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Journal of Chromatography A, 739 (1996) 191–198

JOURNAL OF  
CHROMATOGRAPHY A

## Analysis of disparate levels of anions of relevance to corrosion processes

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### Abstract

The application of an analysis approach which combines matrix matching of electrolyte with sample with direct UV detection for anion analysis of low levels (ppm) of some anions in the presence of large levels (on the order of 1 M) of chloride or sulfate is reported. By replacing the standard chromate electrolyte with one based on the dominant anion (e.g., NaCl), a matrix match for the anion is achieved. The development of the method and the effects of the concentration of the electroosmotic flow modifier on the selectivity of the analysis are described. In addition, the application of the method to several corrosion studies is presented.

**Keywords:** Corrosion; Electroosmotic flow modifier; Buffer composition; Inorganic anions

### 1. Introduction

In corrosion studies, there are many instances in which the anionic species of interest may be present at mM concentrations while the major anion present (typically chloride) occurs at concentrations of the order of 1 M. Anions of interest in such studies include the sulfur species such as sulfide, sulfite, thiosulfate and tetrathionate, and oxyanions such as molybdate, tungstate, nitrate and nitrite. These species are of interest due to their origin in the corroding metal substrate as alloying elements (i.e., S, Mo, W, N). Their role in the mitigation or acceleration of the localized corrosion processes involving chloride ions continues to be an object of controversy [1–5]. Alloying elements can affect corrosion processes by changing the nature of the

interfacial kinetics of importance [3], forming a protective barrier in the form of an oxide film [4], or by forming soluble, inhibiting species that modify the corrosivity of the solution [5]. While a great deal of work has characterized the effects of alloying elements on the nature, thickness and composition of the passive film that forms on engineering materials, and substantial work has characterized their effects on the interfacial kinetics, few measurements exist on the nature of the soluble species that form from these alloying elements during dissolution of the material. This lack of data is due to the small masses of material of interest and the inherent analytical difficulty of measuring small amounts of one species in the presence of large amounts of another. In the case of corrosion, the dominant anion present tends to be chloride. Ion chromatography (IC) has been used [6–8] to study these processes, but can be limited in its ability to handle disparate levels. CE has been found to be more robust for such applica-

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tions, but sometimes still requires method modification to handle disparate levels.

The use of an analysis approach which combines matrix matching with direct UV detection for anion analysis in CE has been developed and applied to a number of corrosion applications. By replacing the standard chromate electrolyte [9] with one based on the dominant anion (e.g., NaCl), a matrix match for the anion is achieved, but at the loss of universal detection via indirect UV. For chromophores such as the sulfur species and the oxyanions, this loss of universality in detection is actually a benefit, as it allows a more rigorous determination of a species, as all of the anion species of interest except sulfate in these investigations absorb fairly strongly at 214 nm. The development of the method, the results of some electrolyte modifications, and its application to several corrosion studies are presented.

## 2. Experimental

The CE system used for all experiments was the Waters Quanta 4000 (Waters Corporation). Fused-silica capillaries (Polymicro Technology) of 75  $\mu\text{m}$  I.D. and 60 cm length were used. The polyimide coating was burned off to create a detection window 52 cm from the injection end. New capillaries were conditioned by purging with 0.5 M KOH for 3 min, followed by a 15-min purge with deionized water (from a Millipore Milli-Q UV Plus water purification system, water resistivity of 18 M $\Omega$ -cm) and a 25 min purge with electrolyte. Used capillaries were cleaned weekly by following the above procedure. Capillaries were electrolyte specific.

Hydrostatic sampling was used with a sampling time of 30 s and a height of 10 cm. The capillary was purged with electrolyte for 2 min before each run and with deionized water at the end of each day. All analyses were carried out at room temperature (23  $\pm$  2°C) using a negative power supply at 20 kV.

