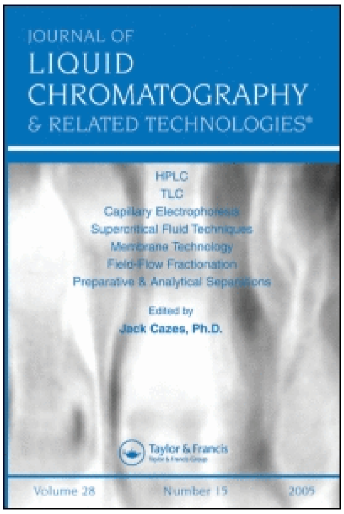

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SEPARATION AND DETERMINATION OF CHROMIUM(VI), MOLYBDENUM(VI) AND VANADIUM(V) IN STEEL USING CAPILLARY ION ELECTROPHORESIS WITH DIRECT UV DETECTION

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ABSTRACT

The application of capillary ion electrophoresis to the separation and determination of chromium (VI), molybdenum (VI) and vanadium (V) with direct on-column UV detection at 254 nm is described. Using a cathodic injection and anodic detection scheme, Cr(VI), Mo(VI) and V(V) were separated in about 4 min in a fused silica capillary column, with a phosphate buffer of pH 12.0, at an applied voltage of 15 KV, followed by direct UV detection. An electro-osmotic flow modifier, namely a cetyltrimethylammonium bromide (CTAB), is necessary to shorten the migration times of these ions. Incorporating citrate into the electrophoretic buffer markedly improves the sensitivity and efficiency.

The influence of several experimental parameters on both sensitivity and efficiency was investigated. Linearity of calibration graphs is observed for about three orders of magnitude with sub-ppm detection limits.

The applicability of the method to the analysis of steel samples is demonstrated. The peak response is strongly dependent upon ionic strength of sample solution and appropriate measurers, such as standard addition, must be used to account for differences in standard and sample conductance.

INTRODUCTION

High performance capillary zone electrophoresis (CZE) is a technique for the separation of charged species in small capillaries at electric field strengths in the range of 10 to 30 KV. It is a highly efficient separation method, capable of yielding excellent resolution of ionized compounds based on the combined effects of electrophoresis and electro-osmosis. The majority of CZE applications have involved the separation of biological macromolecules. However, the technique is amenable to the separation of any ionic species. Although the earliest report of electrophoretic separations of inorganic cations appeared in 1967,[1] the lack of a universal detection scheme for nonchromoplloric analytes hampered early development of separations for inorganic anions. This method has been introduced into inorganic analysis only in the last 3 years.[2-5]

When applicable, the simplest means of monitoring inorganic ions separated by CZE is direct UV absorbance.[6-8] Unfortunately, many ions do not demonstrate significant absorbance at convenient wavelengths and may not be detectable using direct UV detection without complexing agents and a bare fused-silica capillary. A fairly promising approach of overcoming these problems is based on the addition of complexing components to the electrophoretic buffer. These complexing agents can selectively moderate the mobility of metal cations, owing to the formation of metal complexes of different stability within the capillary. This CZE separation mode was first proposed by Foret et al.[9] in combination with indirect UV detection for the separation of lanthanides and then intensively developed by Weston et al.[10]

Another promising possibility for complexation CZE is the complete conversion of metal ions into negatively charged chelates, which can move with different mobilities in the opposite cathode to anode direction. In addition, direct spectrophotometric detection of metal chelates can be performed. Popular ligands for the metal cation separations include cyanide,[11,12] 8-hydroxyquinoline-5-sulfonic acid,[13,14] 4-(2-pyridyazo)-resorcinol,[15] lactate,[16,17] EDTA[18] and α-hydroxyisobutyric acid.[19] According to these solutions, a new separation technique for the analysis of inorganic and organic ions, called capillary ion electrophoresis (CIE) has recently been introduced.[20] This paper presents a method for the separation and determination of Cr(VI), Mo(VI) and V(V) using direct UV detection by CIE. In this paper, complexing agents only help to improve the sensitivity and efficiency. They do not solve the detection problem nor do they make possible indirect detection.

