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DETERMINATION OF METAL ION COMPLEXES IN ELECTROPLATING SOLUTIONS USING CAPILLARY ZONE ELECTROPHORESIS WITH UV DETECTION

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SUMMARY

Capillary zone electrophoresis with on-column UV detection at 214 nm was used to detect and determine iron cyanide complexes in liquid samples from zinc electroplating processes. Using a cathodic injection and anodic detection scheme, hexacyanoferrate(II) and -(III) ions were separated with baseline resolution in under 5 min. A linear relationship between peak area and concentration was obtained for both ions, and the detection limit was lower than 10 μM . The experiments were extended to detect the presence of zinc hydroxo complexes in plating solutions. The electrophoretic mobility of this species was determined from the migration times, sampling simultaneously the zinc species at the cathode and adenosine, a neutral molecule that migrates with the electroosmotic flow, at the anode. The results seem to indicate the presence of the doubly charged species $Zn(OH)_4^{2-}$ in Zn^{II} solutions at $pH > 10.5$.

INTRODUCTION

Electroplating has significant applications in metal processing for a variety of products in the electronics, automobile and construction industries. Often, electroplating solutions consist of complex mixtures of ionic and non-ionic compounds and contain one or two major components, additives and minor constituents as impurities. Both additives and minor constituents contribute, in many instances, to the quality of the final product. On the other hand, many of these species are harmful to the environment. Therefore, it is very important to monitor these substances during the electrolytic process and before the exhausted electroplating solutions are discharged into natural waters.

Both high-performance liquid and ion chromatography¹ are useful in solving these analytical problems. Different experimental methodologies for the determination of the constituents of electroplating solutions have been described^{2,3}.

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An alternative approach to this problem is to use capillary zone electrophoresis (CZE), in which a narrow band of the sample is introduced into a capillary and subjected to electrokinetic separation. In this way, the different components in a given sample can be determined if suitable conditions for detection are applied.

In this paper, the results of the separation of hexacyanoferrate(II) and -(III) ions are reported. The results were applied to the determination of the iron cyanide complexes existing as impurities in samples from zinc electroplating processes. Because these solutions contain mixtures of zinc cyanide and zinc hydroxo complexes, the last part of this work was dedicated to identifying the latter type of complexes in industrial water and to providing experimental information in order to ascertain the charge of these species in a highly alkaline medium.

EXPERIMENTAL

Instrumentation

The CZE system has been described elsewhere⁴. A polyimide-clad fused-silica capillary of 75 μm I.D. (Polymicro Technology, Phoenix, AZ, U.S.A.) was used together with a high-voltage power supply (Hypotronics, Brewster, NY, U.S.A.) of 0–30 kV with reversible polarity. Samples were introduced into the cathodic end of the capillary by gravity (sampling time 10 s at a height of 7 cm of the inlet with respect to the outlet). In this way, the biases associated with electrokinetic sampling were avoided⁵. By placing a JASCO UV spectrophotometer (UVIDEC-100 V), modified for CZE experiments, near the anode, detection was affected at 214 nm. The data were recorded using analog-to-digital conversion with the help of an IBM PC/XT computer.

Reagents and solutions

$\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ and $\text{Na}_3\text{Fe}(\text{CN})_6$ analytical grade (J. T. Baker, Phillipsburg, NJ, U.S.A.) were used without further purification. Standard solutions of both compounds were prepared in distilled, deionized water. $\text{Zn}(\text{OH})_4^{2-}$ standard was prepared by dissolving known amounts of $\text{Zn}(\text{NO}_3)_2$ (J. T. Baker) in 0.5 M sodium hydroxide solution. The electrolytic buffer was a mixture of NaH_2PO_4 and Na_2HPO_4 (20 mM, pH 7). The electroplating solution, prepared by dissolving solid zinc oxide and sodium cyanide in excess of sodium hydroxide solution, contained approximately 152 mg/l of Zn, 29 mg/l of Fe, 50 mg/l of Cu and minor amounts of Cr and Cd. The pH of the solution was 12.6. This electroplating solution was kindly provided by Electrite (East Palo Alto, CA, U.S.A.).

