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## Particle Separations by Electrophoretic Techniques

N. E. Ballou  
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March 1996

Prepared for the U.S. Department of Energy  
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Pacific Northwest Laboratory  
Operated for the U.S. Department of Energy  
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Richland, Washington 99352



## Summary

A new method for particle separations based on capillary electrophoresis has been developed and characterized. It uniquely separates particles according to their chemical nature. Separations have been demonstrated with chemically modified latex particles and with inorganic oxide and silicate particles. Separations have been shown both experimentally and theoretically to be essentially independent of particle size in the range of about 0.2  $\mu\text{m}$  to 10  $\mu\text{m}$ .

The method has been applied to separations of  $\text{UO}_2$  particles from environmental particulate material. For this, an integrated method was developed for capillary electrophoretic separation, collection of separated fractions, and determinations of  $\text{UO}_2$  and environmental particles in each fraction.

Experimental runs with the integrated method on mixtures of  $\text{UO}_2$  particles and environmental particulate material demonstrated enrichment factors of 20 for  $\text{UO}_2$  particles in respect to environmental particles in the  $\text{UO}_2$ -containing fractions. This enrichment factor reduces the costs and time for processing particulate samples by the lexan process by a factor of about 20.

This work was performed for the Office of Nonproliferation and National Security, the U.S. Department of Energy, by staff within the Chemical Sciences Department, Pacific Northwest National Laboratory.



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# Introduction

Methods are required that will sharply reduce the time and costs needed for identifying and isolating selected kinds of particles from sample matrices by the lexan method. A new concept for particle separation by capillary electrophoresis techniques has been proposed and has been developed in this project to provide fast separation of particles according to their chemical nature. Uranium oxide particles are separated from other particles (e.g., oxides, silicates) in samples to effect concentration of the uranium oxide particles by factors of ten or more. This increase in concentration provides a corresponding decrease in the amount of time and cost required for the lexan processing.

Capillary electrophoresis (CE) is a relatively new separations technique that was introduced in its present format by Jorgenson and Lukacs<sup>1</sup>. It is widely used to separate aqueous ionic species in capillary tubes according to their different velocities in high electric fields. Compared to other separation methods it is characterized by speed and high separation efficiencies. Experimental parameters affecting separations are capillary material and dimensions; buffer solution composition, concentration and pH; electric field strength; and surfactant type (if any) and concentration. Quality of separations are characterized by numbers of theoretical plates (efficiency), selectivity, and resolution.

Particles suspended in aqueous solutions develop electric charges on their surfaces. The kind and size of charge depends on the chemical nature of the particle and the composition and pH of the suspending solution. As with ions in solution, electrically charged particles will move with characteristic velocities in an electric field. This is the basis for the proposed separation of particles according to their chemical nature.

Successful demonstration of the concept of separating chemically different kinds of particles by capillary electrophoresis was accomplished initially with chemically modified latex particles<sup>2</sup>. The effects of experimental parameters on the quality of such separations were subsequently determined and evaluated<sup>3</sup>. An important result from that study was the determination that electrophoretic heterogeneity of the latex particles causes broadening of the particle zones in CE separations. Other characteristics of the separations (e.g., efficiency, selectivity, resolution) were determined. As a result of zone broadening, values of these quantities were found to be less than such values observed in separations of ions in aqueous solutions.

Extension of the CE technique to separation of naturally occurring particles was accomplished with oxide particles ( $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{TiO}_2$ ,  $\text{Sb}_2\text{O}_5$ ,  $\text{UO}_2$ ) and real-world particulate samples. Evaluated in these studies were methods and media for particle suspensions, effects of CE operating parameters on quality of particle separations, methods for collection of separated particle fractions, and degree of enrichment of uranium oxide particles in respect to matrix particles in real-world particulate samples. Details of these studies have been presented in a series of topical reports<sup>5-10</sup> that should be referred to for further information. In this report we present a summary of the CE particle separation studies.



# 1.0 Experimental Section

## 1.1 Apparatus and Instrumentation

Initial experiments with latex particles were performed on a laboratory-built, non-thermostated CE system. All subsequent experiments were performed on either a P/ACE 2000 or P/ACE 2050 (Beckman Instruments, Palo Alto, CA) programmable/automated CE system. Fused silica capillaries (Polymicro Technologies, Phoenix, AZ) were used and had nominal dimensions of 100  $\mu\text{m}$  i.d. and 360  $\mu\text{m}$  o.d. Total lengths of the capillaries were typically 37 cm, with the distance from the inlet to the detector being about 30 cm. The detection wavelength of the UV absorbance detector was set at 254 nm. The temperature of the capillary was maintained at  $25.0 \pm 0.1^\circ\text{C}$ .