CIE is a branch of capillary electrophoresis (CE) which is optimized for the rapid analysis of low molecular mass anions and cations. Separations by CIE are based on differences in the electrophoretic mobilities of the injected ions.[21,22] Electrophoretic mobilities are influenced by the structural properties of solutes such as size, shape, Stokes' radius, charge and mass, in addition to the interaction of those solutes with the carrier electrolyte. Each of these variables is affected by properties of the electrolyte, such as pH, ionic strength or viscosity. CIE offers many advantages for the analysis of inorganic and organic acid anions in aqueous matrices. Rapid, highly efficient separations with different selectivities, simplicity and economy are obtained. The technique has been successfully applied to the analysis of a variety of anionic solutes in several complex sample matrices.[23,24]

So far, little attention has been given to studies of the separation and determination of Cr(VI), Mo(VI) and V(V) by CIE. This paper presents a method for the separation and determination of these ions by CIE. The migration behaviour and the optimization of the separation conditions for these three ions, by controlling the electrophoretic buffer parameters, are discussed here. In this paper, both qualitative and quantitative aspects of the application of CIE for the analysis of trace Cr(VI), Mo(VI) and V(V) in moderate ionic strength practical samples are discussed.

EXPERIMENTAL

Instrument

A Waters (Milford, MA, USA) Quanta 4000 capillary electrophoresis system, equipped with a negative high voltage power supply, was used throughout this study, with a Model 820 data station. Polyamide-coated fused-silica capillaries, 51.7 cm total length, 75 μm internal diameter, were obtained from Yong Nian Photoconductive Fibre Factory, Hebei, China. A window for on-column detection was created, 7.3 cm from the end of the capillary. Direct UV detection was accomplished with a Hg lamp and a 254 nm optical filter. Hydrostatic sample mode was selected for injection and sample time was set at

30 s. The separation voltage applied was -15 KV. Data acquisition rate was 20 points/s. The electro-osmotic velocity was measured with formyl amine ($HCONH_2$).

Before each run, a 3 min purge of the capillary with electrolyte was programmed. All operations were at room temperature. All conditional experiments were completed using 10 μg/ml of Cr(VI), 20 μg/ml of Mo(VI) and 10 μg/ml of V(V) (present in the forms of CrO_4^{2-}, MoO_4^{2-} and VO_3^-, respectively).

Reagents

All chemicals were of analytical, reagent grade. All solutions were prepared using filtered, degassed and deionized distilled water.

The phosphate carrier electrolytes were prepared as 6.0 mmol/L solutions containing 2.0 mmol/L of citrate (Beijing Chemical Plant, China) and 0.15 mmol/L of CTAB. The pH of the electrophoretic buffer was adjusted to 12.0 by addition of an appropriate volume of concentrated KOH solution.

Na_2CrO_4, Na_2MoO_4 and NH_4VO_3 were obtained from Beijing Chemical Plant, China. Stock standard solutions of each of these ions were prepared in distilled water at a 1.000 mg/mL concentration. Less concentrated standard solutions were prepared by dilution from the stock solution.

Procedure

At the beginning of each experimental day, it was sufficient to rinse the capillary with deionized water for about 15 min. However, in order to keep the capillary clean, the capillary was flushed with 0.5 mol/L KOH solution after being used three or four days.

Experiments were performed to optimize the CIE system. Unless otherwise specified, the standard conditions used for individual parameters of the system are: -15 KV run voltage, 30s hydrostatic loading time and a working electrolyte consisting of 6.0 mmol/L of phosphate, 2.0 mmol/L of citrate and 0.15 mmol/L of CTAB. Detection was by UV absorbance at 254 nm. Before each run, the capillary is purged for 3.0 min under vacuum.

When doing conditional experiments, the standard sample mixture was diluted using distilled water. When making a calibration curve (peak area versus concentration of analyte of interest), the standard solutions were diluted using electrolyte buffer (6.0 mmol/L phosphate + 2.0 mmol/L citrate).

Sample Preparation

About 0.5 g of steel samples is weighed accurately and dissolved by HCl and a few drops of HNO_3. Adjust the pH of the sample solution to more than 13 with NaOH. In order to ensure that all of chromium, molybdenum and vanadium in samples can be converted to CrO_4^{2-}, MoO_4^{2-} and VO_3^{-}, heat the above sample solution as 30% H_20_2 is dropped into it. Remove the ferric hydroxide precipitate produced in the solution by centrifugation and remove surplus H_20_2 by heating. Finally, the sample solution is diluted to an accurate volume for determination.

