

Determination of Size Distribution of Nano-particles by Capillary Zone Electrophoresis

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Abstract: A new method was developed for the determination of the size distribution of nano-particles by capillary zone electrophoresis (CZE). Scattering effect of nanoparticles was studied. This method for the determination of size distribution was statistical.

Keywords: Capillary zone electrophoresis, polystyrene latex, particle size distribution.

Nanosized materials can exhibit unique features in the electric, optical and catalytic aspects. For all purposes the characterization of the particles is needed. The classical way to determine the size distribution is transmission electron microscopy (TEM). This method is time consuming and relatively bad statistics. An attractive alternative is size exclusion chromatography (SEC). Advantages are short analysis time, good statistics, coupling abilities with optical spectroscopy. However, problems may occur when the particles have a very high surface activity¹. Thus, a fast analysis method with less surface effects is of great interest. The capillary electrophoresis (CE) can be served such a method. CE has been successfully applied for the separation of silica sols, modified latex, polystyrene (PS) latex and colloidal metal oxides².

The aim of this article is to investigate the applicability of capillary zone electrophoresis (CZE) for the size distribution determination of nanoparticles. PS size standards are the only particles in nanosized materials that are available commercially in a large assortment of sizes. So, the PS latex is used in our study.

Experimental

For the CE experiments, a 1229-HPCE system (Beijing New Technology Institute, Beijing, China) with UV detector monitoring at 214 nm was used. The total and effective lengths of the capillary were 70 cm and 55 cm, respectively. Sample injection was accomplished by gravity feed. The injection height difference was maintained at 9 cm and injection time was maintained 20 s. A λ -16 UV-Vis spectrophotometer (PE Company, USA) was used to measure absorbance of PS

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suspension in the 190 to 350 nm wavelength range. A 90 Plus Particle Size Analyzer with Zeta Potential Option was used to determine the size distribution of PS latex and Zeta potential of PS suspension. PS standards (PS20, PS50, PS90, PS125 with mean diameter 20 ± 1.5 , 50 ± 2 , 92 ± 3.7 , 125 ± 4 nm, respectively) were from Duke Scientific Corporation, all other reagents were of analytical grade.

Results and Discussion

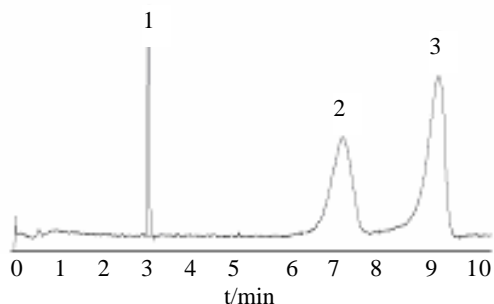
Dispersion of PS latex

Nanoparticles were prone to agglomerate owing to smaller particle size and larger specific surface area. Therefore, the first requirement of this method was to start from a suspension that is as stable as possible. The goal was achieved by dispersing PS latex in a running buffer (same as CE operation) for 5 minutes in an ultrasonic bath. This de-agglomerating agent worked by increasing the repulsive electrostatic forces between the particles. The values for the zeta potentials of PS50, PS90 and PS125 suspension were -42, -50, -71 mV, respectively. The absolute values of zeta potentials were higher, so these suspensions can be considered to be stable for CZE.

CZE separation of PS latex

Figure 1 showed the separation of a mixture of PS50 (peak 2) and PS125 (peak 3) in a 5.0 mmol/L Na_2CO_3 , 1.25 mmol/L NaHCO_3 (pH 10.82) buffer. The time denoted t_0 (peak 1) was characteristic of a neutral species (DMSO) transported through the capillary solely by the electroosmotic flow. DMSO was added as an internal standard to improve precision. **Figure 1** also showed this separation was taken place in a size-dependent manner. This size-dependent manner allowed one to determine the size distribution of nanoparticles by CZE.

Figure 1 Electropherogram of PS50+PS125



1. DMSO; 2. PS50; 3. PS125

Calibration of diameter and content

Data from absorption spectrum of PS latex showed that the migration times of PS latexes were dependent on the particle sizes and sample injection quantity. Controlling the same quantity of injection in each run, the effect of injection amount on migration time can be avoided. Thus, the migration time of particles only related to the particle diameter.

The different mean diameters of the standards are essential for the migration time. The idea of associating the particle diameter data from laser particle sizer with migration time was brought forward. In particular, a calibration plot of migration time vs. particle diameter was prepared by associating the corresponding diameters of three cumulative percentiles (5%, 50%, 95%) of particle distribution of PS50 and PS125 (determined by laser particle sizer) with the corresponding migration time of three cumulative percentiles (5%, 50%, 95%) of area of PS50 and PS125 (from electropherogram of PS50 and PS125 mixture, see **Figure 1**). The calibration plot was: $d = 22.393t - 112.75$, $r = 0.9974$, where d was the particle diameter (nm), t was the adjusted migration time of particle (minute).

The result of research showed: (1) For a certain concentration, the absorption peaks blue-shifted as the size of PS nanoparticles decreased. (2) For a certain size of PS latex, the absorption peaks blue-shifted as the concentration of PS nanoparticles decreased. These phenomena might be owing to the attribution of the light scattering. A correction equation was established to correct the scattering effect. The details were as follows:

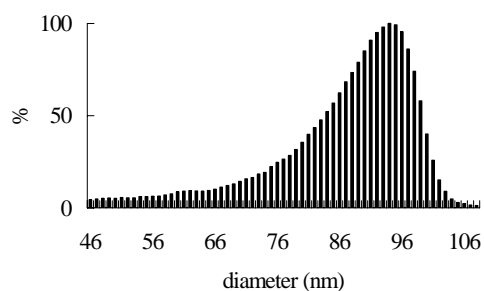
The PS latexes with the same concentration but different mean diameters had different absorbency. Five plots ($A_i = k_i c_i + b_i$) were constructed in which absorbency of different mean diameter PS latexes were plotted vs. corresponding concentration. The slopes of these calibration plots (k_i) were different. Therefore, a calibration plot was constructed in which k was plotted vs. diameter (different particle size). The parameter “ k ” indicated the relationship between different mean diameter and absorbency in a certain concentration range. Thus, the calibration equation from the calibration plot was the correction equation of detection response vs. concentration. That was, $k = 6.986 \times 10^{-4} \times d + 0.0806$, $r = 0.9665$, where k was the slope of plot, d was the diameter of particle. This equation indicated the relationship between absorbency and diameter of particles in a given continuous diameter range.

Application

Two methods including photon correlation spectroscopy (PCS, instrument: laser particle sizer) and CZE (instrument: CE system) were adopted to measure the average diameter (d_{pcs}) of PS90. Here, d_{pcs} was defined by the following equation:

$$d_{\text{pcs}} = \frac{\sum N_i d^6}{\sum N_i d^5}$$

d_{pcs} depended on light scattering, N_i was the number of particles in a given diameter, d was diameter of particles.

Figure 2 Histogram of PS90 size distribution scale bar is 1 nm

The mean diameters (d_{pcs}) were 92 nm and 89 nm for PCS and CZE respectively. This result showed that d_{pcs} obtained by these two methods were almost the same. CZE gave an integral picture of the size distribution with perfect statistics (see **Figure 2**), whereas the number of counted particles in TEM method was limited.

Conclusion

CZE is a promising method for the size determination of nanometre-sized colloidal particles. The result is statistical. However, it should be stressed that each kind of colloid has its own calibration and optimum conditions owing to its different property.

References

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Received 21 November, 2003