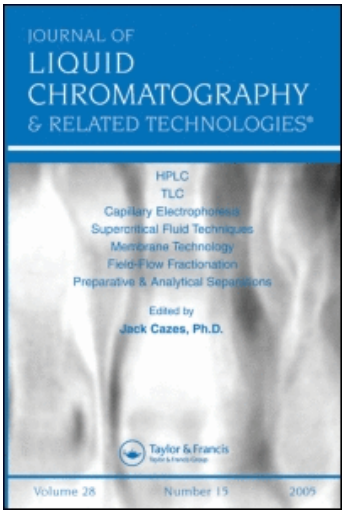

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Separation of Lanthanides and Quantification of Hydronium ION by Capillary Zone Electrophoresis

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To cite this Article Zhang, Y. , Shamsi, S. A. , Peña, M. Sánchez , Thibodeaux, S. and Warner, I. M.(1996) 'Separation of Lanthanides and Quantification of Hydronium ION by Capillary Zone Electrophoresis', Journal of Liquid Chromatography & Related Technologies, 19: 20, 3315 — 3332
To link to this Article: DOI: 10.1080/10826079608014582
URL: http://dx.doi.org/10.1080/10826079608014582

J. LIQ. CHROM. & REL. TECHNOL., 19(20), 3315-3332 (1996)

SEPARATION OF LANTHANIDES AND QUANTIFICATION OF HYDRONIUM ION BY CAPILLARY ZONE ELECTROPHORESIS

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ABSTRACT

The effects of acetate (Ac^-) concentration on the separation of lanthanides from hydronium ion (H_3O^+) in capillary zone electrophoresis is investigated. The effects of sample acidity and buffers on the H_3O^+ peak have been studied. A mixture of 14 rare earth metals, along with H_3O^+, can be baseline separated in less than nine minutes by use of a ternary buffer system [sodium acetate (NaAc) /α-hydroxyisobutyric acid (HIBA) / UV CAT-1]. In contrast, replacing NaAc by equal molar sodium chloride (NaCl) in the buffer decreases the electroosmotic flow without enhancing selectivity and resolution of lanthanides. All of these results suggest that the higher mobility H_3O^+ ion elutes slower than would be predicted. The late appearance of H_3O^+ at pH=4.4 is attributed to the weak acid-base equilibria of HIBA and HAc in the buffers as H_3O^+ migrates through the capillary. The improved separation of metal ions from H_3O^+ by the addition of sodium acetate is also due to the equilibrium of the weak acid (HAc).

In addition, H_3O^+ has been quantitatively detected by use of creatinine as a UV absorbance reagent. The calibration curve was linear for the amount of H_3O^+ up to 0.70 nanomoles in a solution containing 8 mM creatinine. The limit of quantification is about 0.03 nanomoles.

INTRODUCTION

The detection and quantification of individual lanthanides are important for environmental considerations since rare earth metals are widely used in metallurgy, electronics, ceramics, and optics.[1] Both cation[2-3] and anion[4-5] exchange HPLC methods have been employed for the separation and detection of lanthanides. Capillary electrophoresis (CE), with its high separation efficiency and ease of operation, has been reported for the separation and analyses of lanthanides.[6-11]

Lanthanide separations in CE usually require the addition of anionic complexing agents in the electrolyte. This is mainly due to the similarity of the electrophoretic mobilities of the lanthanides that typically range from 72 to 67 x 10^{-5} cm^2/V-s across the period from La^{3+} to Lu^{3+}.[6] Various complexing reagents, such as α-hydroxyisobutyric acid (HIBA)[6,11] and lactate[7-8] have been added to the buffer in order to improve the separation of lanthanides. Since the majority of the lanthanides lacks suitably efficient absorption bands, indirect UV detection has been mainly used.[6-11]

It should be noted that the rare earth metal ions (in particular chloride salts) usually require the addition of nitric acid, not only to promote dissolution but also to decrease possible precipitation of the lanthanide cations in aqueous solution ($La^{3+} + 6\ H_2O = La(OH)_3\ (s) + 3\ H_3O^+$).[12] The lanthanide standards typically used are either metal salts of nitrates,[8] oxides,[6-8] or the metal ion solution in 1 % HNO_3.[9-10]

The study reported here reveals that the resolution and selectivity of lanthanides and hydronium ion are significantly reduced by injection of an acidic sample when HIBA is the only component. For these reasons, an alternative compound, sodium acetate, is used as a modifier.

