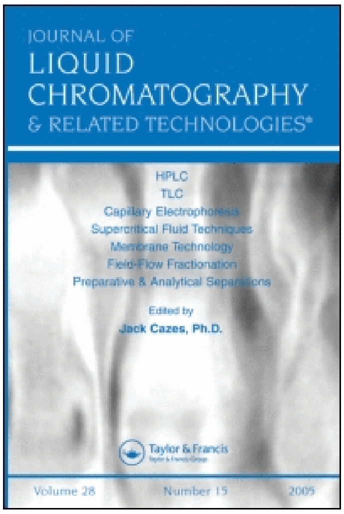

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Chromatography of Suspensions. An Absolute Particle Size Detector Based on Turbidity-Spectra Analysis

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CHROMATOGRAPHY OF SUSPENSIONS. AN ABSOLUTE PARTICLE SIZE DETECTOR BASED ON TURBIDITY-SPECTRA ANALYSIS

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ABSTRACT

Herein is reported the theoretical basis for an absolute particle size detector based on turbidity-spectra analysis for the chromatography of spherical suspensions in the submicron range. A suitable detector for this purpose would be a variable wavelength spectrophotometer with very rapid scan in the wavelength range, 200-900 nm. It is proposed that such a detector be used with a liquid chromatograph which separates a spherical particle suspension according to size. An absolute detector of this kind would, to a large extent, overcome limitations of the chromatographic technique such as relatively poor resolution, flow rate variations and the lack of a particle diameter-retention volume calibration curve.

INTRODUCTION

The very promising analytical techniques which measure particle size distribution of spherical suspensions by chromatography (liquid exclusion chromatography LEC), hydrodynamic chromatography (HDC) and capillary particle chromatography (CPC) all suffer from a serious lack of resolution (1,2). Large corrections for axial dispersion are required to obtain absolute particle size

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distributions and particle diameter averages (1,2). It is unlikely that development of improved column packing materials would reduce axial dispersion significantly, as the major cause of dispersion is the very small diffusion coefficients of the relatively large particles in suspension. The most promising approach appears therefore to be the development of an absolute detector coupled with a chromatograph. The theoretical basis for such an absolute detector based on turbidity-spectra analysis will now be given.

THEORY

Equation (1) forms the basis of a turbidity-spectra analysis for the measurement of particle size distribution of a spherical suspension (3,4).

$$\tau = N \int_0^\infty K\left(\frac{n}{n_m}, \frac{D}{\lambda_m}\right) \frac{\pi D^2}{4} f(D)dD \qquad \text{--- (1)}$$

where $\tau = \frac{1}{\ell} \ln\left(\frac{I_o}{I}\right)$ --- (1a)

and is the turbidity of a dilute suspension of non-absorbing spherical particles in the absence of multiple scattering

ℓ is the cell path length

Io is the intensity of the incident beam

I is the intensity of the transmitted beam

N is the total number of particles per unit volume

K is the extinction coefficient and depends on two dimensionless groups, $\frac{n}{n_m}$ and $\frac{D}{\lambda_m}$

n is the refractive index of the particle

n_m is the refractive index of the suspending medium

D is the particle diameter

λ_m is the wavelength of light in the suspending medium

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$F(D)$ is the frequency distribution with $F(D)dD$ being the number fraction of particles in the diameter range, $D-D+dD$

The extinction coefficient K is a known function of $\frac{n}{n_m}$ and $\frac{D}{\lambda_m}$ and calculated using the Mie theory (5). In principle, the measurement of turbidity as a function of wavelength should permit one to solve equation (1) for N and the parameters of the frequency distribution, F(D). Unfortunately, this is practical only when F(D) is a well-behaved unimodal distribution. The turbidity-spectra analysis is therefore of very limited use as a method of particle size determination for suspensions having a complex size distribution. This limitation is, however, largely overcome when the turbidity-spectra analysis is applied to the contents of the chromatograph detector cell. Due to axial dispersion in column chromatography, the contents of the detector cell will be a mixture of different sized particles. However, with reasonable resolution the size distribution in the detector cell should be reasonably narrow and unimodal and turbidity-spectra analysis should provide an accurate measure of N(v), the number of particles per unit volume in the detector cell, and the mean and variance of a two - parameter frequency distribution ($\bar{D}(v)$ and $6^2(v)$). The argument, v, is the retention volume. With no resolution, the contents of the detector cell and the suspension injected would have the same particle size distribution. A knowledge of N(v), $F(D, \bar{D}(v), 6^2(v))$ and $\bar{D}(v)$ would permit the calculation of the absolute particle size distribution of the original suspension. $\bar{D}(v)$ is the particle diameter - retention volume calibration curve and gives a measure of peak separation as a function of particle diameter and $6^2(v)$ gives a measure of peak broadening for different sized particles. In some instances it may be of interest to measure the retractive index of the particles and relate this to a material property. For example, the refractive index might be used to give a measure of the copolymer composition of latex particles. One could therefore treat the refractive index ratio as an unknown and consider the particle diameter-retention volume calibration curve as known from prior calibration.

CONCLUDING REMARKS

A theoretical basis for an absolute particle size detector to be used for the chromatography of spherical suspensions has been outlined. It now remains to experimentally verify the validity of the proposed theoretical scheme using recently developed spectrophotometers with rapid scan such as the Tracor Northern TN-1710 Diode Array Rapid Scan Spectrometer.

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