RESULTS AND DISCUSSION

pH of Phosphate Electrolytes

The pH of the electrolyte solution used for separation can have a large effect on the separation of Cr(VI), Mo(VI) and V(V). The effect of pH on the migration times of the three ions can be seen in Figure 1. For the purpose of comparison, experimental conditions such as concentration of phosphate and concentration of CTAB were kept 10 mmol/L and 0.15 mmol/L, respectively. The applied voltage was -15 KV and the temperature was at 22.5 ±1°C.

There are three effects worth noting. Firstly, as the pH is lowered, the migration times increase, due to the decrease in the EOF. Likewise, as the pH is increased, the migration times decrease, due to the increase in the EOF.

The second point of interest is that, in addition to the change in mobility due to the EOF, the pH is also affecting the oxidation states of the three ions. As the pH is decreased, the three ions are easy to condense. There is a balance between CrO_4^{2-} and $Cr_2O_7^{2-}$ in solution. Decreasing pH helps to form $Cr_20_7^{2-}$. By contrast, increasing pH favors formation of CrO_4^{21}. MoO_4^{2-} can be condensed to form $Mo_7O_{24}^{6-}$ at pH 6 and $MO_8O_{26}^{4-}$ at pH 1.5-2.9. VO_3^{-} can be condensed to form $V_2O_7^{4-}$ at ,approximately pH 10.0, $H_2V_4O_{13}^{4-}$ at about pH 9.0 and $H_4V_5O_{16}^{3-}$ at approximately pH. When the pH was below 10.0, the peak of V(V) did not appear in the electropherograms, due to its condensation. The experimental result showed that V(V) was the easiest to condense among the

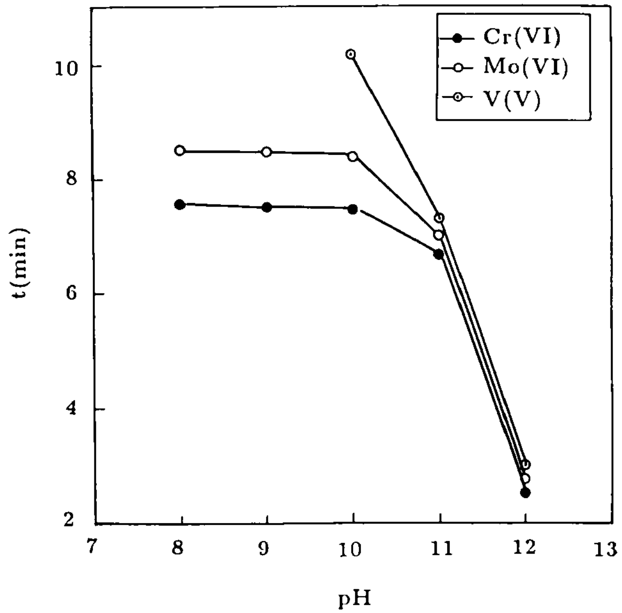

Figure 1. The effect of pH on the migration times of the three ions. When the pH was above 10.0, Cr(VI), Mo(VI) and V(V) were, respectively, present in the forms of CrO_4^{2-}, MoO_4^{2-} and VO_3^-. Later we will discuss the migration order of the three ions in the present work.

Thirdly, the carrier ion-phosphate displays large changes in mobility due to changes in pH. This phenomenon can be seen from the peak shapes. When the pH was at 12.0, the mobility of phosphate was close to the mobilities of the three ions, leading to symmetrical peaks and high efficiency. When the pH was at 12.0, the migration times were shortest for the three ions. If the pH was above 12.0, highly alkaline solutions could change the behavior of the inner surface of the capillary, resulting in poor reproducibility. Owing to the above reasons, 12.0 was selected as the most suitable pH.

Influence of the Concentration of Phosphate

The effect of the concentration of phosphate on the separation behavior of the ions was studied while keeping CTAB at 0.15 mmol/L and pH at 12.0. The ionic strength of electrolyte was mainly controlled by the concentration of phosphate. The ionic strength of the background electrolyte plays three

