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Effects of Analyte pH on the Accuracy of Capillary Zone Electrophoresis as a Quantitative Analytical Technique

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complexed and free species can be determined. The Benesi-Hildebrand equation was then used to calculate the charge complexation constant. The factors which affect the formation of a charge transfer complex between the electron donor and electron acceptor species are: aromaticity, solvent interaction, and concentration of species in solution. N-substituents were found to have little effect on the formation of a charge transfer complex. This poster will present data obtained for each of the aforementioned effects.

- 170. CAPILLARY ISOTACHOPHORETIC DETERMINATION OF DIBUTYLPHOSPHATE AND MONOBUTYLPHOSPHATE IN ORGANIC MATERIALS.** Catherine Peters, Department of Chemistry, Eastern Oregon State College, La Grande OR 97850-2899, Karen Wahl, Pacific Northwest Laboratory, P.O. Box 999, Richland WA 99352-0999

In the nuclear energy industry tributyl phosphate (TBP) is used in the regeneration of fuel elements due to its extracting power derived mainly from its phosphoral group. TBP slowly degrades in use as a result of attack by acids and in nuclear applications by radiation into dibutyl phosphate (DBP) and monobutyl phosphate (MBP). A method was developed to detect these degradation products. Capillary isotachopheresis (CITP) was chosen as the separation mechanism due to its small sample and buffer volume requirements (nl-ml respectively) and short run times (<30 min). The preliminary results from studies on the detection and quantitation of DBP and MBP using the reversed anionic mode of CITP and UV detection at 220 nm suggests a linear plot for relative analyte plug width versus concentration in the range 0.001M-0.01M. Analyte steps produced in the isotachopherogram were identified by spiking the samples and observing the corresponding changes in the analyte plugs.

- 171. ELECTROCHEMICAL STUDIES OF VANADATE IN AQUEOUS SOLUTION AT NEUTRAL pH.** E. Alejandro, I. Nieves, Department of Chemistry, Univ. of Puerto Rico-Humacao, PR 00791.

Eventhough Vanadate being in trace amounts in biological systems, plays an important role physiological processes (inhibition of the Na⁺-K⁺-ATPase and various of oxidation-reduction reactions). The electrochemical behavior of vanadium species have been the focus of intense studies using various methods. But such studies have been performed at extreme low and high pH. At neutral aqueous pH at 0.1-1.0 mM range the monomeric or dimeric forms of vanadium predominate as vanadate (V(V)) and vanadyl (V(IV)) in the absense of oxidizing agents. Therefore the electrochemical study at physiological pH is very important. The oxidation-reduction chemistry is characterized by multiple oxidation states which may produce different chemical species adding even more complexity of the system. Our studies using vanadate are performed in aqueous buffered (HEPES 0.05M) solutions at pH 7.4 with 0.1 KCl and low concentration (10 μ M) which mimic physiological conditions. Our group have been characterizing vanadate by Cyclic Voltammetry, (CV) using a 273 A Electrochemical Analysis System (PAR) using Hg and Glassy Carbon as working electrode against Ag/AgCl (sat.). The CV obtained depend greatly on concentration, initial potential and the number of cycles. The intensity of the peaks show a gradual increase with cycles and eventhough there is a reduction, that at higher concentration, present a splitting, that also depends on of the initial potential. We prestend to analyze the system in the presence of physiological important species such as Ouabain and/or ATP. Supported by NIH-MARC Grant 5T34 GM08156-10

- 172. ASSESSMENT OF THE USE OF ELECTROCHEMICAL SENSORS IN THE DETECTION OF NITROGEN-CONTAINING EXERCERGONIC COMPOUNDS**
Timothy W. Marin, IBC/5700 College Rd./Lisle, IL 60532/ Kohlbeck 302

The use of pyrolysis has been seen to effectively decompose trinitrotoluene (TNT), generating nitrogen oxides, which can be selectively detected with electrochemical sensors. It was

determined that electrochemical sensors would be capable of employment in the detection of TNT and other explosive materials in soil samples. The oxidative or reductive reaction taking place within the sensor upon contact with nitrogen oxides produces a microamp signal approximately 160 times as large as that obtained from background noise for the pyrolysis of 20 ppm TNT, exhibiting the high sensitivity of the sensor. Chemical filters were deployed to prevent the interference of other electrochemically active gases and were found to successfully remove SO₂, H₂S, and NO₂, to 95% or better. This method was developed for use with the Site Characterization and Analysis Penetrometer System (SCAPS) for the detection of nitrogen-containing soil pollutants.

- 173. SINGLE CELL ELECTROCHEMICAL DETECTION OF CATECHOLAMINE RELEASE FROM PC12 CELLS.** Robert T. Kennedy and Karen Burton, University of Florida, Gainesville, and Linda Brecci, Southwest Missouri State University, Springfield, Missouri 65804.

Vesicular release of catecholamines was studied at the single cell level. Electrochemical techniques are a valuable tool in the study of neurons; however, mammalian neurons are very difficult to work with in the laboratory and stop proliferation once they have matured. A clonal line of rat adrenal pheochromocytoma (PC12) cells exhibit many of the physiological properties of cultures of sympathetic ganglion neurons and are studied as a model for the developing sympathetic nerve. Stimulation of PC12 cells with nicotine/K⁺ produced current spikes with area proportional to molar quantities of dopamine and norepinephrine expected for exocytotic release. PC12 cells which were exposed to nerve growth factor (NGF) for 5-6 days grew interconnecting processes. These smooth processes have larger areas, or varicosities, at various distances from the cell body. Nicotine/K⁺ stimulation of these differentiated PC12 cells resulted in vesicle release at the varicosities consistent with the smaller size of the varicosities vs. the cell body. Little or no catecholamine release was observed from the cell body of differentiated cells, and no vesicle release was observed from the smooth processes.

- 174. EFFECTS OF ANALYTE pH ON THE ACCURACY OF CAPILLARY ZONE ELECTROPHORESIS AS A QUANTITATIVE ANALYTICAL TECHNIQUE.** Michael A. Janusa, Lawrence J. Andermann, Mark H. Nannie, Dant A. Sandras, Department of Physical Sciences, Nicholls State University, Thibodaux, Louisiana, 70310

The determination of the concentration of inorganic species both charged and neutral can be accomplished by using capillary zone electrophoresis (CZE). Capillary zone electrophoresis is the fastest growing analytical separation technique. There are many factors that effect electroosmotic flow; pH is one of the major factors effecting electroosmotic flow. It has been shown previously that the buffer pH has a dramatic effect on the electroosmotic flow and may essentially stop electroosmotic flow at low pH. Another pH that is equally important is the pH of the analyte. Herein, it is shown that the pH of the analyte is a very crucial factor for obtaining accurate results with CZE. Experimental evidence shows that the pH of the standards and sample analyte, must be similar in order to optimize resolution and accuracy with CZE.

- 175. THE ANALYSIS OF WATER SOLUBLE INKS BY CAPILLARY ELECTROPHORESIS.** Analytical Chemistry. A. McManus, E. Rohde, W.R. Heineman, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221

The analysis of inks is important in the provision of trace evidence in forensic science. Most frequently thin layer chromatography is used - simple, yet laborious technique. Capillary electrophoresis (CE) is a relatively young but versatile separation technique. We used CE for