

Date of Report: October 6, 2003

EPA Agreement Number: R828771-0-01

Center Name and Institution of Center Director: Center for Hazardous Substances in Urban Environments, Johns Hopkins University

Identifier Used by Center for Project: RP#5

Title of Project: "Speciation of chromium in environmental media using capillary electrophoresis with multiple wavelength UV/visible detection"

Investigators and Institutions: Principal Investigator: Alan T. Stone, Johns Hopkins University, Co-Investigator: Charles R. O'Melia, Johns Hopkins University

Type of Research: Laboratory and Basic

Project Period: September 1, 2002 to October 6, 2003

Objectives of Research: Appraising extents of contamination, predicting future contaminant migration behavior, and devising mitigation schemes all rely heavily upon the quality of chemical analysis information. In addition to total elemental concentrations, it is often worthwhile to obtain speciation information. With chromium, for example, it is widely accepted that oxidation state determinations are important. Although the diphenylcarbazide (DPC) colorimetric test can distinguish Cr(III) from Cr(VI), it is subject to interferences and may yield misleading results. Information beyond oxidation state, e.g. the number and identity of ligands coordinated to the central metal ion, is important too. Neutral Cr(III) complexes, for example, partition and adsorb to soils in ways quite distinct from cationic and anionic complexes.

Capillary electrophoresis (CE) is a promising new analytical method that offers the opportunity of obtaining speciation information that is more reliable (e.g. oxidation state determination) and more complete (coordination information) in comparison to methods currently employed by environmental professionals. CE separates analyte molecules based upon differences in the charge and hydrodynamic radii. Multiwavelength UV-visible detection, in turn, is inexpensive and easy to maintain. Our objective is to develop the analytical methodology to obtain chromium speciation information from aqueous samples relevant to hazardous waste sites using this new technique.

Progress Summary/Accomplishments: We began work with a new Beckman-Coulter MDQ capillary electrophoresis system in January 2002. As noted in the previous progress report, the Cr^{VI} species HCrO₄⁻ and CrO₄²⁻ are easily distinguished from a wide range of Cr^{III}-containing low molecular-weight complexes. Diode-array multi-wavelength detection (from 190 to 600 nm) allows us to use the wavelength of maximum absorbance (λ_{max}) for each chromium species in generating calibration curves. If a discernable CE peak appears, from our experience a detection limit of at least 50 ppb (1 μ M) can be obtained.

Let's suppose that an unknown peak appears in an electropherogram. Since full spectra are recorded by our UV-visible diode-array detector, Cr^{III} and Cr^{VI} are readily distinguished owing to their different values of λ_{\max} (wavelength of maximum absorbance). What additional information can we obtain from the time required for electromigration to the detector?

Citric acid, secreted by plant roots into soils, is a common and naturally-occurring chelating agent. The potential exists for the solubilization of sorbed or precipitated Cr^{III} at hazardous waste sites. To illustrate this point, citric acid has been brought into contact with amorphous Cr^{III} (hydr)oxide solid (Figure 1). A single new peak appears in the electropherogram. The observed electrophoretic mobility (μ_{obs}) reflects contributions from the effective electrophoretic mobility (μ_{eff}) and the electroosmotic flow (μ_{eof}):

$$\mu_{\text{obs}} = \mu_{\text{eff}} + \mu_{\text{eof}} \qquad \mu_{\text{eff}} = \frac{L_d}{t_m} \cdot \frac{L_t}{V} - \mu_{\text{eof}}$$

where L_d is the capillary length to the detector, L_t is the total capillary length, t_m is the time for the peak to reach the detector, and V is the applied electric field (in volts). μ_{eof} is known from the time required for the analyte to reach the detector.

Figure 2 represents our efforts to "calibrate" electrophoretic mobility in terms of the molecular charge of the analyte, using complexes of Cr^{III}, Co^{III}, Co^{II}, and Ni^{II}. A clear linear relationship exists; as the charge of the complexes becomes more anionic, the electrophoretic mobility becomes increasingly more negative. Based on this graph, we can quite justifiably conclude that the Cr^{III}-citrate complex possesses a charge of -1. (This is the expected charge, based on Cr^{III} coordination of one alcoholate and two carboxylate groups of the citrate molecules.)

Based upon this finding, we can conclude that the molecular charge of unknown peaks is readily obtained by CE.

Aqueous samples collected from the field sometimes must be stored for hours or for days before analysis can be performed. What changes accompany sample storage?