The ions of interest for pH are hydroxide, deuterium and hydronium.[13] The CE method with indirect UV detection has been used previously[14-15] for the separation and detection of hydroxide ion. Although Barger, *et al.* reported

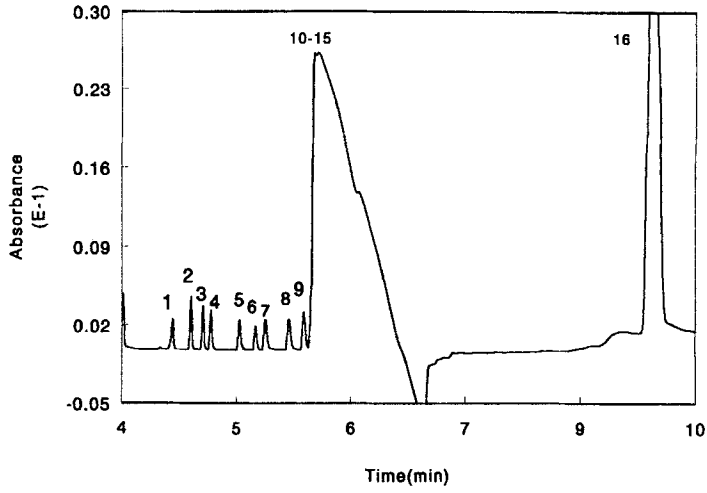


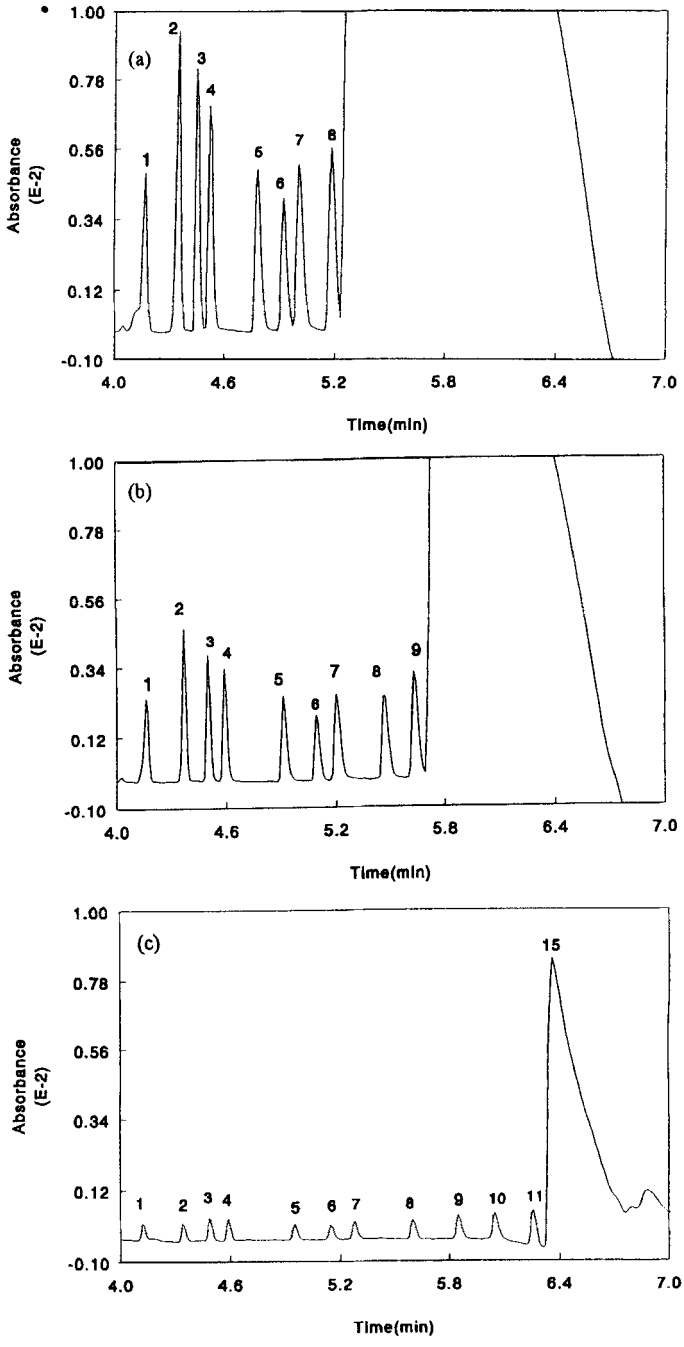
Figure 1. Electropherogram of a 5 ppm lanthanide standard mixture obtained by use of electrolyte buffer I (6.5 mM HIBA, 5 mM UV CAT-1, pH=4.4). Pressure injection was for 5 sec. Separation voltage was +20 kV, current 6 TA. Indirect UV detection at 214 nm. Peak identification: 1. La^{3+}; 2. Ce^{3+}; 3. Pr^{3+}; 4. Nd^{3+}; 5. Sm^{3+}; 6. Eu^{3+}; 7. Gd^{3+}; 8. Tb^{3+}; 9. Dy^{3+}; 9. Dy^{3+}; 10. Ho^{3+}; 11. Er^{3+}; 12. Tm^{3+}; 13. Yb^{3+}; 14. Lu^{3+}; 15. H_3O^+; 16. Electroosmotic flow (EOF).

observing "the acid peak (H^+)",[16] the detection of the hydronium ion (H_3O^+) has not been thoroughly studied. In this manuscript, the effects of acetate concentrations on the separation of lanthanides from H_3O^+ are reported. The H_3O^+ is also quantitatively measured.