## 1.2 Preparation of Solutions and Sample Suspensions

Various buffer solutions at selected concentrations and pH values were prepared for determining electrophoretic behavior and separability of different particle kinds under given buffer conditions. Carbonate, pyrophosphate, phosphate, borate, and acetate buffers were prepared from appropriate combinations of their salts, acid salts, and acids. Concentrations were from 1-10 mM, and pH values centered around their respective  $\text{pK}_a$  values.

Suspensions of oxide particles in the buffer solutions were prepared from commercially-available oxide powders while suspensions of real-world samples were prepared from collected environmental samples. Concentrations of oxide particles in the buffer solutions were typically 0.015 volume percent. Concentrations of uranium dioxide in other oxide and environmental particle mixtures were about 80 ppm. Diameters of the uranium dioxide particles ranged from 0.2  $\mu\text{m}$  to 13  $\mu\text{m}$ . Nominal diameters of the other oxide particles were in the range of 0.2  $\mu\text{m}$  to 0.8  $\mu\text{m}$ .

## 1.3 Analytical Procedure

Before initiating CE runs, the capillary was first conditioned with washes of NaOH, deionized water, and operating buffer solution. Satisfactory performance of the system was then verified by measuring the electroosmotic flow rate using acetone (0.5 vol% in the running buffer) as the neutral marker. Between runs with a given oxide, the capillary was rinsed for several minutes with the operating buffer solution. Between runs of different oxides, the capillary was rinsed with NaOH solution, deionized water, and operating buffer solution. At the end of each day the capillary was thoroughly rinsed with deionized water and the ends left immersed in water overnight.

Suspensions of particles in buffer solutions were generated by ultrasonication of particles/buffer solutions for about 5 minutes. Before loading a particle suspension into a capillary it was agitated several minutes by hand, ultrasonicated for about 5 minutes, and then again manually agitated for several minutes. Particle suspensions were injected into a capillary hydrodynamically (by pressure). Sample plug lengths were typically 1% of the total capillary length. The runs were performed under constant voltage with applied electric field strengths of 100-500 V/cm.

## 2.0 Results and Discussion

### 2.1 Separations of Chemically Different Latex Particles

The original demonstration of the feasibility of separating chemically different kinds of particles by CE was accomplished with various samples of commercial suspensions of latex particles having different numbers of attached carboxylate or sulfate groups in the different samples<sup>2</sup>. The degree of separation of different kinds of particles in two-component and seven-component mixtures was determined for different pH values of phosphate buffer solutions and for different applied potentials. Most effective separations were accomplished with the phosphate buffer at a pH of 10.71 and a concentration of 5 mM and at an applied potential of 35 kV (636 V/cm). Quality of separations was characterized by efficiency (number of theoretical plates), selectivity, and resolution for different pH and applied potential values. Efficiencies ranged from about 400 to 3000. Selectivities ranged from about 0.1 to 0.4, and resolution values ranged from 0.8 to 2.3. Electrophoretic mobilities steadily increased with applied potential with the nonthermostated CE system initially used. This increase was believed to be due to a rise in temperature from increased Joule heating of the solution; this caused a reduction of viscosity and a concomitant rise in electrophoretic mobilities.

Further characterization of CE separations of latex particles was performed on a thermostated (P/ACE 2000) system<sup>3</sup>. In this system, even at high electric field strengths from about 400 to 650 V/cm, the increase in electrophoretic mobility was less than 10% as compared to about 45% in the nonthermostated CE system. Theoretical analyses and experimental determinations were made of the dependencies of zone variance (peak broadening), efficiency, selectivity, and resolution on parameters of the CE system. From this, we determined that more than 90% of zone variance was due to electrophoretic heterogeneity of the particles. We also determined that in the thermostated system efficiencies, selectivities, and resolution were essentially independent of electric field strength except at the highest field strengths. This is in contrast to their generally large variations in the nonthermostated system.