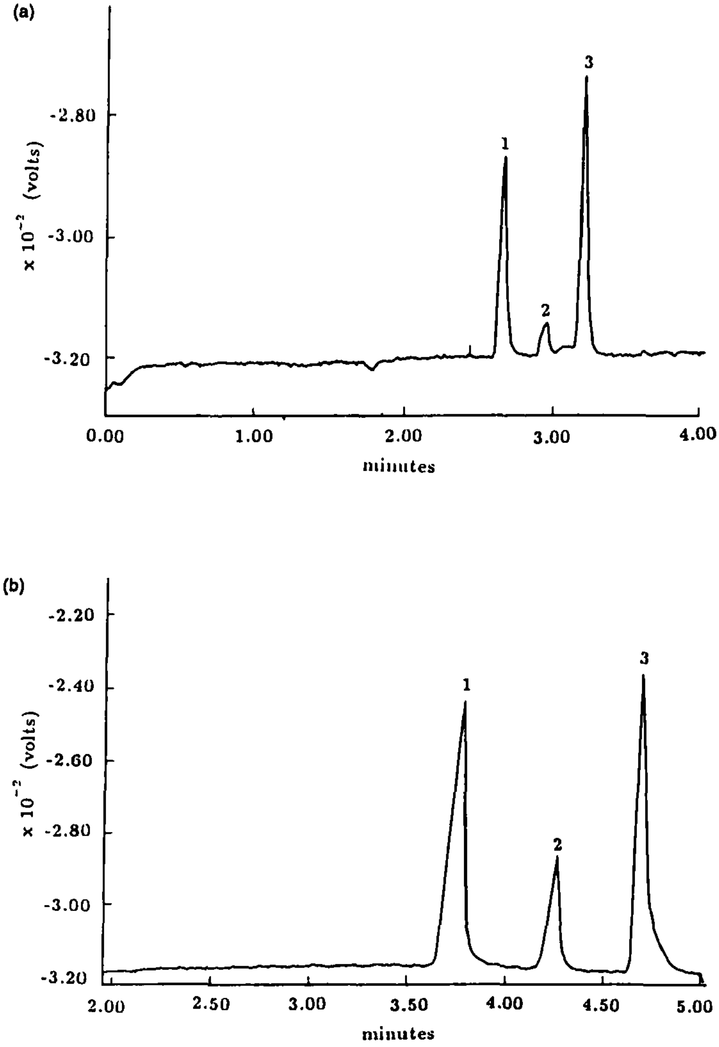

Figure 2. Effect of citrate addition to the phosphate electrolyte on the separation of Cr(VI), Mo(VI) and V(V). Capillary(75 Hm), 51.7 cm length. (a) Electrolyte composed of 6.0 mmol/L phosphate, 0.15 mmol/L CTAB. (b) Electrolyte was same as electrolyte (a), but with 2.0 mmol/L citrate, pH = 12.0, -15 KV applied for separation. Direct UV detection at 254 nm, anode detection. Gravity injection, 10 cm for 30 s. Peaks: 1= Cr(VI) (10.0 µg/mL); 2 = Mo(VI) (20.0 µg/mL); 3 = V(V) (10.0 µg/mL).

different roles in the CZE separations. Firstly, increasing concentration of background electrolyte decreases the EOF. Secondly, it increases efficiency due to higher field strength.[25] Thirdly, it produces higher current, resulting in the inability to effectively dissipate heat. This effect is manifested as noise and baseline aberrations. Taking the three effects into account, we selected 6.0 mmol/L phosphate as optimum concentration, which produces an acceptable current (54.7 μA) to minimize noise while maintaining good peak efficiency.

Influence of the Concentration of Citrate

The influence of citrate addition to the capillary electrophoresis electrolyte was investigated while keeping phosphate at 6.0 mmol/L, CTAB at 0.15 mmol/L, pH at 12.0 and the applied voltage at -15 KV. Figure 2 shows the effect of citrate addition to the phosphate electrolyte system. The second electropherogram in Figure 2 shows the separation of Cr(VI), Mo(VI) and V(V) in an electrolyte similar to that used for the first electropherogram, but with the inclusion of 2.0 mmol/L citrate.

The addition of citrate increases the viscosity and the ionic strength of the electrolyte, resulting in a decrease of electro-osmotic flow. The decrease in EOF results in a small increase in the migration times of the three ions. The addition of citrate causes a change in current due to the increase of ionic strength of electrolyte. But the change in current is not large. The current increased from 54.7 μA at 6.0 mmol/L phosphate to 71.6 μA at 6.0 mmol/L phosphate and 2.0 mmol/L citrate. The change in current was acceptable and did not cause significant increase in baseline noise. It must also be noted that there is a striking increase in efficiency. The efficiency increases with the increase of the concentration of citrate due to the increase of the ionic strength of the electrolyte.