EXPERIMENTAL

Apparatus

Separations were performed by use of a Beckman (Fullerton, CA) P/ACE System 5510 capillary electrophoresis instrument, equipped with: 1) a 0-30 kV high-voltage built-in power supply, 2) 200, 214, 254, and 280 nm selectable wavelengths for UV detection, and 3) software System Gold for system control and data handling.



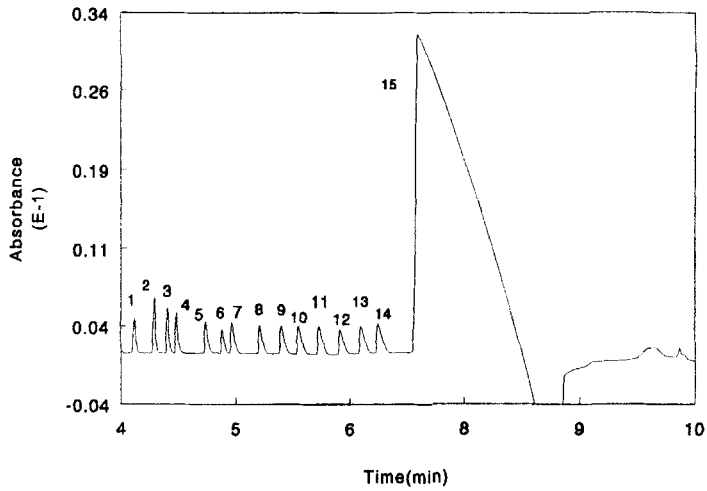


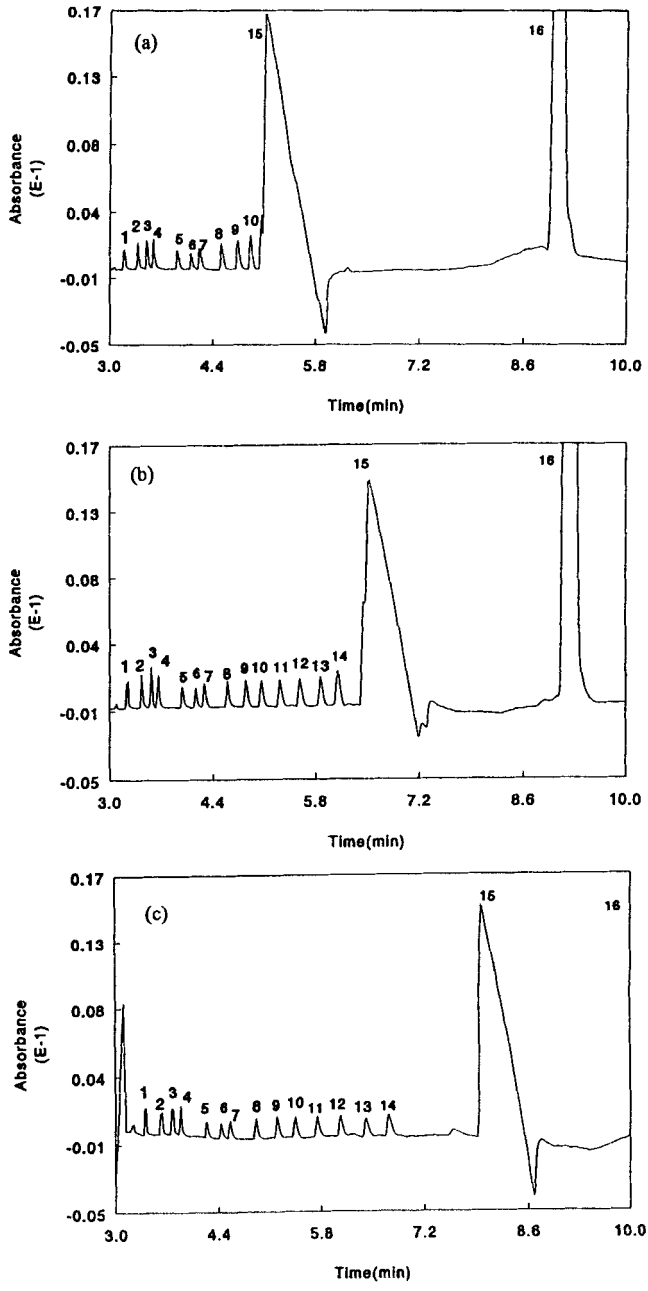
Figure 3. Electropherogram in the presence of HAc for a 5 ppm lanthanides standard mixture using buffer II (4.25 mM HIBA, 10 mM UV CAT-1, pH adjusted to 4.4 by use of 0.1 M HAc). Pressure injection for 5 sec. Separation voltage 20 kV. Peak identification and other conditions are as noted in Figure 1.