### 2.2 Preparation of Particle Suspensions

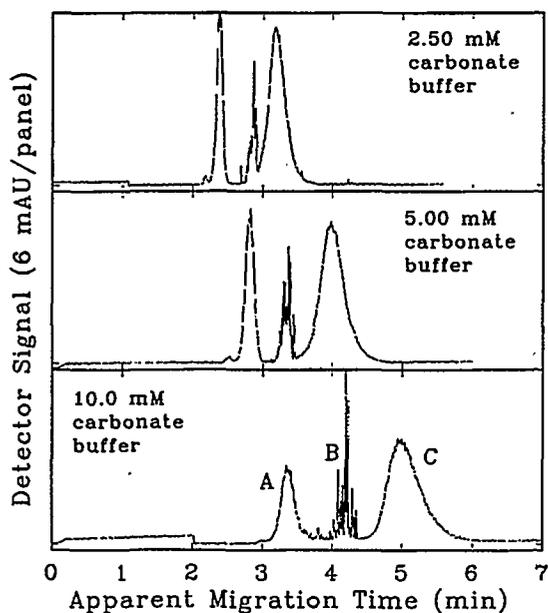
Dry particle samples that are to be separated by CE must first be converted into quasi-stable suspensions in appropriate buffer solutions. Manual and mechanical agitation and ultrasonication were evaluated for this purpose. None of them alone was sufficient. We found that ultrasonication was generally required with some agitation before and after the ultrasonication in order to establish satisfactory suspensions. The specific combination used was determined on a case-by-case basis as judged by the apparent stability of the suspension. Agitation and/or ultrasonication of a sample suspension immediately before loading it into a capillary was generally found to be necessary.

## 2.3 Effects of Capillary Electrophoresis Parameters on Separations of Common Oxide Particles

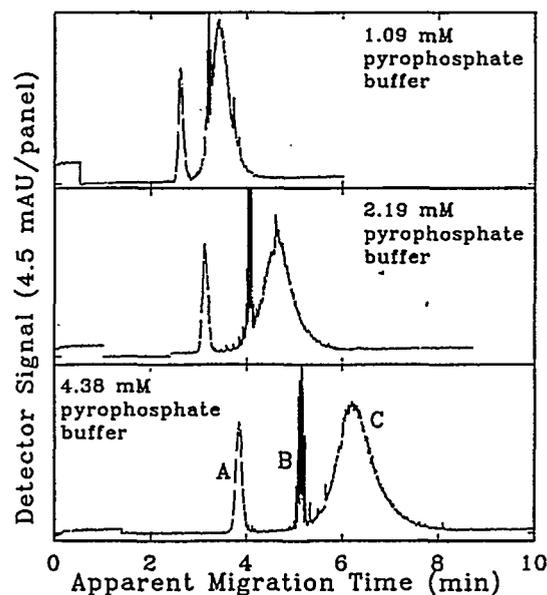
Separation of chemically different kinds of particles by CE was extended from latex particles to common oxide particles<sup>5</sup>. The electrophoretic behavior of such particles under various CE operating conditions was determined to demonstrate feasibility of separation and to establish optimum separation conditions. The primary parameters effecting CE particle behavior are capillary dimensions, nature and concentration of the buffer solution, pH, and electric field strength. The effects of each of these on electrophoretic behaviors of such commonly occurring particles as  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{TiO}_2$  were determined.

A capillary i.d. was selected that balanced the need for a large i.d. to provide as great a sample capacity as possible with the need for a small i.d. to limit Joule heating. An i.d. of about  $100\ \mu\text{m}$  was selected as most suitable. A capillary length of about 37 cm was selected that was sufficient to provide adequate separations while limiting the length of time required for separations.

Electrophoretic behavior of the above oxides was determined at various concentrations of carbonate and pyrophosphate buffers at pH values of 10.6 and 10.2, respectively. Separations of mixtures of the oxides were accomplished at several concentrations of both buffers. Representative separation results are presented in Figures 1 and 2.



**Figure 1.** Capillary Electrophoretic Separations at Three Carbonate Buffer Concentrations of a Mixture Containing 0.015 vol% Each of (A)  $\gamma\text{-Al}_2\text{O}_3$ , (B)  $\text{Fe}_3\text{O}_4$ , and (C)  $\text{TiO}_2$  Particles. The electric field strength was 300 V/cm for all three separations.



**Figure 2.** Capillary Electrophoretic Separations at Three Pyrophosphate Buffer Concentrations of a Mixture Containing 0.015 vol% Each of (A)  $\gamma$ - $\text{Al}_2\text{O}_3$ , (B)  $\text{Fe}_3\text{O}_4$ , and (C)  $\text{TiO}_2$  Particles. The electric field strength was 300 V/cm for all three separations.