The effect of citrate on the sensitivities of the three ions was also investigated. Figure 3 demonstrates the influence of the concentration of citrate on the sensitivity. In Figure 3, the units for the peak areas are microvolts (corrected for migration times). Since this quantity varies with the zone velocity, the peak areas corrected for migration times were used throughout the report. From Figure 3, we can see, when the concentration of citrate was below 2.0 mmol/L, the peak areas of the three ions increase with the increase of the concentration of citrate, partly due to the decrease in adsorption of the three ions. When the concentration of citrate was above 2.0 mmol/L, the peak areas decrease with the increase of the concentration of citrate. The reason for this

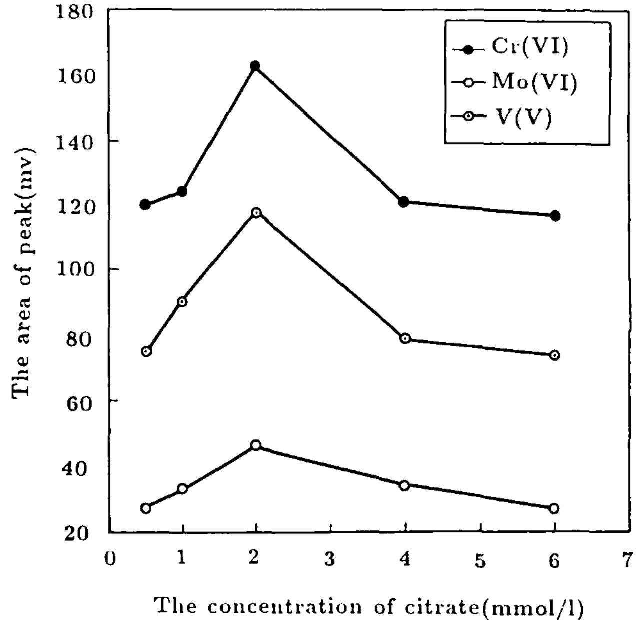

Figure 3. The effect of concentration of citrate on the sensitivities for determination Cr(VI), Mo(VI) and V(V).

observation needs to be explored in greater detail. 2.0 mmol/L of citrate proved to be the best compromise between efficiency, acceptable baseline noise level and sensitivity.

Influence of CTAB

For a normal bare silica capillary, the direction of electro-osmotic flow is from anode to cathode. Cr(VI), Mo(VI) and V(V) are anions under the experimental conditions. A cathode injection and anode detection scheme was used. The three ions migrate from cathode to anode under the applied voltage. In order to minimize the time of analysis, it is desirable to produce an electro-osmotic flow in the same direction as the migration of the analytes. The surfactant CTAB, as an EOF modifier, is used in the electrolyte. CTAB dynamically coats the inner wall of the fused-silica capillary and imparts a positive charge on the wall and changes the EOF towards the anode, thus augmenting the apparent mobility of the three ions. The influence of concentration of CTAB on the migration times was studied. Increasing the

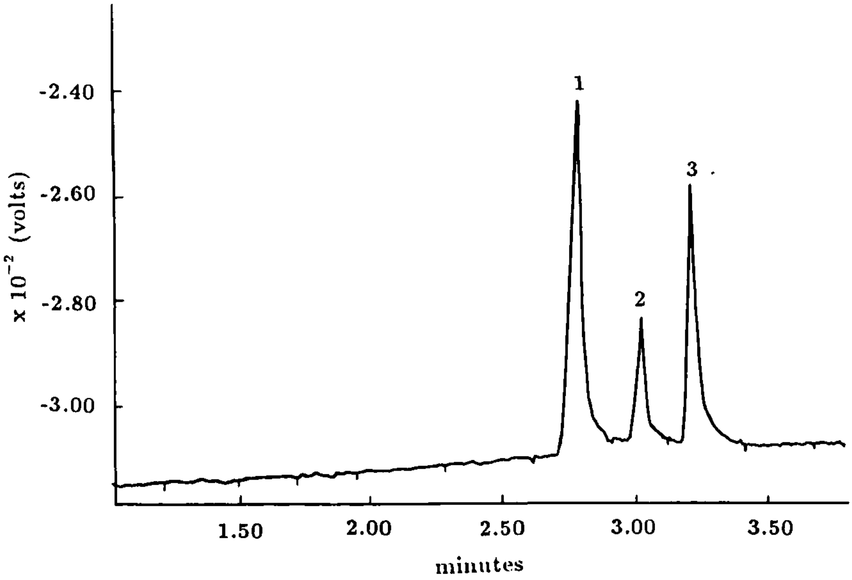

Figure 4. Effect of sodium chloride concentration on the separation of Cr(VI), Mo(VI) and V(V). Experimental conditions: capillary (75 μm), 51.7 cm length; Electrolyte composed of 6.0 mmol/L phosphate, 2.0 mmol/L citrate and 0.15 mmol/L CTAB, pH=12.0; -15 KV applied for separation. Direct UV detection at 254 nm, anode detection. Gravity injection, 10 cm for 30 s.; Peaks: 1 = Cr(VI) (5.0 μg/mL); 2 = Mo(VI) (5.0 μg/mL); 3 = V(V) (5.0 μg/mL)