Direct UV detection at 214 nm was used for the analysis of molybdate, tungstate, thiosulfate, sulfide and sulfite in the presence of either high concentrations of chloride or sulfate (>300 ppm). The electrolyte used when examining high-Cl<sup>-</sup> solutions was deionized water containing 25 mM NaCl (Fisher reagent grade) and differing amounts of OFM Anion-BT (Waters Corporation) with a pH of 10.5. In some

cases, the OFM was put in the hydroxide form by passing it through Bio-Rad AG 1-X2 anion-exchange resin which had been previously rinsed several times with 0.1 M NaOH and high-purity water. The electrolyte used for high-SO<sub>4</sub><sup>2-</sup> solutions was deionized water containing 1.5 mM Na<sub>2</sub>SO<sub>4</sub> (Fisher reagent grade) and 2 mM osmotic flow modifier (OFM) Anion BT in the hydroxide form, with the pH adjusted to 10.5. All pH adjustments were made using NaOH or HCl (Fisher reagent grade).

## 3. Results and discussion

One example of the analytical difficulties encountered in corrosion studies is the study of the effect of alloyed sulfur on the crevice corrosion of stainless steel in neutral chloride solutions [10]. While substantial phenomenological evidence of the deleterious effects of alloyed sulfur on the crevice corrosion resistance of various alloys exists [11–14], the mechanism which is responsible has not been unambiguously delineated. Typical crevices would contain solutions with a chloride to sulfur species ratio of the order of 200:1. When the standard chromate electrolyte was used for anion analysis of a standard containing 600 ppm Cl<sup>-</sup> and ppm levels each of several sulfur species, the electropherogram of Fig. 1a was obtained. The large chloride concentration dominates and encompasses any sulfur species peaks that may be present. This type of result provided the impetus for the remainder of the work.

The balance of the results are presented and discussed in three subsections. The first section discusses the method development including the effects of the form of the osmotic flow modifier and its concentration. The second section discusses an application of the method to the measurement of low levels (mM) of sulfur species in the presence of molar levels of chloride during the crevice corrosion of stainless steels. The third section describes the results from another application in the study of the passive dissolution of Al–Mo and Al–W alloys.

### 3.1. Development of method

Fig. 2 shows the results for the chloride electrolyte with direct UV detection for a standard containing 600 ppm chloride, 5 ppm thiosulfate, 7.5

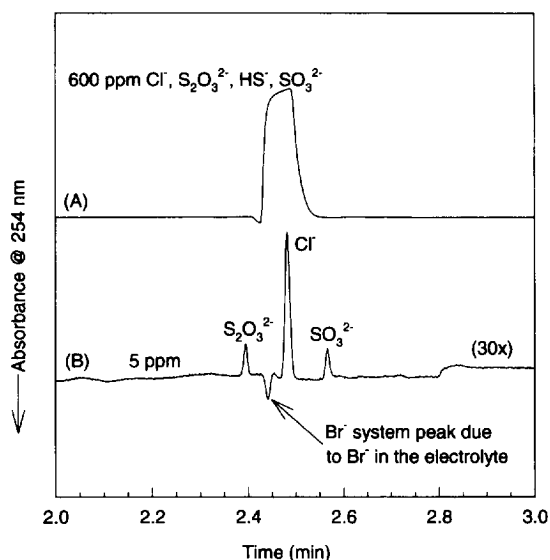


Fig. 1. (A) Electropherogram of a standard containing sulfur species (5 ppm thiosulfate, 7.5 ppm sulfide and 5 ppm sulfite) that are hidden in the large (600 ppm) chloride peak. (B) Standard containing 5 ppm chloride, 7.5 ppm sulfide, 5 ppm thiosulfate and 5 ppm sulfite. Note the absence of any peak for sulfide. Electrolyte: 5 mM chromate electrolyte, 0.5 mM OFM-BT, 20 kV, indirect detection at 254 nm.

