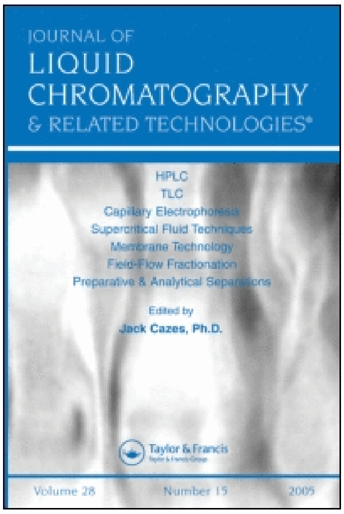

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# CHARACTERIZATION OF SILICA SOLS USING CAPILLARY ZONE ELECTROPHORESIS

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## ABSTRACT

Separations of silica sols ranging in size from 5 to 500 nanometers have been accomplished with capillary zone electrophoresis (CZE). Separations were achieved by free-zone electrophoresis in 50-µm internal diameter (id) fused silica capillaries filled with pH 9.0 ammonia buffers; detection of separated bands was accomplished via on-capillary turbidity measurements at 190 nm. Separations are relatively fast and moderately high-efficiency, with essentially baseline resolution of sub-100 nanometer sols differing by a factor of 2 accomplished in under 20 minutes. The ionic strength of the separation buffer was found to have a significant effect on the resolution and electrophoretic mobilities of the silica sols, with higher ionic strengths substantially improving resolution of smaller silica colloids while greatly increasing the elution time of the larger silica sols. Several areas of application of the CZE technique for separation and characterization of charged particulate species are discussed.

## INTRODUCTION

Capillary electrophoresis (CE) has been used in recent years for the separation of numerous types of samples, ranging from small ions (1,2) to peptides (3), proteins (4,5), and nucleic acids (6,7). The technique is not limited to soluble molecules, but can also be used for the separation of particulate materials as well. For example, CZE has been used to separate submicron-sized polystyrene spheres (8) and viral particles (9).

This report extends the CE technique to the separation of colloidal silica particles with diameters in the range of 5 to 500 nm; silica colloids of these dimensions are conventionally used to prepare porous particulate microspheres for liquid-phase chromatographic columns as well as for making catalysts, for use as binders, stiffening agents, anti-friction agents, etc., and for many other uses (10). Characterization of these colloidal materials is important, as the nominal size and the size distribution of silica sols have a substantial impact on their physical properties.

Conventional methods of characterizing these materials include electron microscopy (11), hydrodynamic chromatography (12,13) or capillary hydrodynamic fractionation (14-17), sedimentation field-flow fractionation (18,19), and size-exclusion chromatography (20).

Electron microscopy does not involve any separation process; sol size characterization can be achieved by relative measurements from electron-photomicrographs. Hydrodynamic chromatography does involve separation of the colloidal species by size, although the precision of the measurements is poor because of the relatively low resolving power of the method (12). Capillary hydrodynamic chromatography and capillary hydrodynamic fractionation likewise appear to have a cut-off for colloids at around 100 nm (15). Both sedimentation field-flow fractionation and size-exclusion chromatography have demonstrated utility for characterization of colloids in this size region, though detection of smaller particle sizes is hampered somewhat by the large band-broadening characteristics of these techniques.

CE appears to offer a unique approach to separating colloidal species. Inherently efficient CE separations yield sharp bands, facilitating detection; in addition, CE separations provide high discrimination between sols of different sizes. High-efficiency separations of the smaller colloids can be achieved in capillaries of larger diameters than those used for hydrodynamic separations, thus alleviating some of the detection difficulties of the separated bands in the 1 to 10 micron internal diameter capillaries used for hydrodynamic fractionation. Rapid CE separations (<20 minutes) are possible on unstable colloidal systems that can rapidly undergo aggregation.

# EXPERIMENTAL SECTION

## Apparatus

Separations were done in a capillary electropherograph constructed from an in-house design (9). Several improvements in the original design of system have been implemented. These include installation of temperature-control in the CZE cabinet using a J-type thermocouple temperature controller (Cole Parmer Instrument Co., Chicago, IL) and a Teflon-insulated resistance heating element (Cole Parmer Instrument Co.). Temperature control of +/-1/2° C is possible over a range of 30 to 65° C using this system.

The detection system of the original apparatus was improved by installation of a high-intensity deuterium lamp (ISCO, Inc., Lincoln, NE) and substitution of rectangular 50 x 300 micron slits for the circular pinholes used in the previous design. These modifications increase light throughput in the optical system and improve detector response characteristics. Finally, the Hewlett Packard LAS data acquisition system used previously was replaced with a Perkin Elmer/Nelson (Cupertino, CA) data system for these studies.