The mixed standard solution was diluted using 6.0 mmol/L phosphate and 2.0 mmol/L citrate solution.

Table 1

Calibration Data Between 0.5 to 50 μg/mL for the Three Ions

Component	Slope	y intercept	Correlation Coefficient
Cr(VI)	9.88	1.39	0.9998
Mo(VI)	1.29	0.59	0.9997
V(V)	10.4	-0.05	0.9997

The unit of the peak area is microvolts. The unit of C is μg/mL.

concentration of CTAB above 0.10 mmol/L decreases the migration times. Decreasing the concentration of CTAB below 0.10 mmol/L did not appreciably change the magnitude of the reversed EOF, resulting in a little change on the migration times of the three ions. In this paper, 0.15 mmol/L of CTAB was selected.

Quantitation

The usefulness of the method for quantitative monitoring of the three ions was evaluated by means of calibration and reproducibility experiments. In order to study the peak area reproducibility and the variation of the peak areas with concentration, several consecutive runs with different standard solutions were made. As shown in Table I, valid calibration plots could be obtained for the three ions. The precision of five consecutive determinations was evaluated at 5 ppm for the three ions. All analytical conditions were as described in the Experimental section. The results, calculated as relative standard deviations (R.S.D.) of peak areas, along with the concentrations of Cr(VI), Mo(VI) and V(V) in the standards used for the repeat runs, are 4.5%, 7.2% and 3.0% respectively. The detection limits of Cr(VI), Mo(VI) and V(V) achieved at 2 times the signal-to-noise ratio are 0.2 μg/mL, 1.0 μg/mL and 0.2 μg/mL, respectively.

Application

From the sample pretreatment, we know that high concentrations of sodium chloride are introduced into the sample solution. Thus, the sample solution has high ionic strength, which has an effect on the separation behavior of Cr(VI), Mo(VI) and V(V). In order to analyze the amounts of the three ions in the sample, an experiment was performed in which CZE analysis was done with solutions containing a constant amount of Cr(VI), Mo(VI) and V(V), 5, 5, and 5 μg/mL, respectively, and from 10 to 40 mmol/L sodium chloride. Figures 4-8 show the effect of sodium chloride concentration on the migration behavior of the three ions.

From Figures 4-8, we can draw the conclusion that the lower the ionic strength of the sample, the greater will be the enhancement of efficiency and sensitivity, and the shorter the migration times of analytes. When the concentration of sodium chloride is above 20 mmol/L, the Cr(VI) peak is not separated from the Mo(VI) peak. After addition of a constant

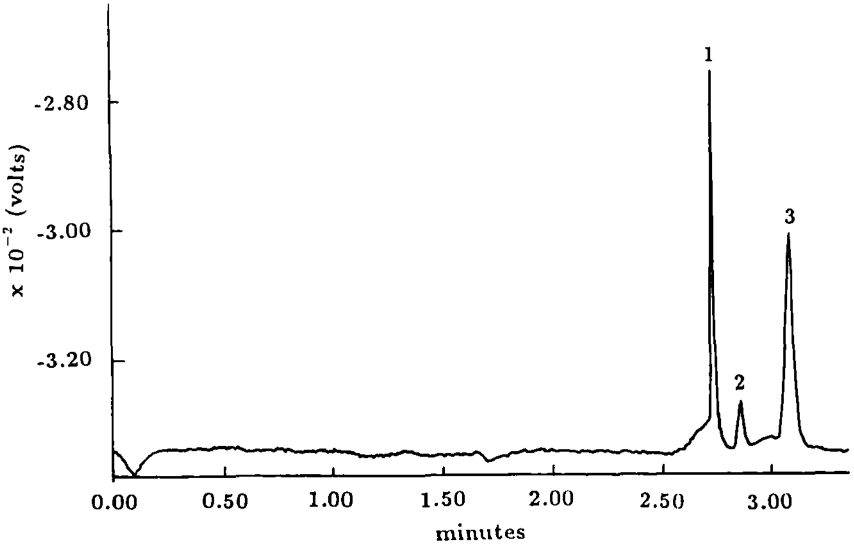

Figure 5. The diluting solution was same as Figure 4, but with 10 mmol/L NaCl.