Figure 3 shows data obtained from the dissolution of Cr^{III} (hydr)oxide solids by nitrilotriacetic acid (NTA) ethylenediaminetetraacetic acid (EDTA) and iminodiacetic acid (IDA). Under the conditions employed, concentrations of Cr^{III} complexes with inorganic anions are negligible. Concentrations of discrete Cr^{III}-containing species are denoted by open circles. Total dissolved chromium concentrations determined by atomic absorption spectrophotometry (AAS) are denoted by filled circles. All the samples were collected, filtered, and then stored until analysis at the end of the experiment. In the experiments with NTA and EDTA, 80 % or more of total dissolved chromium can be attributed to discrete CE peaks. In other words, the complexes were not adversely affected by up to ten days of storage. IDA is a substantially weaker complexing agent, and the effects of sample storage are more severe. Our interpretation of these findings is that the acetate buffer employed in these experiments gradually replaced IDA within the inner coordination sphere of Cr^{III}. As a consequence, speciation information in the presence of this weaker complexing agent was lost during storage.

Publications/Presentations:

Carbonaro, R.F.; Stone, A.T. "Capillary Electrophoresis Analysis of Cr(III) and Cr(VI) Aqueous Speciation", Symposium on Emerging Technologies in Hazardous Waste Management: Current EPA Focus Areas", Division of Industrial & Engineering Chemistry, American Chemical Society 224th National Meeting, Boston, MA (August, 2002).

Carbonaro, R.F.; Stone, A.T. "Monitoring Environmental Transformations of Chromium Using Capillary Electrophoresis" [Poster], Environmental Sciences: Water Gordon Conference, Plymouth, NH (June, 2002).

Stone, A.T. "Exploring Transition Metal Ion Reactions In Aquatic Environments - New Insights From Capillary Electrophoresis", Department of Chemistry, Ohio State University, Columbus, OH (March, 2002).

"Redox Reactions in Soils: How Structure and Speciation Influence Reactivity", Environmental Science and Engineering, California Institute of Technology, Pasadena, CA (January, 2003).

Future Activities: Our next six months of research will focus on the following tasks:

Our future work focuses on natural organic matter (NOM)-rich surface waters. "Raw" water samples will contain a wide variety of organic molecules, including molecules that sorb strongly onto silica (SiO_2) and other mineral surfaces. We will also pre-contact NOM-rich surface waters with high surface area silica. This "pre-contacted" NOM will have less interaction with the quartz silica wall of our CE capillary. An important issue under investigation will be the extent to which interaction with this quartz silica wall affects what we are able to discern with CE.

We will spike both raw and pre-contacted NOM with (i) Cr^{III} complexes with relatively weak chelating agents (e.g. oxalate) and with (ii) Cr^{VI} (chromate ion). Type i experiments provide insight into slow rates of metal ion and ligand exchange reactions, and the subsequent speciation. Type ii experiments provide information regarding the redox incorporation of chromium into NOM.

Supplemental Keywords: - na -

Relevant Web Sites: - na -

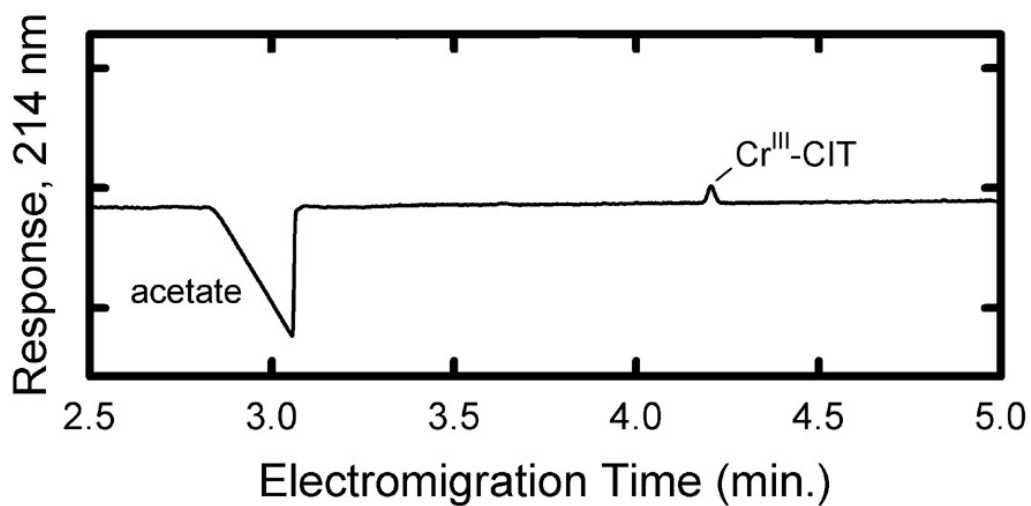


Figure 1. Characterization of a dissolved Cr^{III} complex with citrate by capillary electrophoresis. 100 μ M was added to 1 mM Cr^{III}(OH)₃ · xH₂O at pH 4.02. The peak at 4.2 minutes grew over a period of 12 days, and was attributed to a Cr^{III} complex with citrate. The electrophoretic mobility of this peak was -1.78×10^{-4} cm²/V-s, consistent with a monovalent anionic metal complex. Experimental conditions: 10 mM NaCl, 5 mM acetate.