The temperature was controlled by use of a fluoroorganic fluid provided by Beckman. The fused-silica capillaries 57 cm x 75 μm I. D. (50 cm to detector) were also obtained from Beckman. In all experiments, the operating temperature was set at 23 °C. The run voltage was +20 or + 30 kV. Indirect UV detection was performed at 214 nm.

Materials

UV-CAT-1, a proprietary UV absorption reagent was purchased from Waters Chromatography Division (Milford, MA). The compounds α-hydroxybutyric acid (HIBA, 99 %), creatinine (98 %), $LaCl_3$ (99.9%), $CeCl_3$ (99.9 %), $PrCl_3$ (99.9 %), $SmCl_3$ (99.99 %), $TbCl_3$ (99.99%), $EuCl_3$ (99.99 %) and $Tm(NO_3)_3$ (99.9 %) were all purchased from Aldrich Chemical Company

Figure 2. (left) Electropherograms showing the influence of injection size on the separation of lanthanides. Pressure injection at (a)10 sec; (b) 5 sec; (c) 1 sec. Peak identification and other conditions are as noted in Figure 1.



(Milwaukee, WI). Sodium acetate (100.3%) was obtained from Fisher Scientific Company (Fair Lawn, NJ). Acetic acid (99.7%) was purchased from EM Science (Gibbstown, NJ). The other metal standards were purchased as nitrate salts (1000 ppm in 1 % HNO_3) directly from Sigma Chemical Company (St Louis, MO). The $HClO_4$ (70 %) was purchased from Curffin Matheson Scientific, Inc. (Houston, Texas).

Preparation of Electrolyte and Analytes

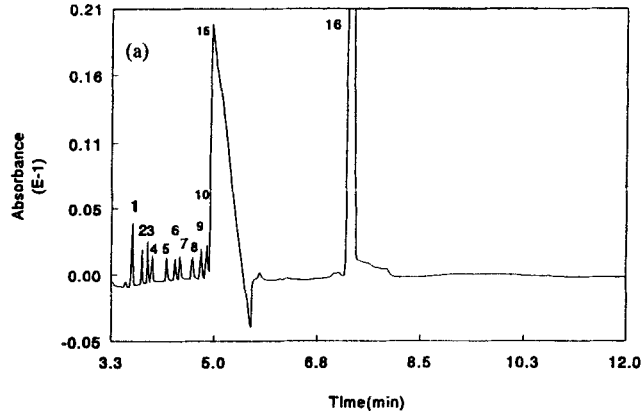
Buffer I, composed of 6.5 mM HIBA and 5 mM UV CAT-1, pH=4.4, was prepared by dissolving 68 mg of HIBA and 64 Tl of UV CAT-1 reagents in 100 mL double distilled water. Buffer II contained 4.25 mM HIBA and 10 mM UV CAT-1. The pH was adjusted to 4.4 by use of acetic acid. Buffer III was composed of 5.60 mM HIBA, 4.29 mM UV CAT-1 with varying concentration of sodium acetate (NaAc) (0.0 mM - 12.0 mM). The pH of the system was adjusted to 4.4 by use of acetic acid.

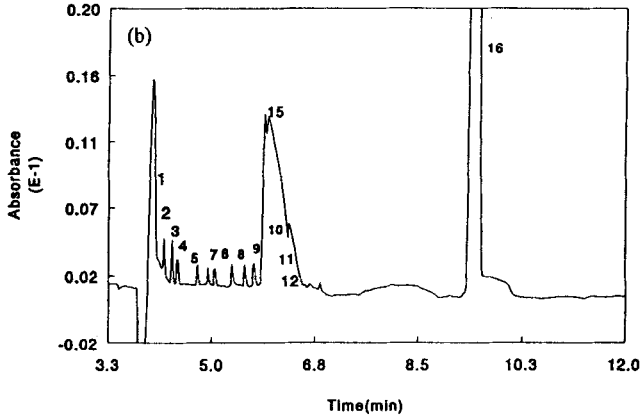
Buffer IV contained the same electrolyte composition as buffer III except for the use of sodium chloride (NaCl), rather than NaAc. Buffer V and VI were made of 4.7 mM HIBA and 3.7 mM UV creatinine, and adjusting the pH to 2.8 and 4.4 by use of 0.2 N HCl, respectively.