## Materials/Supplies/Procedures

Electrophoresis buffers were prepared from 18 megaohm-cm reverse osmosis/deionized water passed through a Barnstead PCS water purification system (Barnstead/Thermolyne Corporation, Dubuque, IA). Ammonium hydroxide (J. T. Baker, Phillipsburg, NJ) and ammonium chloride (Aldrich Chemical Co., Milwaukee, WI) were used to prepare buffers of varying ionic strengths at pH 9.0. Experimental colloidal silica sols of known sizes were obtained in-house at Du Pont. The sizes of these sols were determined by sedimentation field flow fractionation and confirmed by transmission electron microscopy measurements.

Capillaries (50 µm id, 350 µm od) were acquired from Polymicro Technologies (Phoenix, AZ). Capillaries for free-zone electrophoresis were cleaned by flushing with 1 M KOH for 10 to 15 minutes using house vacuum to pull the solution through the capillary. The capillaries were then flushed with 18 megaohm-cm water until the effluent had a neutral pH.

Samples, suspended in the electrophoresis running buffer, were introduced by timed hydrostatic injection at the anode. Detection was at 190 nm via turbidity measurements.

## RESULTS AND DISCUSSION

Colloidal silica particles are inherently negatively-charged in buffers of neutral and alkaline pH and adsorption of these particles onto the nonderivatized silica capillary wall is not a problem as with materials containing positively charged sites such as proteins (5). The electrophoretic mobility of a charged colloidal particle, which is dependent on the force exerted on it by an electric field tempered by viscous drag from the solution through which it moves, is a complex function of particle radius, thickness of the electrical double layer and the shear surface around the particle, surface charge density on the particle, and solution viscosity within the double layer of the particle (21). However, it can be predicted *a priori* that the electrophoretic mobility of larger sol particles will be greater (towards the anode for negatively charged silica colloids) than smaller particles, and hence larger sols should reach the detector later than smaller ones (when injected at the anode in a nonderivatized silica capillary with electroosmotic flow in the direction of the cathode). Also, changes in buffer pH, ionic strength, and chemical composition should have substantial impact on the capillary zone electrophoretic separation of particles, with buffer ionic strength greatly influencing resolution of different size colloids because of its role in determining the magnitude of the Stern, shear, and double layer thicknesses (21,22) associated with the colloidal particles. The effect of buffer ionic strength is illustrated in the following separations.

Figure 1 (Panel A) shows the separation of a mixture of 5, 8.5, 44, 94, and 250 nm silica sols in a 2.5 mM $NH_4OH$, 4.65 mM $NH_4Cl$ (0.5 X) pH 9.0 buffer. Samples were introduced into the capillary at the

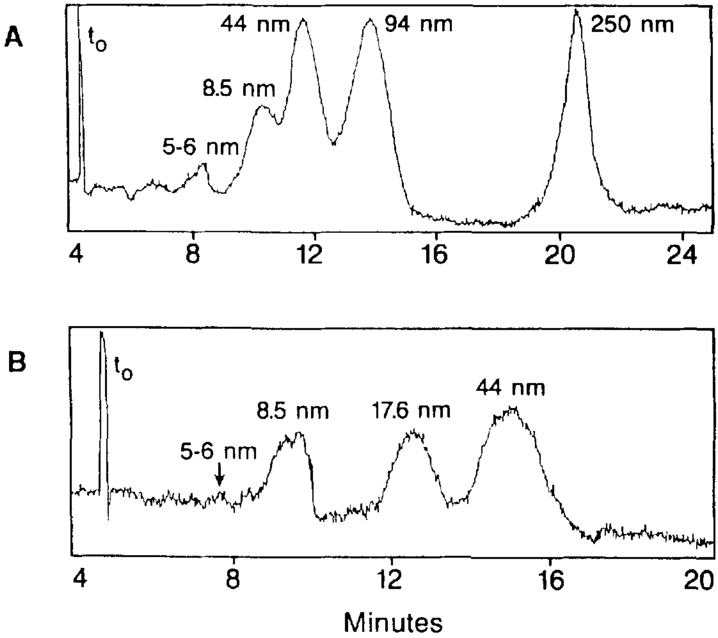

FIGURE 1

Effect of Buffer Concentration on Elution Time of Silica Sols in CZE. A. 0.5X Buffer - 2.5 mM $NH_4OH$, 4.65 mM $NH_4Cl$, pH 9.0. B. 2X Buffer - 10 mM $NH_4OH$, 18.6 mM $NH_4Cl$, pH 9.0. Separations were done in a 101 cm length (61 cm anode section before the detector) of 50 μm id fused silica capillary; sample was injected hydrostatically for 5 - 10 seconds at 15 cm head pressure. Detection was by light-scattering at 190 nm. Separation voltage was 0 to 30 kV linear ramp in 30 seconds; then hold at 30 kV.

anode and were transported to the cathode via the bulk electro-osmotic flow; separation was achieved by differential electrophoretic migration counter to the electro-osmotic flow (i.e. towards the anode), with the larger colloids having higher electrophoretic mobilities than the smaller colloids. The time denoted $t_0$ is characteristic of a neutral species (flow marker) transported through the capillary solely by the electroosmotic flow.