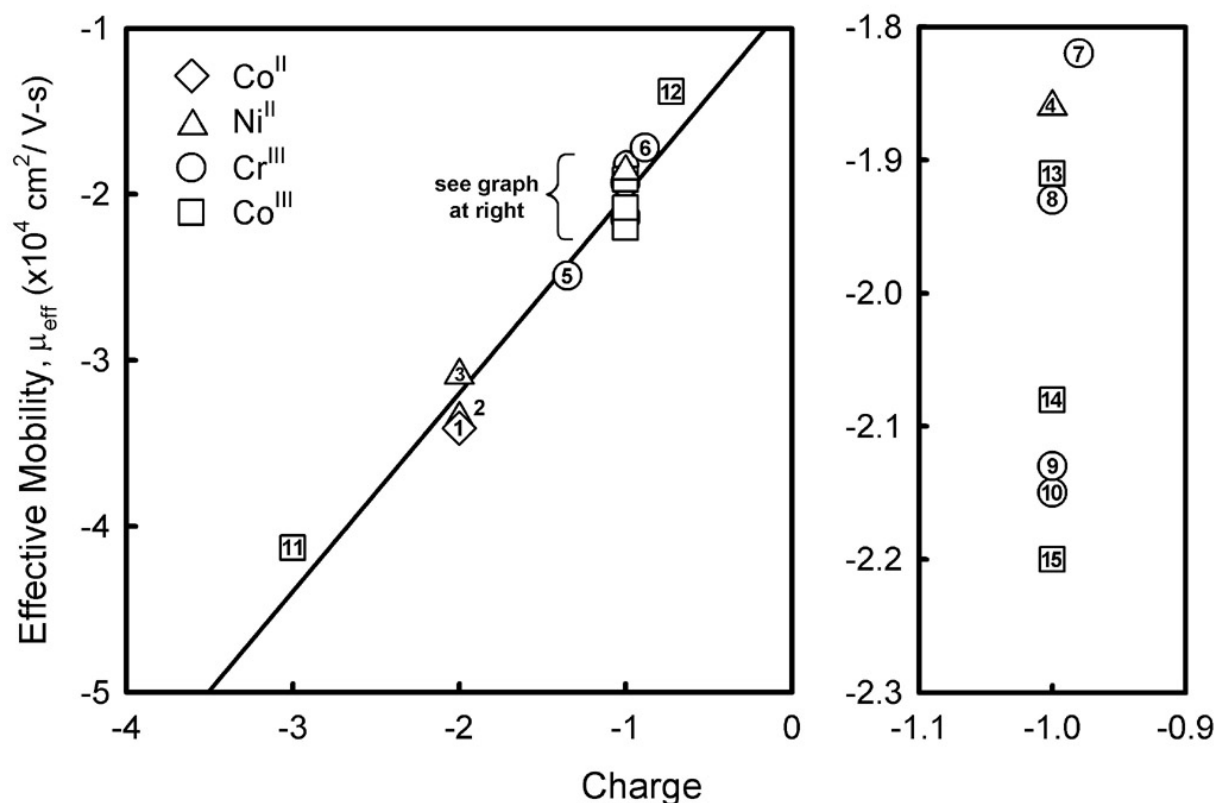


Figure 2. Effective mobility versus charge for monomeric Co^{II} , Ni^{II} , Cr^{III} and Co^{III} aminocarboxylate complexes. The average molecular charge of each complex was computed at the pH of the CE buffer (7.10) using pK_a values reported in the literature. The identity of each data point is as follows: 1. $[\text{Co}^{\text{II}}(\text{edta})]^{2-}$ 2. $[\text{Ni}^{\text{II}}(\text{edta})]^{2-}$, $[\text{Ni}^{\text{II}}(\text{tmdta})]^{2-}$ 3. $[\text{Ni}^{\text{II}}(\text{cdta})]^{2-}$ 4. $[\text{Ni}^{\text{II}}(\text{H}_2\text{O})(\text{hedta})]^-$ 5. $[\text{Cr}^{\text{III}}(\text{edta})]^-$ 6. $[\text{Cr}^{\text{III}}(\text{OH})(\text{hedta})]^-$ 7. $[\text{Cr}^{\text{III}}(\text{OH}_2)(\text{OH})(\text{nta})]^-$ 8. $[\text{Cr}^{\text{III}}(\text{cdta})]^-$ 9. $[\text{Cr}^{\text{III}}(\text{tmdta})]^-$ 10. *u-fac*- $[\text{Cr}^{\text{III}}(\text{ida})_2]^-$ 