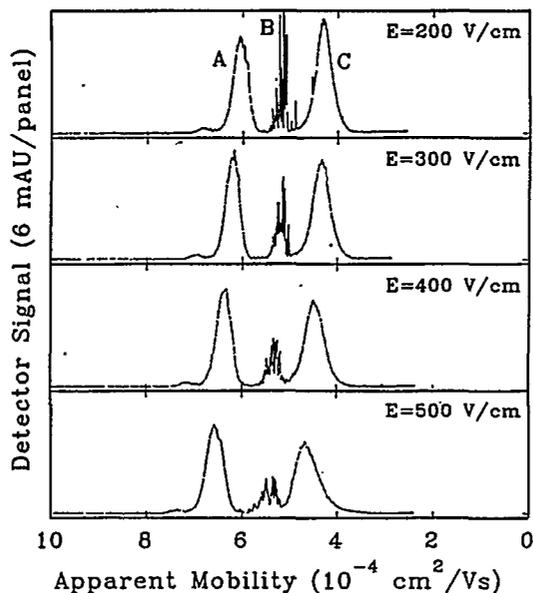
Selectivity, efficiency, and resolution values were calculated and analyzed for the data in Figures 1 and 2. As is shown by the figures, all selectivities between different types of oxide particles increased significantly with increasing buffer concentration. This is consistent with modern electrophoresis theory<sup>4</sup>, which predicts that the selectivity between particles that are similar in size but that differ in surface charge density should increase with increasing buffer concentration. Different types of oxide particles have different isoelectric points and, therefore, should have different surface charge densities in a given pH buffer solution. In addition to buffer concentration effects, the above data also reveal that buffer type can have a significant effect on the selectivity observed between given oxides. Comparison of Figures 1 and 2, for example, shows that the selectivity between  $\text{Fe}_3\text{O}_4$  and  $\text{TiO}_2$  is higher in carbonate buffer than in pyrophosphate buffer. Another example is that  $\gamma$ - $\text{Al}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  are easily separated in carbonate buffer (Figure 1), whereas these two oxides co-migrate in pyrophosphate buffer (not shown).

For the mixtures separated in carbonate buffer, efficiencies decreased considerably with increasing buffer concentration. On average, efficiencies decreased by a factor of 2 when going from 2.5 mM to 10 mM carbonate buffer. On the other hand, for the mixtures separated in pyrophosphate buffer, efficiencies showed no significant trend with changing buffer concentration. We obtained highest separation resolutions for the mixtures separated in carbonate buffer at the lowest buffer concentrations because the efficiency losses more than offset the selectivity gains as the buffer concentration was

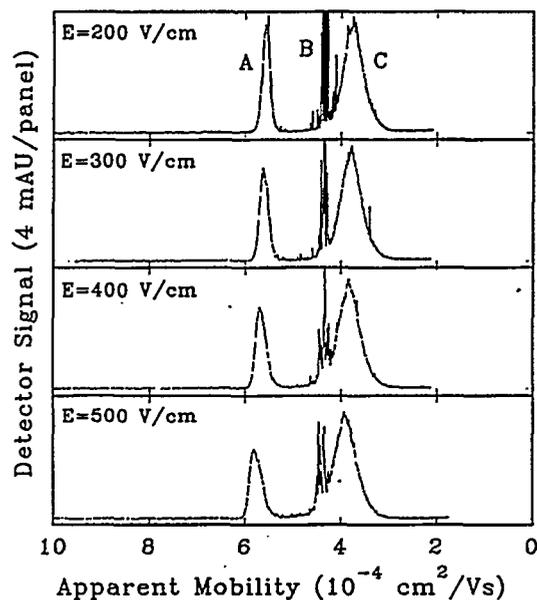
increased. Conversely, we found that separation resolutions in pyrophosphate buffer consistently increased with increasing buffer concentration due to the essential independence of efficiency on buffer concentration.

From the above results, it can be concluded that optimal separations are obtained either at low (2.5 mM) carbonate buffer concentration or high (4.4 mM) pyrophosphate buffer concentration. Because separations run faster at lower buffer concentrations (Figures 1-2), carbonate buffer has the advantage of speed over pyrophosphate buffer when optimum resolution is sought.

The effect of electric field strength (E) on quality of separations of oxide particles was also investigated. Representative results are presented in Figures 3 and 4. To compare electropherograms obtained at different E, it is useful to normalize the migration times by converting them to mobility values. The apparent mobility of a particle is the sum of its electrophoretic mobility and the electroosmotic mobility of the buffer solution. This conversion to apparent mobilities was done for the data in Figures 3 and 4. The figures qualitatively show that E does not have a large effect on the quality of CE separations of oxide particles. This is consistent with theory and with results obtained previously for chemically modified latex particles<sup>3</sup>.