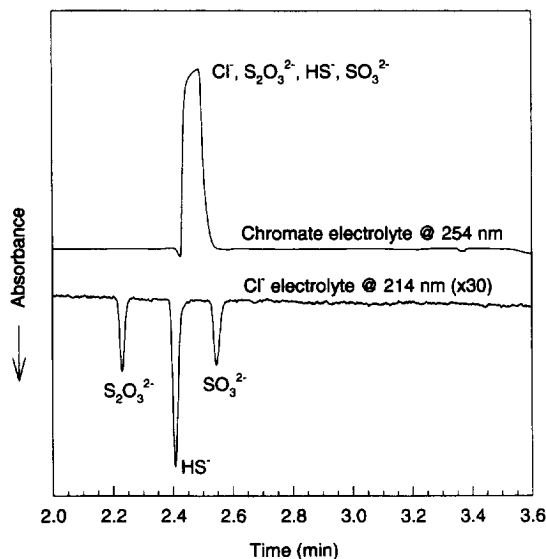


Fig. 2. Electropherogram of same sample as in Fig. 1 but using chloride electrolyte (25 mM NaCl, 0.5 mM OFM in OH form, pH 10.2) with direct UV detection at 214 nm for a standard containing 600 ppm chloride, 5 ppm thiosulfate, 5 ppm sulfide and 5 ppm sulfite.

ppm sulfide and 5 ppm sulfite. The presence of the 600 ppm chloride had no adverse effects on the separation. The regression statistics for standards run in this electrolyte over a concentration range of 0.5 to 16 ppm showed good linearity using peak area ( $r^2=0.998$ , 0.993 and 0.999 for thiosulfate, sulfide and sulfite, respectively). Excellent linearity is observed for all of the sulfur species. Fig. 3 shows the effect of the form of the electroosmotic flow (EOF) modifier on the electropherogram. When used in the Br form, a large, positive baseline disturbance occurred just before the thiosulfate peak. The bromide in the electrolyte electrostacked, causing the deviation at the bromide peak position. The size of the baseline disturbance was found to increase with increasing ionic strength of the sample. When the EOF modifier was transformed into the hydroxide form, the baseline disturbance disappeared, as shown in Fig. 3b. This transformation improved the ability to quantitate the thiosulfate peak more accurately.

The EOF modifier concentration was used to change the selectivity of the separation, which can aid in the analysis of more complex samples. As shown in Fig. 4, with an EOF modifier concentration of 2 mM, thiosulfate and nitrate comigrate. In-

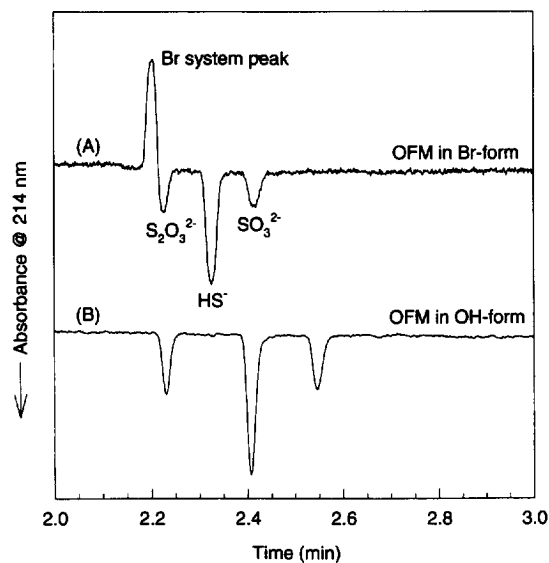


Fig. 3. Comparison of chloride electrolyte with the EOF in the (A) Br form and (B) OH form. Sample is a standard containing 600 ppm chloride, 5 ppm thiosulfate, 7.5 ppm sulfide and 5 ppm sulfite. Note the removal of the baseline aberration just before the thiosulfate in the OH form electrolyte.

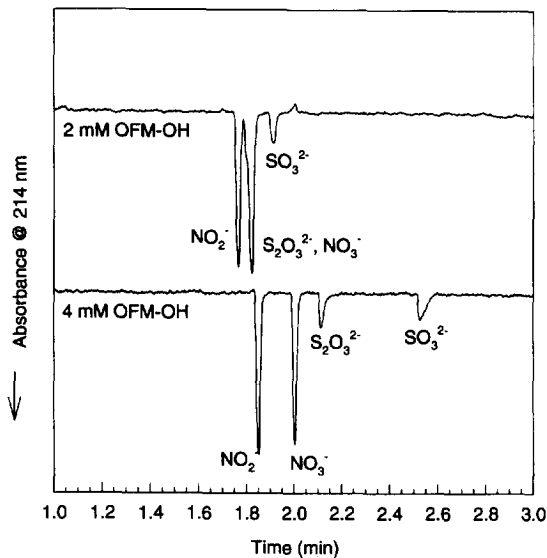


Fig. 4. Increasing the OFM concentration from 2 to 4 mM in the chloride electrolyte improves the separation by changing the selectivity. Note the near-complete comigration of thiosulfate and nitrate in the 2 mM OFM solution, while excellent separation was achieved in the 4 mM OFM solution.