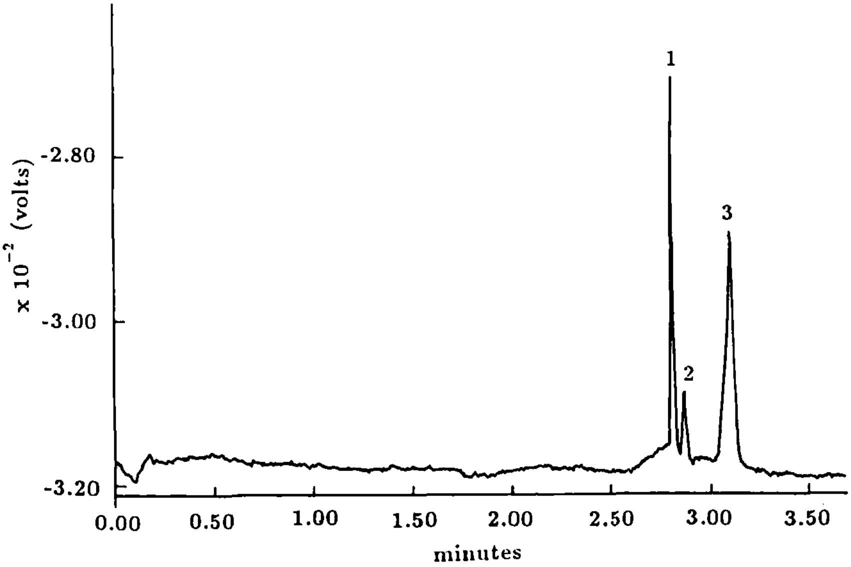

Figure 6. The diluting solution was same as Figure 4, but with 20 mmol/L NaCl.

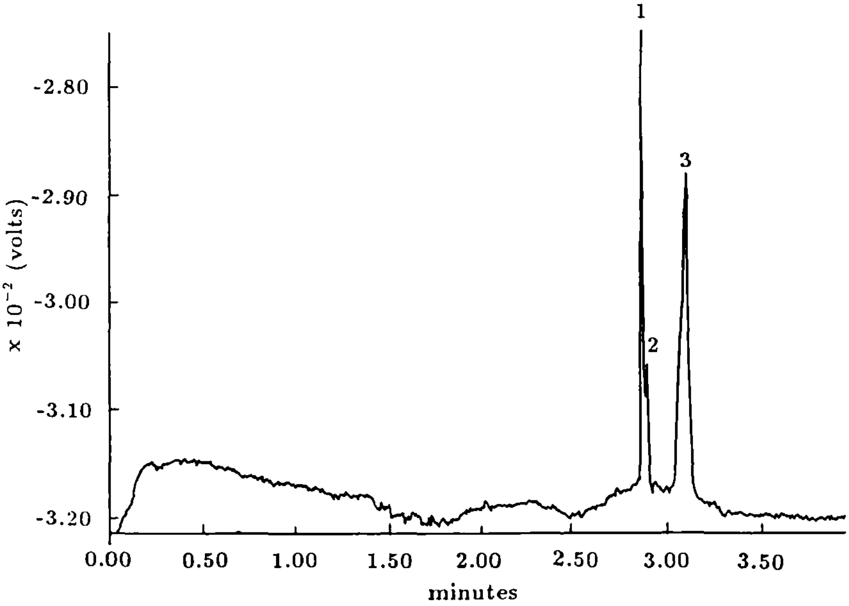

Figure 7. The diluting solution was same as Figure 4, but with 30 mmol/L NaCl.