**Figure 3.** Capillary Electrophoretic Separations at Four Electric Field Strengths of a Mixture Containing 0.015 vol% Each of (A)  $\gamma\alpha$ - $\text{Al}_2\text{O}_3$ , (B)  $\text{Fe}_3\text{O}_4$  and (C)  $\text{TiO}_2$  Particles in 5.00 mM, pH 10.6 Carbonate Buffer. The x-axis was normalized with respect to electric field strength by converting units from apparent migration time to apparent mobility.



**Figure 4.** Capillary Electrophoretic Separations at Four Electric Field Strengths of a Mixture Containing 0.015 vol% Each of (A)  $\gamma$ - $\text{Al}_2\text{O}_3$ , (B)  $\text{Fe}_3\text{O}_4$ , and (C)  $\text{TiO}_2$  Particles in 2.19 mM, pH 10.2 Pyrophosphate Buffer. The x-axis was normalized by converting units from apparent migration time to apparent mobility.

Selectivity, efficiency, and resolution values were calculated for the data shown in Figures 3 and 4. The most significant trend, which is most easily observed in Figure 4, is that the selectivity between  $\text{Fe}_3\text{O}_4$  and  $\text{TiO}_2$  decreases and the selectivity between  $\text{Fe}_3\text{O}_4$  and  $\text{Al}_2\text{O}_3$  increases with increasing  $E$ . Another consistent trend for the data in Figures 3 and 4 is that the efficiencies of the particle zones decrease with increasing  $E$ . This is most easily observed by the broadening of the  $\text{TiO}_2$  peak in Figure 3 and the  $\gamma$ - $\text{Al}_2\text{O}_3$  peak in Figure 4 with increasing  $E$ . Analysis of the calculated separation parameters indicated that for  $E > 300$  V/cm the apparent mobilities of the particle zones significantly increased, the efficiencies of the particle zones significantly decreased and the resolutions of the separations significantly decreased relative to the values of these parameters for  $E \leq 300$  V/cm. Therefore, for the buffer and capillary conditions used herein, oxide particle separations should be performed at  $E \leq 300$  V/cm.

Separability of different polymorphic forms of one oxide (i.e.,  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ ,  $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\gamma$ - $\text{Al}_2\text{O}_3$ ) was demonstrated<sup>6</sup>. This was also the case for the anatase and rutile forms of  $\text{TiO}_2$ . However, in this case samples of rutile from two different suppliers gave different migration times, although they were different from migration times of anatase. Additional samples and measurements are needed to better define behavior of these polymorphs of  $\text{TiO}_2$ .

Reproducibility is an important factor in CE separations and it was determined here for oxide particle separations<sup>5</sup>. In a series of triplicate runs of 9 different three-component oxide particle mixtures the relative standard deviations (RSDs) of the apparent migration times for the 27 peaks ranged from 0.1% to 1.2%, with the average RSD being 0.44%. This is as good as is typically obtained for ionic analytes, and in consideration of the limited stability of the oxide particle suspensions

is especially noteworthy. In addition, excellent reproducibility in peak width, peak height, and peak shape were demonstrated in overlay plots of electropherograms of replicate particle separation runs at various given buffer concentrations.

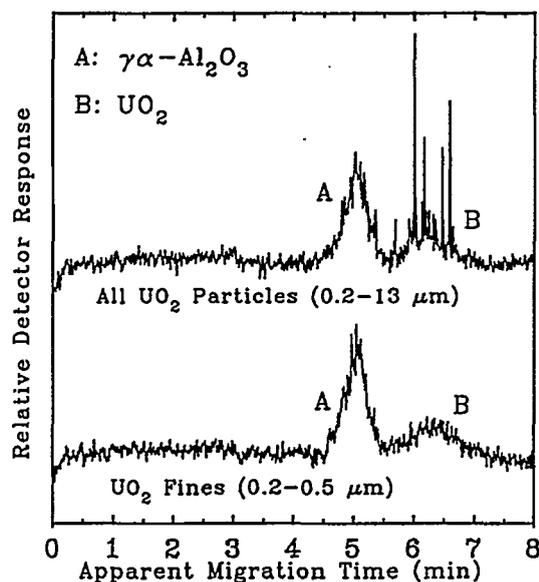
## 2.4 Separations of Uranium Oxide Particles from Other Types of Particles

As initially stated in this report, the purpose of this research is to develop and demonstrate a CE method for separation of uranium oxide particles from other types of particles. Successful separations of common oxide particles from each other by CE, as described above, leads next to determinations of the CE behavior of uranium oxide particles and their separability from other types of particles. This was done with particles of the common oxide,  $\text{Al}_2\text{O}_3$ , and with samples of environmental particulate material<sup>5</sup>.