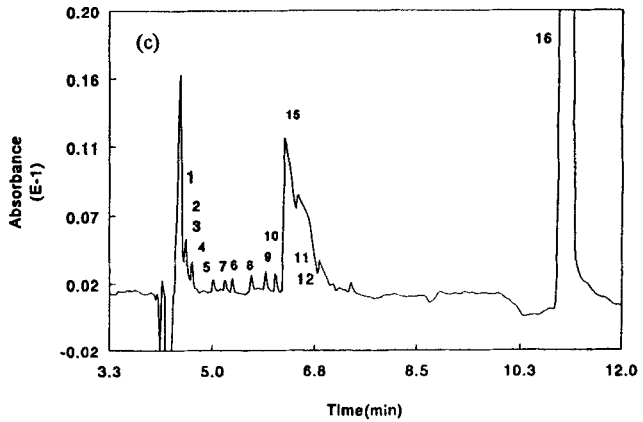
Buffer VII composed of 4.7 mM HIBA and 3.7 mM creatinine with varying concentration of NaAc (0.0 mM, 4.0 mM, and 8.0 mM), and adjusting the pH to 4.4 by use of 0.2 N HCl. Buffer VIII contained 4.7 mM HIBA with various molar concentrations of creatinine (2.0 mM - 10.0 mM), and adjusting the pH to 2.8 by use of 0.2 N HCl.

The stock solutions of the lanthanide standards were prepared in 1 % HNO_3 as 1000 ppm and then diluted to 5 ppm. All buffer solutions and metal ion standards were prepared using double ion-exchange, deionized water, and then filtered through a 0.45 μm membrane syringe filter purchased from Nale Company (Rochester, New York).

Figure 4. (left) Electropherograms illustrating the effects of various concentrations of NaAc on the separation of 5 ppm lanthanide standard mixture. Buffer III (5.60 mM HIBA, 4.29 mM UV CAT-1, pH 4.4) at various NaAc concentrations of (a) 0.0 mM; (b) 4.0 mM; (c) 8.0 mM. Peak identification and other conditions are as noted in Figure 1.







RESULTS AND DISCUSSION

Hydronium (H_3O^+) Peak in Lanthanide Mixture

Figure 1 shows an electropherogram for a mixture of 14 lanthanides using Buffer I. Although buffer I is a recommended electrolyte for alkali, alkaline earths, and some transition metals,[17] its use for the separation of lanthanides (when dissolved in 1 % HNO_3 solution) is limited. As noted, buffer I can only separate the faster eluting lanthanides (peaks 1-9), whereas the slower eluting rare earths (peaks 10-14) overlap with a large triangular shape peak (peak 15). Note that the area of the triangular peak is much larger than that of the metal ion peaks. Therefore, this peak is not likely due to an impurity. One could simply claim that this is a system peak.

Over the years, researchers have efficiently studied system peaks in HPLC with indirect detection.[18-20]. The HPLC system peaks have been shown to be generated by the sample concentration, the injected volume of sample, the nature of the sample ion, the sample pH, and the eluent pH as well as its concentration.[21] One normally labels the systematic appearing peaks during separations as systems peaks before undertaking comprehensive studies.

In reality, system peaks which show up can often be identified and studied. Although the mechanism of appearance of system peaks is clear in HPLC, its appearance in CE is still under investigation .[22]

We believe that peak 15 is due to the H_3O^+ ion since all metal standards were dissolved in 1 % HNO_3 solution to prevent hydrolysis of lanthanides. The H_3O^+ concentration in the lanthanide mixture was calculated to be about 12 mM, whereas the average concentration of metals was about 0.034 mM. The electropherogram in Figure 1 also exhibits a rectangular peak (peak 16) appearing at 9.5 min. This peak which corresponds to elution of the neutral water molecules has been used previously as an electroosmotic flow marker in indirect UV detection.[23]

Figure 5. (left) Electropherograms illustrating the effects of various concentration of NaCl on the separation of 5 ppm lanthanide standard mixture. Buffer IV (5.60 mM HIBA, 4.29 mM UV CAT-1, pH 4.4) at various NaCl concentrations (a) 0.0 mM; (b) 4.0 mM; (c) 8.0 mM. Peak identification and other conditions are as noted in Figure 1.