Resolution of the smaller colloids can be dramatically improved by increasing the ionic strength of the separation buffer. Figure 1 (Panel B) shows the separation of a mixture of 8.5, 17.6, and 44 nm silica sol particles in a more concentrated (2X) buffer (10 mM $NH_4OH$, 18.6 mM $NH_4Cl$, pH 9.0) in less than 20 minutes. Bands of the 8.5 and 44 nm sols, which overlapped substantially in Figure 1, Panel A are now completely resolved from each other as well as from an intermediate-size (17.6 nm) sol species.

Mixtures of larger sol particles, which would be eluted late in these relatively concentrated buffers, can be resolved in very dilute buffers, as illustrated in Figure 2, which shows the separation of 94, 250, and 500 nm sols in a 0.1X ammonia buffer (pH 9.0). Again, essentially baseline resolution of sol species that differ by a factor of two in diameter can be achieved in under 15 minutes in this buffer system.

Figure 3 shows the dependence of the elution times of particles of various sizes on the strength of the buffer in which the separations were run. At very low ionic strength, colloids of different sizes are co-eluted just after the electroosmotic flow marker ($t_0$); as the ionic strength is increased, smaller particles are eluted somewhat later and

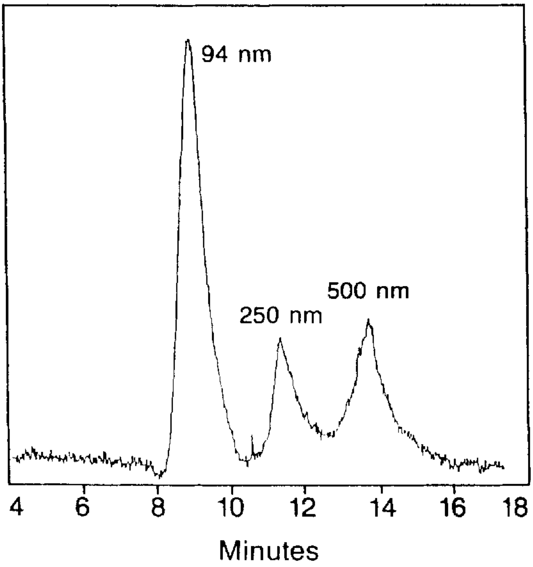

FIGURE 2

CZE Separation of Colloidal Silica Sols of Larger Particle Diameters. 0.1X Buffer - 0.5 mM $NH_4OH$, 0.93 mM $NH_4Cl$, pH 9.0. Separations were done in a 100 cm length of 50 μm id fused silica with 60 cm anode section located before the detector. Injection was hydrostatic at 15 cm head pressure for 5 sec. Other conditions same as Figure 1.

are resolved into discrete bands, whereas larger particles elute much later. Optimum separation of the smaller silica sols is achieved in higher ionic strength buffers, though at the expense of reduced dynamic range of the separation because the larger particles elute together late as very broad bands.

This effect is demonstrated in Figure 4, which shows no separation of small silica sols in a 0.1X buffer system (Panel A), partial