RESULTS AND DISCUSSION

Experimental methodology

In a typical CZE system with a fused-silica capillary, the direction of the electroosmotic flow is from the anode to the cathode and the sample is injected at the anode. The electroosmotic flow-rate is often so strong that all the analytes, even those with negative charge, will move toward the cathode. In this work, however, the ionic mobilities of the highly negatively charged metal cyanides are so large that they will not be carried from the anode to the cathode, making their detection impossible if they are

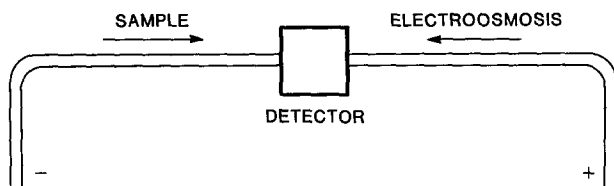


Fig. 1. Diagram of the CZE system used. Note that the sample is injected at the cathode and the highly charged negative complex ions move against the electroosmotic flow.

injected at the anode. Consequently, we choose to inject the sample at the cathode and place the detector near the anode (see Fig. 1). Under these conditions, the species of interest will migrate toward the anode and against the electroosmotic flow. The separation of hexacyanoferrate(II) and -(III) ions is shown in Fig. 2.

Quantitation

Several consecutive runs with different standard solutions were made in order to study the reproducibility of the migration times and the variation of the peak areas with concentration. The reproducibility of the migration times and the values of the correlation coefficients ($r > 0.99$) of the straight-line fits indicate that CZE can be used for both qualitative and quantitative analyses of liquid samples containing anionic metal species. We found the following migration times and standard deviations: 258.8 ± 1.3 s for $\text{Fe}(\text{CN})_6^{4-}$, 315.2 ± 1.9 s for $\text{Fe}(\text{CN})_6^{3-}$ and 629.4 ± 4.1 s for $\text{Zn}(\text{OH})_4^{2-}$. These values were measured for a capillary length of 75 cm, an applied voltage of 25 kV and a distance between the inlet and the detector of 25 cm.

Analysis of electroplating solutions

In order to find the best experimental conditions for the analysis of the different ions in the sample, the pH of the original solution was first adjusted to 9.5 and then several dilutions were made. In this way, we avoided working with highly alkaline solutions that may change the behavior of the inner surface of the capillary. For the detection of the different metal cyanides, we found the ideal dilution to be 1:6 either in

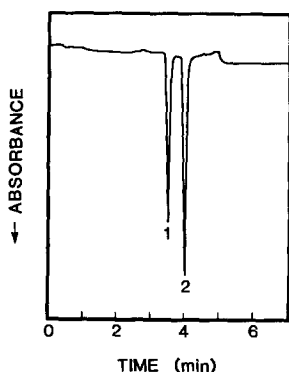


Fig. 2. Electropherogram of a mixture of iron cyanide complexes: (1) $\text{Fe}(\text{CN})_6^{4-}$; (2) $\text{Fe}(\text{CN})_6^{3-}$. Conditions: applied voltage, 25 kV; capillary length, 86 cm; concentration of ions, 10^{-4} M; phosphate buffer, 20 mM (pH 7).

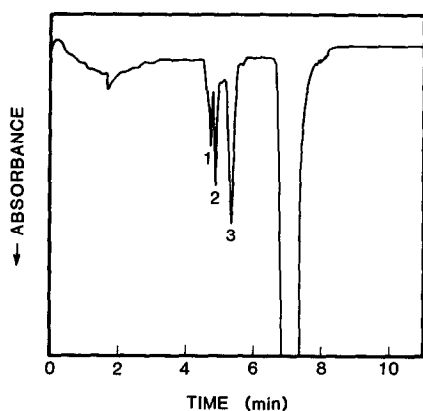


Fig. 3. Electropherogram of electroplating solution containing Zn, Fe and Cu cyanide complexes; 1:6 dilution with buffer, pH 9.5. Peak 1 is not identified; peak 2 is $\text{Fe}(\text{CN})_6^{3-}$; peak 3 may correspond to $\text{Cu}(\text{CN})_4^{2-}$; the large peak off-scale is $\text{Zn}(\text{OH})_4^{2-}$. In the electropherogram of the electroplating solution after chemical treatment to remove heavy metal anions, no significant peaks were observed.