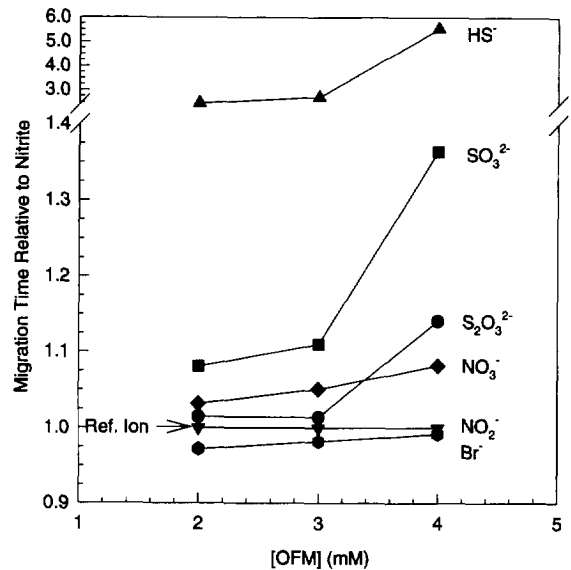


Fig. 5. Relative migration times (reference ion=nitrite) as a function of OFM concentration. Note the break in the migration time scale for sulfide and the strong effect of OFM concentration on the weak acid anions above 3 mM.

ing the EOF modifier concentration from 2 to 4 mM increased the migration time of thiosulfate relative to nitrate, allowing baseline resolution. As shown in Fig. 5, the migration times of the weak acid anions (in this case, the sulfur species) are much more strongly affected than the hard acid anions by increasing the EOF modifier concentration. The weak acid anions are more strongly affected by an EOF modifier concentration above 3 mM due to their hydrophobicity and the presence of micelles of the EOF modifier at these concentrations [14]. Under these conditions, the weak acid anions will tend to form equilibrium ion-pairs, which are more neutral and hence have longer migration times. Note the extremely strong effect on sulfide in Fig. 5 which shows that at 4 mM EOF modifier, the migration time of sulfide is 10.04 min. The sulfide peak under these conditions is extremely well-shaped, as will be shown later. Note that it is critical for accurate  $\text{HS}^-$  quantitation that the pH of the electrolyte be maintained at least one pH unit above its  $\text{p}K_a$ . As the electrolyte pH decreases, the  $\text{HS}^-$  will become neutral, distorting its peak shape and decreasing its response.

### 3.2. Analysis of sulfur species from a corroding stainless steel crevice

As shown in Fig. 1, low levels of sulfur species cannot be determined with the standard chromate method if large concentrations of chloride are also present. As part of a study aimed at delineating the mechanism by which alloyed sulfur decreases the resistance of stainless steels to localized corrosion, studies of the local chemistry that develops inside crevices have been performed. A variety of actual crevice solutions were analyzed. The experimental details of the crevice corrosion experiments can be found elsewhere [10,15]. A typical electropherogram from an active crevice corrosion site is shown in Fig. 6, showing that sulfide was the only sulfur species in the crevice solution. These measurements have been used to discount the theory that thiosulfate production from the dissolution of MnS inclusions in the stainless steel are responsible for the initiation of crevice corrosion [16,17]. At no point in the testing in chloride solutions was thiosulfate detected in a solution removed from a crevice. If thiosulfate was added to the bulk, it accelerated the attack and was concentrated in the crevice, but no thiosulfate was