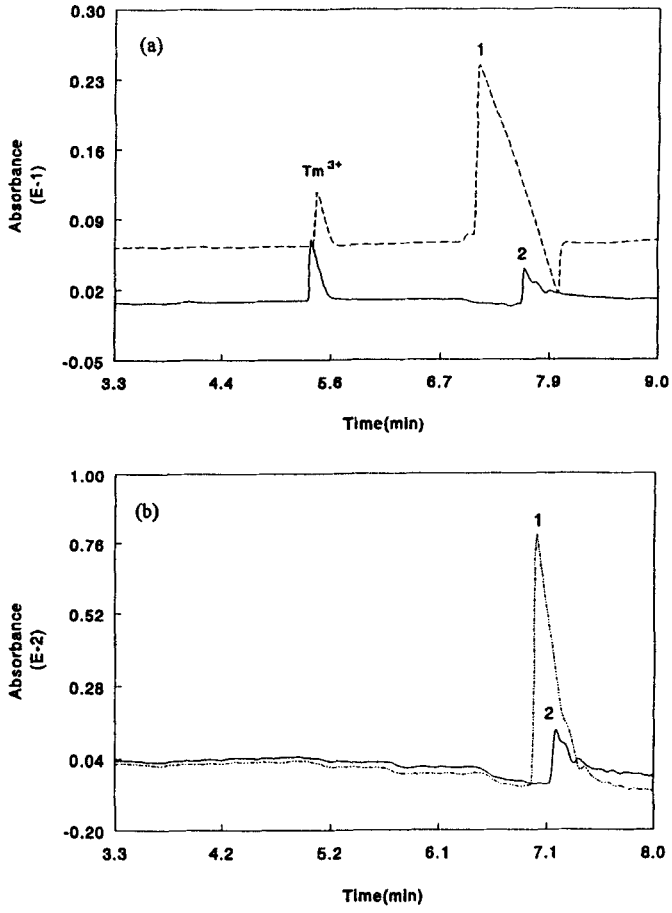


Figure 6. Electropherograms of (a). a 35 ppm Tm^{3+} dissolved in water and 6 mM HNO_3; (b). 6 mM HNO_3 and neutralized 6 mM HNO_3 by addition of 0.1 M NaOH. Buffer conditions are as noted in Figure 1.

Effects of Injection Sizes on the Separation of Lanthanides from H_3O^+ Ion

The injection volume of the lanthanide mixtures was found to exert a large influence on their resolution from the H_3O^+ peak. Figure 2 a-c shows the influence of different injection volumes on the migration time and resolution of the peaks. As expected from capillary zone electrophoresis separations, decreasing the injection size increases resolution at the expense of longer migration time. Resolution of 11 out of 14 lanthanides was possible only at the

lowest limit of injection size (1 second for this particular instrument). However, three metal peaks (Tm^{3+}, Yb^{3+}, Lu^{3+}) still co-eluted with the H_3O^+ peak. This is because the higher injection volume contains higher concentrations of HNO_3 resulting in an increasing overlap of the H_3O^+ peak with the metal ion peaks.

Effects of Acetate Concentrations on the Separation of Lanthanides from H_3O^+

To improve the separation of the lanthanides, the pH of buffer II (containing 10 mM UV CAT-1 and 4.25 mM HIBA) was adjusted with 1 % acetic acid to a pH of 4.4. As illustrated in Figure 3, acetate has a significant effect on the resolution of lanthanides from H_3O^+, resulting in complete baseline separation of all metal ions. The order of migration of lanthanides was similar to that reported previously.[6-11] If the charge-to-mass ratio was the sole consideration for this migration, the H_3O^+ should elute earlier than any of the metal ions. We hypothesize that the association / dissociation equilibria of H_3O^+ with $HIBA^-$ and Ac^- ions (generated from the buffer) causes this migration delay for H_3O^+, resulting in better separation of this ion from the lanthanides. Comparing Figure 3 to Figure 1, it should also be noted that using the same injection time of 5 sec, only 9 metal ions could be resolved from H_3O^+ in the absence of acetic acid.

To test the above assumption, buffer III (containing 5.60 HIBA, 4.29 mM UV CAT-1 with varying concentrations of NaAc) was used to study the migration behavior of lanthanides and H_3O^+. The electropherograms generated in Figures 4 a-c demonstrate that the higher the concentrations of NaAc, the greater the increase in migration time for the metals and H_3O^+. Note that this effect of increasing migration is more significant for H_3O^+. As mentioned before, this is primarily due to the association of H_3O^+ with Ac^-, resulting in the formation of acetic acid (HAc), consequently decreasing the mobility of H_3O^+.

To demonstrate that this enhancement in the resolution of lanthanides from H_3O^+ with the addition of NaAc to the buffer is due to dissociation / association equilibria between H_3O^+ and Ac^-, and not a stacking mechanism, varying amounts of NaCl (a salt of a strong acid and strong base) were added to buffer II. It is apparent in Figure 5 a-c that increasing the concentration of NaCl decreases the EOF. However, the resolution of the slower migrating metal ions (peak 10-14) from the H_3O^+ peak was not improved. In fact, an extra peak (probably due to Na^+) appears early in the electropherograms, which obscures the faster eluting lanthanides (peaks 1-5).