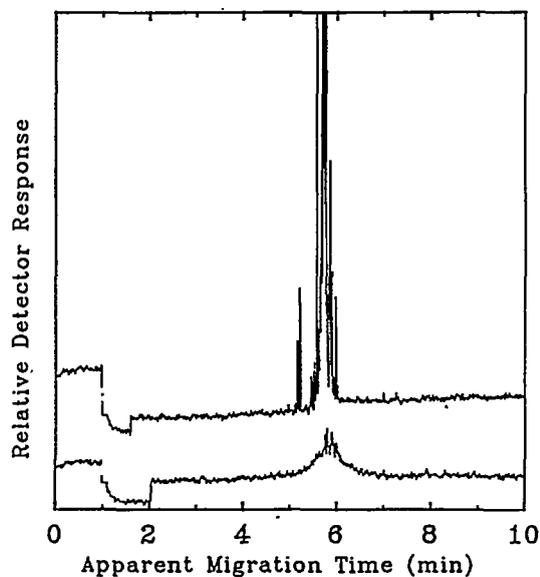
First experiments with uranium dioxide particles showed that satisfactory suspensions could be generated and that the particles were electrophoretically well behaved<sup>5</sup>. However, the peaks in the electropherograms were strongly spiked. This is similar to the peaks for  $\text{Fe}_3\text{O}_4$  in Figures 1-4. Visual observations of suspensions of both oxides showed what appeared to be sizable agglomerates of finer particles. The co-migration of the spike-producing material with the main peak material indicated that the agglomerates are the cause of the spikes. This was confirmed in experiments that demonstrated two important points: 1) co-migration of large particles with small particles, and 2) separation of  $\text{UO}_2$  particles from  $\text{Al}_2\text{O}_3$  particles. These results are presented in the electropherograms in Figure 5. It is clear from Figure 5 that the quality of separation of  $\text{UO}_2$  from  $\text{Al}_2\text{O}_3$  particles is comparable to that shown in the preceding section for common oxide particle separations.

As indicated in Figure 5, electropherograms of  $\text{UO}_2$  suspensions with and without large particles were obtained by first acquiring an electropherogram of a freshly-generated suspension of particles and then acquiring a second electropherogram on particles which remained suspended after a 4-h settling period. Confirmation of co-migration of large and small particles was made with  $\text{Fe}_3\text{O}_4$  particles, as shown in Figure 6. These experimental results are consistent with results of a theoretical analysis of particle size effects on electrophoretic mobilities,  $\mu$ , of particles. The analysis results were derived from the principles given in the modern theory of zeta potentials<sup>4</sup>. In that analysis, for a 30-mM ionic strength solution it was calculated that there would be an increase of only 5% in  $\mu$  in going from a particle diameter of 0.2  $\mu\text{m}$  to 1.0  $\mu\text{m}$  while there would be just a 1.5% increase in  $\mu$  in going from 1.0  $\mu\text{m}$  to 10.0  $\mu\text{m}$  in particle diameter. The absence of a measurable size effect in separations of chemically different kinds of particles by CE is of major significance in permitting straightforward separation of micrometer size particles without complications of particle size effects.

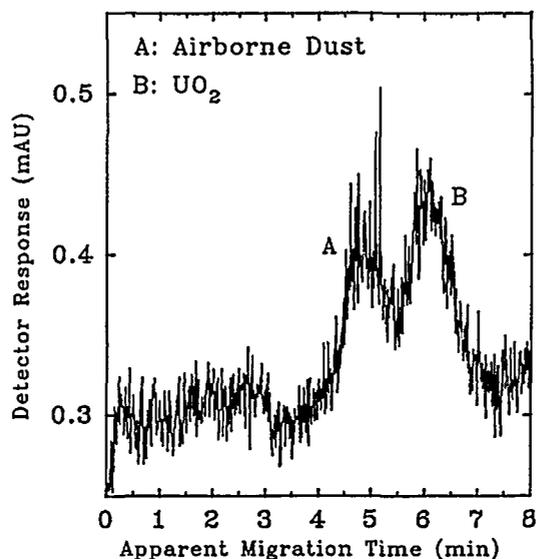
Separation of  $\text{UO}_2$  particles from complex mixtures of particles found in environmental samples was the next major test of the CE method<sup>5</sup>. A local airborne dust sample was collected, suspended in 6 mM, pH 10.7 carbonate buffer, and spiked with  $\text{UO}_2$  suspension. CE runs of this particulate mixture successfully separated  $\text{UO}_2$  particles from a major portion of the dust particles. Results of a run of the mixture are presented in Figure 7. Such separations were tested further with  $\text{UO}_2$  particles and a



**Figure 5.** Capillary Electrophoretic Separations of 17 ppm  $\gamma\alpha$ - $\text{Al}_2\text{O}_3$  and 83 ppm  $\text{UO}_2$  Particles in 6.00 mM, pH 10.7 Carbonate Buffer. The electric field strength was 185 V/cm. The electropherograms are from mixtures containing all  $\text{UO}_2$  particles (top) and containing only those  $\text{UO}_2$  particles that remained suspended for >4 hours (bottom).