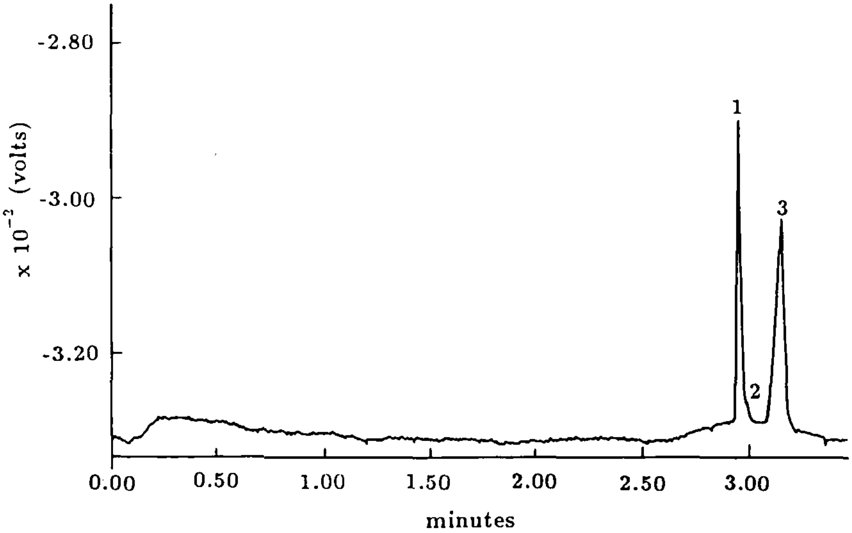

Figure 8. The diluting solution was same as Figure 4, but with 40 mmol/L NaCl.

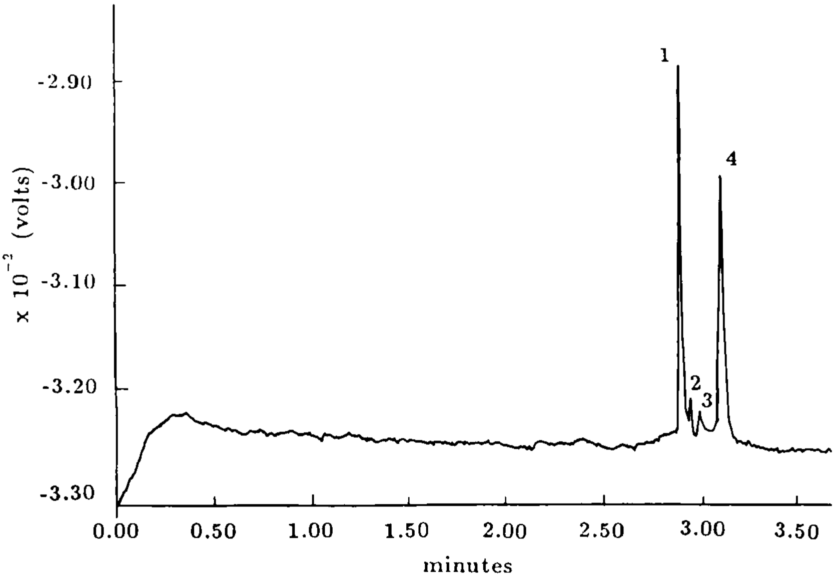

Figure 9. Electropherogram of steel sample solution. Electrophoretic conditions as in Figure 4. Peaks: 1= Cr(VI); 2 = Mo(VI); 3 = Not identified; 4 = V(V).

amount of sodium chloride, lower than 20 mmol/L, the peak area reproducibility and the value of the correlation coefficients of the straight line fits indicate that the approach can be used for quantitative analyses of Cr, Mo and V in steel samples. If the ionic strength of the sample is higher, the approach is less attractive.

In order to analyze the amounts of Cr, Mo and V in the steel sample, the pH of the pretreated sample solution was first adjusted to 12.0 and then several dilutions were made. In this way, the ionic strength of the sample solution was adjusted to be suitable for analysis. According to the distilled sample conductance, adjust the conductance of the standard solutions and make the working curve. Several consecutive electropherograms of the sample were taken.

Figure 9 shows a representative run. The determined values of the concentrations for Cr, Mo and V are in good agreement with the analytical information provided for the standard steel sample.

CONCLUSION

This is the first example of using capillary electrophoresis for the separation of Cr(VI), Mo(VI) and V(V). A major advantage of such a system is its high selectivity, which permits the separation of Cr(VI), Mo(VI) and V(V) in a short analysis time without interference from other ions. The addition of the citrate to the electrophoretic buffer markedly improves the sensitivity and efficiency. The peak response is strongly dependent upon ionic strength of sample solution and appropriate measures, such as standard addition, must be used to account for differences in standard and sample conductance. The approach was successfully applied for analysis of Cr(VI), Mo(VI) and V(V) in a steel sample.

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