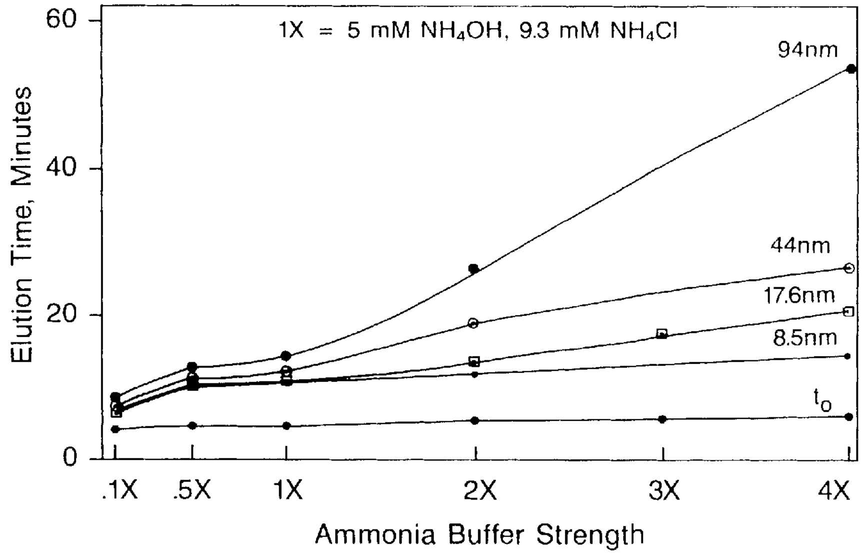

FIGURE 3

Effect of Ammonia Buffer Concentration on Elution Time in CZE. Separation conditions same as in Figure 1, with varying buffer strength as indicated.

separation in the 1X buffer (Panel B), and baseline resolution in the 2X buffer system (Panel C). Also, under the constant pH conditions used here, changes in the buffer ionic strength have little effect on the magnitude of the electroosmotic flow, as evidenced by the constancy of the elution time of a neutral flow marker ($t_o$).

Though CZE has applicability for characterization of small silica sols that are difficult to separate by other methods, a general limitation of all separation methods is the ability to detect separated bands of

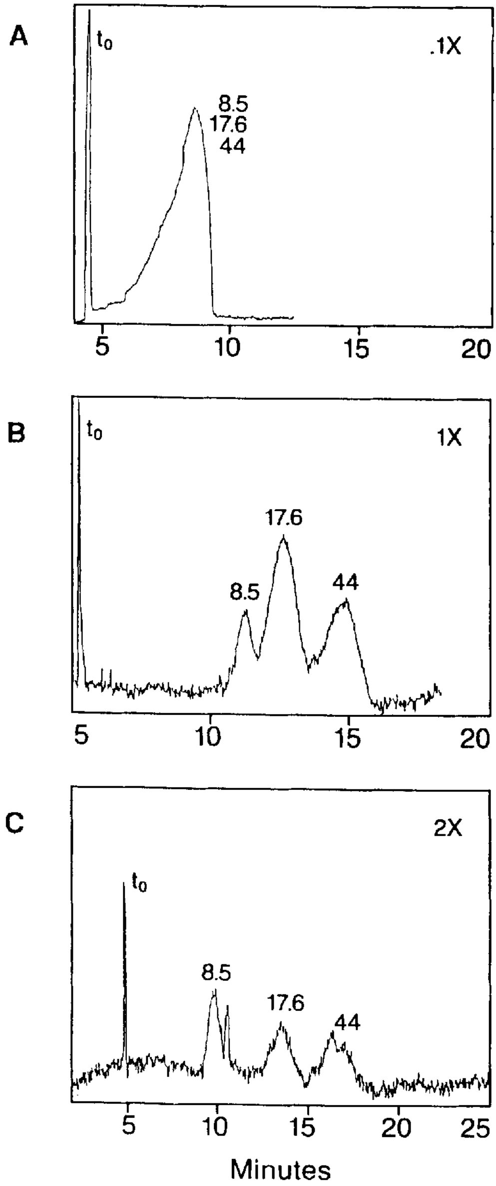

FIGURE 4

CZE Separations Illustrating Effect of Buffer Strength on Resolution of Silica Sols. 1X buffer is 5 mM $NH_4OH$, 9.3 mM $NH_4Cl$. Separation conditions same as in Figure 1.

very small colloidal materials. Detection in the preceding separations was done by turbidity measurements at 190 nm, and even at this low wavelength where small particles exhibit maximal light scattering, detection of colloids with diameters less than 10 nm is difficult. However, capillary electrophoresis, which provides inherently high-efficiency separations, is well-suited to separation of small colloidal species which are difficult to detect when separated by other analytical techniques.

In contrast to separation of small colloids, the detection of large colloidal species is readily achieved; difficulties with even larger colloidal species settling out of solution can be overcome by increasing the density of the buffer to more closely match that of these larger silica colloids. The dynamic range of the separations might also be substantially improved by using a buffer gradient technique (23). With this approach, a high buffer ionic strength would be used to obtain optimum resolution of the smaller colloids; the strength of the buffer would be gradually reduced to improve resolution of the larger species.

Application of CZE to the separation and characterization of a wide range of charged colloidal species should be readily attainable; in addition, with the appropriate software and calibration standards, precise particle-size distribution measurements should be possible. The technique should also be useful for acquiring fundamental information on the effect of ionic strength, pH, etc., on the surface charges of particulate species such as cells (24). In addition, if a charge could be imparted to electrically neutral species (e.g., by adsorption of charged species on the surface), then the technique may be applicable to characterization of many types of neutral colloidal materials as well.

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