**Figure 6.** Capillary Electrophoretic Runs of a 0.014 vol%  $\text{Fe}_3\text{O}_4$  Standard in 6.00 mM, pH 10.7 Carbonate Buffer. The electric field strength was 185 V/cm. The electropherograms are from injections of all particles (top) and of only the fine particles that remained suspended for >60 minutes (bottom).



**Figure 7.** Capillary Electrophoretic Separations of 100 ppm Airborne Dust and 90 ppm  $\text{UO}_2$  Particles in 6.00 mM, pH 10.7 Carbonate Buffer. The electric field strength was 185 V/cm.

variety of environmental samples and with additional types of buffer solutions<sup>7,8</sup>. Particles from ten different samples of airborne dust, soil, and vegetation were used. Their CE behavior and that of  $\text{UO}_2$  were determined in buffer solutions of phosphate at pH 7.2, borate at pH 9.2, and carbonate at pH 10.6.

In each of the buffer solutions the CE behavior of the environmental particulate samples tended to group together. Also, in each of the buffer solutions there was a consistent tendency for the  $\text{UO}_2$  particles to be usefully separable from the environmental particulate material. This is favorable for establishment of conditions for practical separations of  $\text{UO}_2$  particles from environmental particulate material. In applications of the CE method a small test aliquot of the sample particles would be run in the buffers to determine specifically its CE behavior in each buffer. Then the best buffer for separation of  $\text{UO}_2$  particles would be selected and used to process the sample.

## 2.5 Electrophoretic Behavior of Particles of the Three Uranium Oxides

The electrophoretic behavior of  $\text{UO}_2$  particles under various CE operating conditions has been described in the above sections. The electrophoretic behaviors of  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$  were also examined to establish CE conditions for their separations from environmental particulate material<sup>9</sup>.

Suspensions of  $\text{U}_3\text{O}_8$  were prepared in pH 7.2 phosphate, pH 9.2 borate, and pH 10.6 carbonate buffers. In CE runs on the  $\text{U}_3\text{O}_8$  suspensions in phosphate and borate solutions no peaks were observed in the resulting electropherograms. In addition, the particles appeared to dissolve in the phosphate buffer as no particles were visible in the suspension vessel several days after the suspension was

prepared. For the carbonate buffer, reproducible results could not be obtained and a slight yellow color became visible in the buffer solution several days after preparation of the  $U_3O_8$  suspension. To make CE separations of  $U_3O_8$  particles it will be necessary to develop a buffer solution in which  $U_3O_8$  is sufficiently insoluble and that provides a medium for satisfactory CE behavior.

Only limited experiments with  $UO_3$  particles were possible. A suspension of the particles was made in pH 10.6 carbonate buffer solution, and CE runs were made on the suspension. No peaks were detected in the resulting electropherograms. This may be due to some solubility of  $UO_3$  in carbonate solutions. In this case also, to be able to make CE separations of  $UO_3$  particles it will be necessary to develop a buffer solution in which  $UO_3$  is sufficiently insoluble and which provides a medium for satisfactory CE behavior.

## 2.6 Separation, Fraction Collection, and Enrichment Factor for $UO_2$

To determine to what extent  $UO_2$  particles can be enriched in CE-separated particulate material it is necessary to collect fractions of an eluting suspension and to determine relative amounts of  $UO_2$  and sample matrix particles in each of the fractions. An integrated method was developed that accomplishes that<sup>10</sup>.

The method developed for collection of fractions separated by CE was based on sequential collection of the fractions in microvolumes (35  $\mu$ L) of buffer solution. Use of such small volumes was central to the subsequent use of the membrane-filtration method developed for determinations of numbers of  $UO_2$  particles in each fraction. In this method the  $UO_2$  particles in each fraction were recovered on the filter, which was then processed by the lexan technique for determination of the numbers of  $UO_2$  particles on the filter and thus in the collected fraction. The relative numbers of sample matrix particles in each fraction were determined from the electropherogram of the CE run by determination of the fraction of the matrix particle peak area located in each collected fraction.