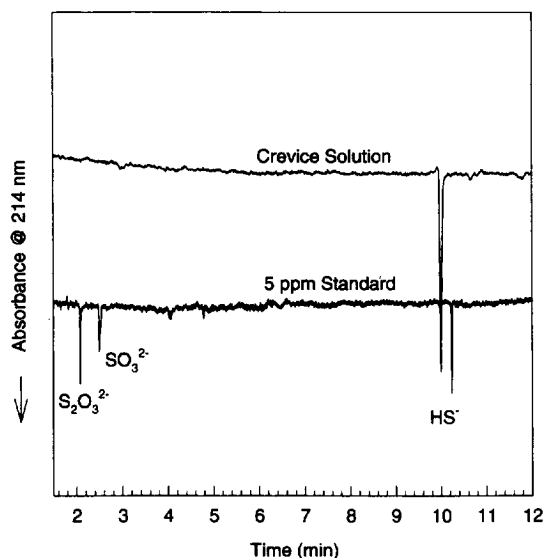


Fig. 6. Electropherogram of solution removed from active crevice of Type 304 stainless steel corroded in 17 mM NaCl at +0.05 V (SCE). The only sulfur species detected was sulfide. Electrolyte: 25 mM NaCl, 4 mM OFM in OH form, pH 10.8.

produced by dissolution of the stainless steel. An estimation of the chloride concentration present at incipient corrosion sites can be made by CE analysis for the metal cations present. Using the corrected concentrations for the cations and electroneutrality, the occluded cell chloride content can be estimated. This concentration increases during the time before crevice corrosion initiates to 0.9 M. Thus, the chloride electrolyte allows small concentrations of sulfide in the presence of large amounts of chloride. Typical concentrations were 10 to 60 mM sulfide in the presence of 0.9 M chloride.

CE was also used to demonstrate that thiosulfate was not formed during dissolution and transformed to another sulfur species during the testing or handling. Fig. 7 shows the decomposition kinetics of thiosulfate in a neutral chloride solution. These data were generated by CE analysis of serially removed aliquots. The horizontal "total sulfur" line, which was calculated from the sum of the soluble sulfur species detected, indicates that no elemental sulfur was produced within the experimental error ( $\pm 4\%$ ). In addition, the thiosulfate was found to be persistently metastable, with no measurable decomposition occurring over the first 3 h. Thus, if thiosulfate had

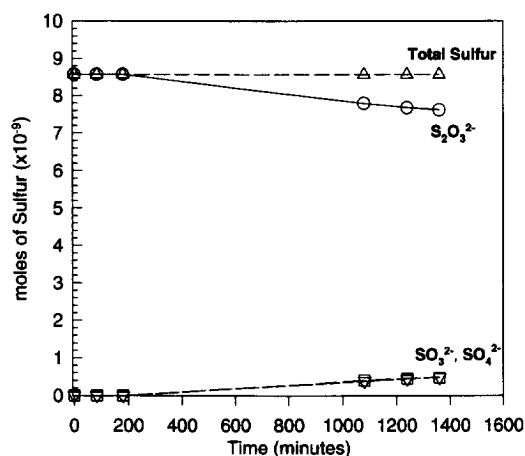


Fig. 7. Decomposition kinetics of thiosulfate in a deaerated, neutral chloride solution containing 2 M NaCl. The total amount of sulfur remained constant within experimental error of the CE analysis ( $\pm 3\%$ ), indicating that no elemental sulfur was formed.

been produced during the 45 min crevice corrosion test, some of it would remain in the rinse solution that was analyzed within 5 min of the stopping of the test.

The use of the chloride electrolyte has allowed estimations of the occluded solution sulfide concentration to be made. At the initiation of crevice corrosion, approximately 6 mM sulfide was present in these crevices along with 0.9 M chloride. Electrochemical measurements on stainless steel in bulk analogues of these solutions have shown that while stainless steel remains passive in 0.9 M chloride, the addition of the 6 mM sulfide was sufficient to cause it to activate and begin active dissolution [10]. During the stabilization of crevice corrosion, the concentration of chloride increased to approximately 3–4 M, and the sulfide concentration increased to levels close to 0.5 M.