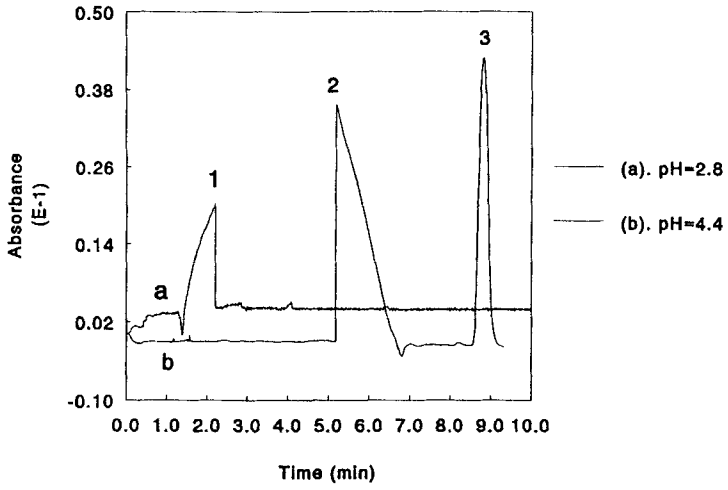


Figure 7. Electropherograms showing the effect of the electrolyte pH on H_3O^+ peak by use of buffer V and VI (4.7 mM HIBA and 3.7 mM creatinine, adjusted the pH by use of 0.2 M HCl). Pressure injection at 5 second. Sample was 11.7 mM $HClO_4$. (a) pH=2.8; (b) pH= 4.4. Other conditions are as noted in Figure 1.

Effects of Sample pH on the H_3O^+ Peak

To further examine the properties of peak 15, the effect of sample pH on the area of this triangular peak was studied. Figure 6 a illustrates the effect of injecting 35 ppm of Tm^{3+} in 6 mM HNO_3 and in H_2O. The peak area of Tm^{3+} is the same in both runs, but a larger triangular peak was observed for the sample dissolved in HNO_3. Furthermore, when aqueous HNO_3 solution was injected (Figure 6 b), the same triangular peak appeared at a slightly shorter migration time of 7.1 min with a tendency toward decreasing in peak height when neutralized with NaOH. Replacing HNO_3 with $HClO_4$ gave similar results. These results suggest that the triangular peak is indeed due to H_3O^+. However, the peak does not appear at the location that one would predict for H_3O^+ ion. The explanation of this observation is given in the following text.

The Effects Of Buffer Concentrations On H_3O^+

The effects of buffer concentrations (pH=4.4) on H_3O^+ peak have also been studied. The concentrations of CAT-1 range from 2.0 mM to 5.0 mM and HIBA from 2.7 mM to 6.8 mM (pH=4.4). Although the elution time of

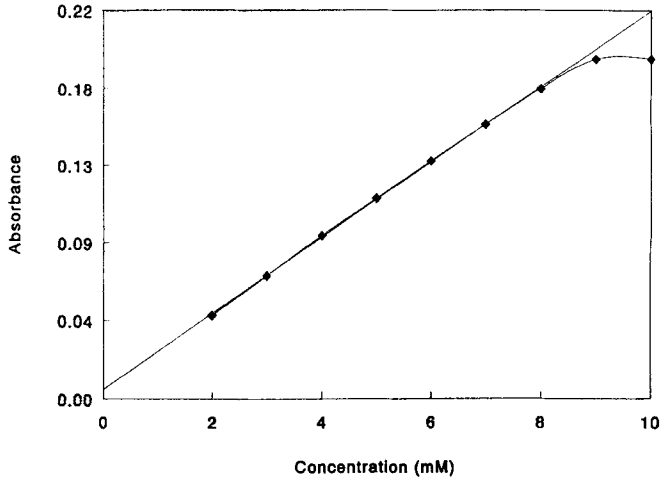


Figure 8. Calibration curve of creatinine as buffer (at pH 2.8). R=0.999. Buffer VIII was used.

H_3O^+ increases as the CAT-1 and HIBA concentrations increase due to the slower EOF, the peak area of H_3O^+, however, does not depend on the concentrations of CAT-1 or HIBA. This suggests that the generation of H_3O^+ peak is not due to the contribution from the running buffer components (CAT-1 and HIBA).

Use Of Creatinine As Absorbance Reagent To Detect And Quantified H_3O^+

Since CAT-1 is a proprietary reagent, the exact chemical compositions are unknown. It is appropriate to use it to separate lanthanides with known conditions of buffers containing CAT-1. However, it is not acceptable to study a chemical equilibrium with an unknown electrolyte component. Therefore, creatinine was used to replace the absorbance reagent CAT-1. The studies focused on H_3O^+. There were no lanthanides in the samples used in the following studies.

The Effects of buffer pH on the H_3O^+ peak

To explain the delayed appearance of H_3O^+, creatinine buffers with different pHs were used to study the behavior of the H_3O^+ ion. Figure 7 a-b are the electropherograms of H_3O^+ in pH 2.8 and 4.4, respectively. The peak

around 2.0 min (# 1) in Figure 7 a (pH=2.8) is fronting, which can be reasonably assigned as the H_3O^+ because of its high mobility.[16] Upon increasing the pH to 4.4, the H_3O^+ peak (#2) migrates slower about 6.0 min (Figure 7 b).