11. $[\text{Co}^{\text{III}}(\text{nta})_2]^{3-}$ 12. $[\text{Co}^{\text{III}}(\text{OH}_2)(\text{OH})(\text{nta})]^-$ 13. $[\text{Co}^{\text{III}}(\text{cdta})]^-$ 14. *u-fac*- $[\text{Co}^{\text{III}}(\text{ida})_2]^-$ 15. $[\text{Co}^{\text{III}}(\text{edta})]^-$, *s-fac*- $[\text{Co}^{\text{III}}(\text{ida})_2]^-$.

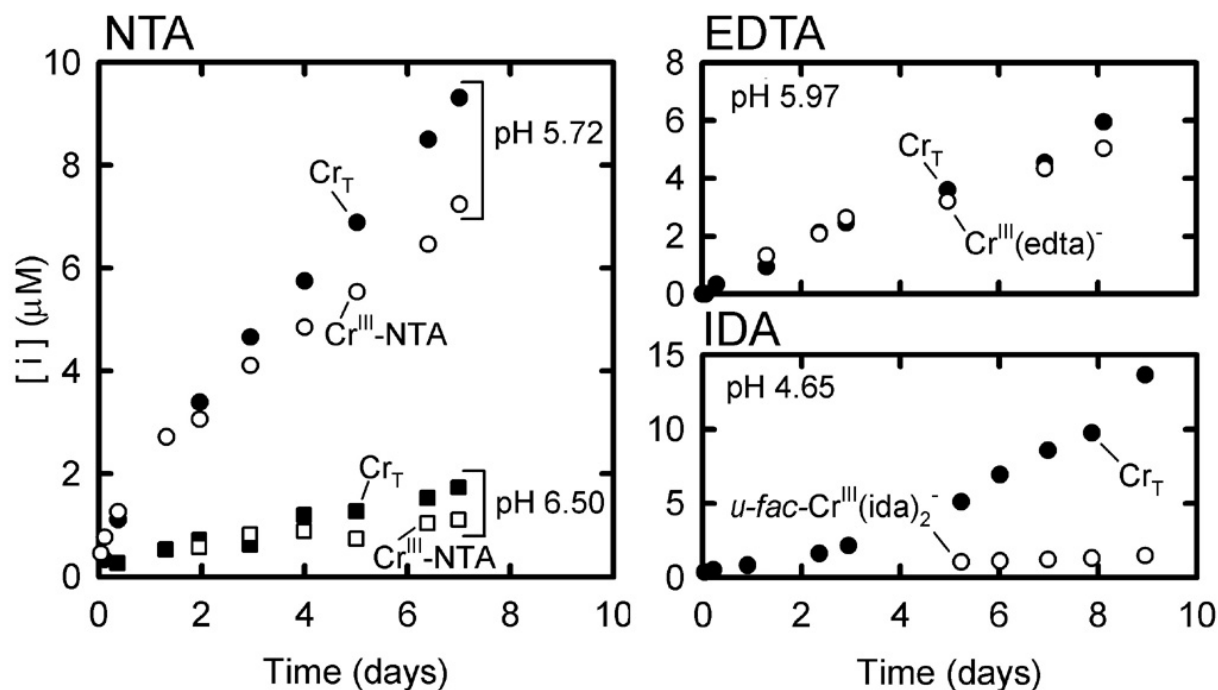


Figure 3. Characterization of dissolved Cr^{III} complexes with IDA, NTA and EDTA by capillary electrophoresis. Measurements of total dissolved chromium, Cr_T (closed symbols), were compared with measurements of individual Cr^{III} complexes by CE (open symbols). The left panel shows results for kinetic experiments with NTA at pH 5.72 and 6.50. The top right panel shows results using for experiments performed at pH 5.97 with EDTA; the bottom right panel shows results of an experiment at pH 4.65 with IDA. 1 mM $Cr^{III}(OH)_3 \cdot xH_2O$, 100 μM L_{tot} , 10 mM NaCl, 5 mM buffer (Acetate or MES).