One method to inhibit chloride-induced crevice corrosion is the addition of non-aggressive anions such as sulfate to the bulk solution [18]. The mechanism by which such additions inhibit localized corrosion is currently under study using the analysis approach outlined. In relation to the development of the critical crevice solution described above (a mixture of mM levels of sulfide and M levels of chloride within the crevice), sulfate could suppress the concentration of chloride by a supporting elec-

trolyte effect, and/or by suppressing the formation of sulfide within the crevice by inhibition of the chemical dissolution of MnS inclusion. Under these circumstances, the dominant anion in the sample was sulfate. Therefore, an analysis electrolyte based upon sulfate was used. Fig. 8 shows the results of using a sulfate electrolyte to allow measurement of the other sulfur species in a crevice solution. Fig. 8a shows an electropherogram from a crevice solution just at initiation, when the bulk solution contains 17 mM chloride, and Fig. 8b shows an electropherogram from a crevice solution in which initiation did not take place due to a higher sulfate content in the bulk (5.8 mM), while Fig. 8c is the electropherogram of a standard. After correcting for dilution, the solutions removed from the crevices were found to contain 6.9 and 8.9 mM sulfide, respectively. The chloride contents were estimated to be 1.2 and 0.62 M, respectively. The chloride contents were estimated by measurement of the cations in the crevice and the electroneutrality condition. Thus, it appears that the sulfate acts primarily to slow the increase in chloride

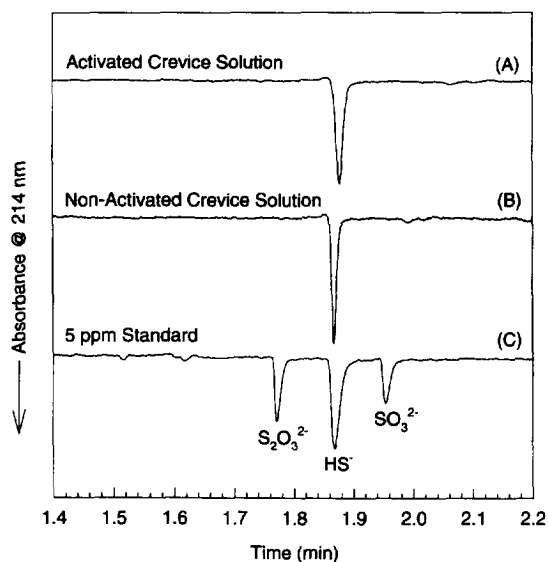


Fig. 8. Analyses of anions in 1.5 mM  $\text{Na}_2\text{SO}_4$ , 2 mM OFM BT, pH 10.5. (A) solution from an active crevice solution just after the initiation of corrosion when the bulk solution contained 17 mM chloride, (B) solution from a crevice in which corrosion initiation did not take place due to the presence of 5.8 mM sulfate in the bulk solution, (C) 5 ppm standard.

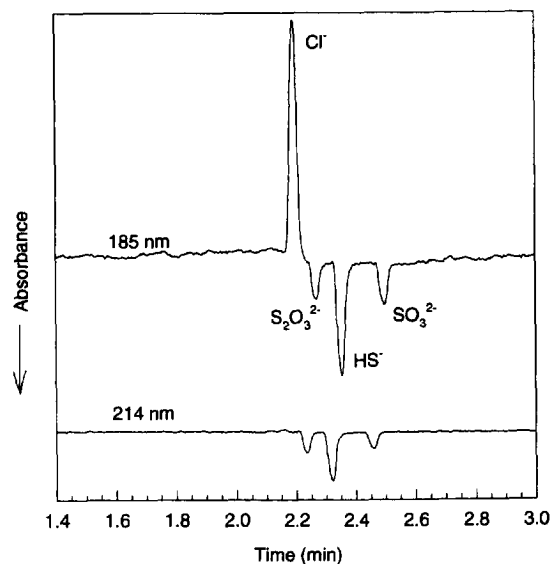


Fig. 9. The effect of detection wavelength on the ability to visualize chloride in the sulfate electrolyte. Note that while chloride is transparent at 214 nm, it can be detected indirectly at 185 nm.

concentration inside the crevice via competitive migration, as discussed elsewhere [10].

Fig. 9 shows the effect of detection wavelength on the analysis using the sulfate electrolyte. Using 214 nm, the high chloride concentration in the solution did not affect the analysis. In cases in which visualization of the chloride is desirable, changing the wavelength to 185 nm allows the chloride peak to be observed. Note that the  $\text{Cl}^-$  peak was detected indirectly. This positive peak for chloride was unexpected, as it would be expected to be UV-active at 185 nm.