water or in the buffer solution. Under these conditions, several consecutive electropherograms of the sample were taken; Fig. 3 shows a representative run, with three different peaks at migration times of *ca.* 5 min. These peaks may be ascribed to the presence of hexacyanoferrate(II) and -(III) ions. In order to determine which of the peaks should be assigned to the different iron complexes, the electroplating solution was spiked with standard solutions of hexacyanoferrate(II) and -(III). The results indicated that the electroplating solution contains Fe^{II} in the form of the anionic complex of formula $\text{Fe}(\text{CN})_6^{3-}$. The concentration of this ion was calculated to be $6 \cdot 10^{-4} \text{ M}$ from the area of peak 2 in Fig. 3. This value of the concentration, which corresponds to 33 mg/l of iron, is in good agreement with the analytical information (29 mg/l) provided by Electrite and obtained from Fe^{II} determination by standard volumetric methods after acid destruction of the complex ion.

The large peak in the electropherogram in Fig. 3 evidently represents one of the major components of the electroplating solution. Hence, the peak may be assigned either to the complex $\text{Zn}(\text{CN})_4^{2-}$ or to a soluble species of general formula $\text{Zn}(\text{OH})_n^{(2-n)-}$, which may exist at high pH. Because the metal cyanide complex absorbs weakly at the detector wavelength and the electroplating solution shows a white precipitate at $\text{pH} < 10.5$ (the standard solutions of the zinc cyanide complex do not precipitate under identical conditions), it may be assumed that the appearance of this peak in the electropherogram is caused by migration of the zinc hydroxo complex. This was experimentally confirmed by using Zn^{II} standards at different pH.

Determination of the ionic mobility of the species $\text{Zn}(\text{OH})_4^{2-}$

In order to ascertain the charge of this species, we injected a Zn^{II} standard at pH 10 at the cathode and also injected adenosine, a neutral marker molecule, at the anode. The resulting electropherogram is shown in Fig. 4. The first peak corresponds to adenosine. From its measured migration times and the known distance between the anode and the detector, the electroosmotic flow-rate was calculated. The second peak corresponds to the species $\text{Zn}(\text{OH})_4^{2-}$. From its migration time and the known distance

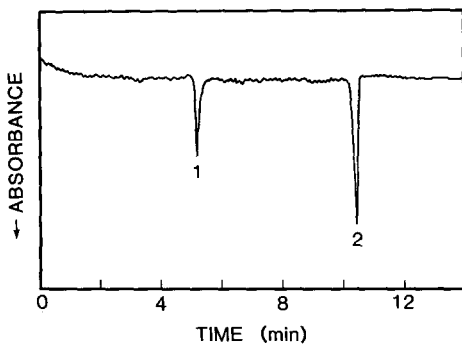


Fig. 4. Electropherogram of adenosine and Zn(OH)_4^{2-} standards. Peak 1 is adenosine and peak 2 is Zn(OH)_4^{2-} .

between the cathode and the detector, the electrokinetic flow-rate was determined. Using the electroosmotic flow-rate determined for adenosine, the electrophoretic flow-rate of the species Zn(OH)_4^{2-} was calculated. Knowing the value of the electric field strength, the ionic mobility of the metallic species was found to be $7.5 \cdot 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$. This value of the ionic mobility is of the same order of magnitude as that quoted in the literature for other divalent ions ($7.4 \cdot 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$ for CO_3^{2-} , $8.2 \cdot 10^{-4} \text{ cm}^2/\text{V} \cdot \text{s}$ for SO_4^{2-})⁶. For this reason, it may be assumed that the zinc hydroxo complex has an electric charge equal to -2 . Consequently, we identify it as Zn(OH)_4^{2-} .

Monitoring industrial waste water

Metal cyanides are generally toxic and should be destroyed before the spent electroplating solutions are discharged into the environment. For this reason, these types of solutions are subjected to chemical treatment in order to eliminate both free and complexed cyanide. The electropherogram of the zinc electroplating solution after chemical treatment showed no significant peaks, indicating that the treatment was satisfactory and that essentially all the metal cyanides had been eliminated.

We conclude that CZE may be a useful technique in the control and analysis of many kinds of industrial waste waters.

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