The integrated method was successfully applied to separations of a mixture of  $UO_2$  particles and airborne dust particles and to determinations of the relative amounts of each particle type in the collected fractions<sup>10</sup>. A suspension of both particle types was prepared in pH 10.6 carbonate buffer solution and separated by CE. An electropherogram showing the separation of the two particle types is shown in Figure 8. Also shown are the locations of separate fractions which were collected across the electropherogram. For two CE runs of this mixture, separated fractions were collected and analyzed for their  $UO_2$  and matrix particle contents in the manner described above. For these two runs, fractions 5 plus 6 were found to contain 5.0% and 5.2% of the dust particles, respectively. Also, for these two runs, fractions 5 plus 6 were found to contain 80% and 84% of the  $UO_2$  particles, respectively. It is thus seen that a 20-fold reduction in the amount of sample particles associated with about 80% of the  $UO_2$  particles was accomplished by CE separations and fraction collections of the  $UO_2$ -dust particle sample.

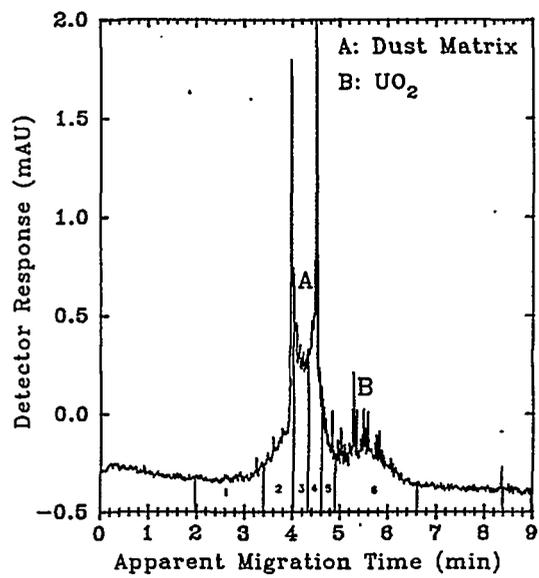


Figure 8. Electropherogram of UO<sub>2</sub>-Spiked Airborne Dust Sample Displaying Six Fraction Collection Intervals

### 3.0 Conclusions

The new method developed herein for separating chemically different kinds of particles by the CE technique can be applied to separations of  $UO_2$  particles from particles of environmental samples. Enrichment factors of about 20 for  $UO_2$  in respect to sample matrix particles can be obtained. This permits a reduction by a factor of about 20 in the costs and time for processing particulate samples by the lexan process.



## 4.0 References

1. Jorgenson JW, and KD Lukacs. 1981. "Zone electrophoresis in open-tubular glass capillaries." *Anal. Chem.* 53, 1298-1302.
2. Jones HK, and NE Ballou. 1990. "Separations of chemically different particles by capillary electrophoresis." *Anal. Chem.* 62, 2484-2490.
3. Petersen SL, and NE Ballou. 1992. "Effects of capillary temperature control and electrophoretic heterogeneity on parameters characterizing separations of particles by capillary zone electrophoresis." *Anal. Chem.* 64, 1676-1681.
4. Hunter RJ. 1981. *Zeta potential in colloid science*. Academic Press, New York.
5. Petersen SL, and NE Ballou. 1993. *Separation of oxide particles by capillary electrophoresis*. PNL-SA-23190, Pacific Northwest National Laboratory, Richland, Washington.
6. Remcho VT, and NE Ballou. 1994. *Electrophoretic behavior of different polymorphic forms and migration time reproducibility for several oxide particulates*. PNL-9806, Pacific Northwest National Laboratory, Richland, Washington.
7. Ducatte GR, and NE Ballou. 1994. *Electrophoretic separations of particles of uranium oxides from those of real-world samples*. PNL-10472, Pacific Northwest National Laboratory, Richland, Washington.
8. Ducatte GR, and NE Ballou. 1995. *Electrophoretic separations of particles of uranium oxides from those of additional real-world samples*. PNL-10579, Pacific Northwest National Laboratory, Richland, Washington.
9. Ducatte GR, and NE Ballou. 1994. *Electrophoretic behavior of particles of different oxides of uranium for various electrophoresis operating conditions*. PNL-10124, Pacific Northwest National Laboratory, Richland, Washington.
10. Ducatte GR, and NE Ballou. 1995. *Capillary electrophoretic separation and fraction collection of particles of real-world samples*. PNL-10845, Pacific Northwest National Laboratory, Richland, Washington.



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