### 3.3. Analysis of molybdate and tungstate from passive dissolution of Al–Mo and Al–W alloys

Metastable aluminum alloys containing high concentrations of alloying elements such as Mo and W have been formed by sputtering and have been found to have exceptional resistance to localized corrosion in chloride solutions [19,20]. The mechanism by which these alloying elements impart such massive

improvement remains unknown. Since many of the alloying elements which improve the corrosion resistance can form oxyanions which are known corrosion inhibitors, a study of the dissolution products formed during electrochemical oxidation of these alloys has been conducted. Fig. 10 shows a standard as well as dissolution solutions from two alloys, an Al–9% (w/w) Mo (Al–9Mo) and an Al–13% (w/w) W (Al–13W) held at an elevated potential in a 0.01 M HCl solution for 12 h. The longer migration times in the samples are due to the lower concentration of chloride relative to the standards. The currents were thus lower and the migration times longer. The use of direct UV detection at 214 nm as well as spiking of the samples allowed verification of the identity of the species. The concentrations of molybdate and tungstate found in these solutions was consistent with surface analysis measurements that have shown the presence of Mo(VI) and W(VI) in the outer portion of the oxide film formed [21]. The presence of these strongly corrosion-inhibiting oxyanions in solution could be the origin of their localized corrosion resistance.

#### 4. Conclusions

Analysis of solutions from corrosion studies can be challenging due to the need to measure small amounts of one species in the presence of large concentrations of another. In the case of anion analysis, a matrix matching approach has been successfully used to study the effects of alloyed sulfur, molybdenum and tungsten on the localized corrosion site chemistry in solutions in which the chloride or sulfate concentrations were 100 to 1000 times higher. These measurements have provided new insights into the mechanisms by which these alloying elements affect corrosion resistance.

The EOF modifier form and concentration can be adjusted to improve the analysis. By placing the EOF modifier in the hydroxide form, the baseline disturbance due to the bromide in the standard electrolyte can be removed. This conversion improved the ability to quantitate the thiosulfate peak, which, at low EOF modifier concentrations, migrates just after the bromide. The EOF modifier concentration was used to change selectivity. Weak acid anions are strongly affected by increases in the EOF modifier concentration, with higher concentrations leading to longer migration times due to the formation of equilibrium ion-pairs. The hard acid anions are much less affected. This difference in selectivity allows complex samples to be analyzed by proper selection of the EOF concentration, moving the weak acid anions to longer migration times.

#### Acknowledgments

The financial support of NSF (DMR-9505760) is gratefully acknowledged. The technical assistance from H. Scully (University of Virginia) in initial method development, E. Principe and B. Shaw (Pennsylvania State University) in the procurement of samples for molybdate and tungstate analysis is also gratefully acknowledged. Equipment support was kindly provided by Waters Corporation (J. Krol).

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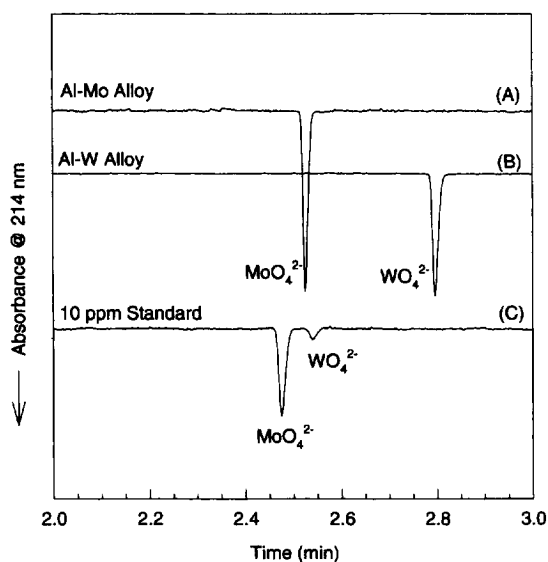


Fig. 10. Electropherograms from dissolution solutions of (A) Al–9Mo and (B) Al–13W held potentiostatically at +0.152 V (SCE) and +0.174 V (SCE), respectively, in 10 mM HCl for 12 h. A standard containing 365 ppm chloride, 10 ppm molybdate and 10 ppm tungstate is also shown (C).

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