As is widely known, the EOF increases as pH increases. However, the H_3O^+ peak migrates slower at a pH of 4.4 than at a pH of 2.8. In order to explain these phenomena, some other factors should be considered. Acid-base equilibrium was discussed by Foret, *et al.*[24] regarding the migration delay of A^- of a weak acid (HA) in capillary electrophoresis. In our case, the H_3O^+ can be delayed by $HIBA^-$ or Ac^- in the buffer due to the acid-base equilibria.

During the separation, the capillary is filled with an electrolyte solution which contains HIBA. As a weak acid, HIBA (pK_a at 3.7), undergoes the following dynamic acid-base equilibrium

$CH_3CH_2CH(OH)COOH$ (**HIBA**) + H_2O 8 $CH_3CH_2CH(OH)COO^-$ (**$HIBA^-$**) + H_3O^+

at pH=2.8	about	88 % [HIBA]
		12 % [$HIBA^-$]
at pH= 4.4	about	17 % [HIBA]
		83 % [$HIBA^-$]

At pH=2.8, almost 90 % of HIBA in the electrolyte is protonated. The concentration of $[HIBA]^-$ is low, thus, a large fraction of the H_3O^+ ions in the sample freely migrates through the capillary without participation in this equilibrium. Therefore, the high mobility of H_3O^+ elutes early and is fronting. In contrast, H_3O^+ migrates slower regardless of the higher EOF at a pH of 4.4. At this pH, most of the HIBA in the electrolyte is disassociated into $HIBA^-$ and H_3O^+. In this case, the concentration of $[HIBA]^-$ in the buffer is higher than at a pH of 2.8. After injection of $HClO_4$ into the capillary, the microenvironment of the sample zone in the capillary is very acidic, which shifts the acid-base equilibrium to form HIBA. However, the total H_3O^+ concentration does not change appreciably. Consequently, the buffer cannot consume this large H_3O^+ concentration. This micro- equilibrium exists throughout the entire capillary as H_3O^+ migrates, resulting in a delay of H_3O^+ elution.

The effect of acetate concentration on the migration behavior of H_3O^+

As is shown in Figure 3, the addition of acetate results in the separation of lanthanides from H_3O^+ in CAT-1 buffer. Similar studies were conducted by use of creatinine (buffer VII) as an absorbance reagent. The electropherograms

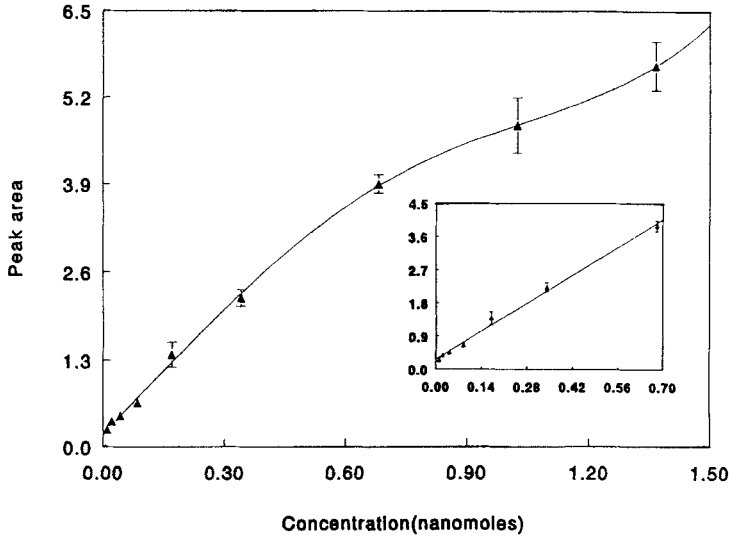


Figure 9. Calibration curve of H_3O^+. The insert figure is the linear plot (R=0.996). Buffer VIII with 8.0 mM creatinine was used. Pressure injection at 5 second. 30 kV. Other conditions are as noted in Figure 1.

revealed that higher Ac^- concentration elongates the elution time of H_3O^+ (electropherograms not shown). As discussed in an earlier paragraph, Ac^- is part of the electrolyte which further delays elution of H_3O^+ due to acid-base equilibrium ($H_3O^+ + Ac^- \rightleftharpoons HAc + H_2O$, $pK_a = 4.8$).

Quantification of H_3O^+

Hydroxyl ion was reported to be quantified by Salomon.[15] Here, we report the quantification of H_3O^+ by use of creatinine buffer at pH 2.8. Figure 8 is a plot of background absorbance intensity as a function of creatinine concentrations. It can be seen that the absorption of the creatinine buffer inside the fused-silica capillary is linear up to approximately 0.18 AU (0.0 mM to 8.0 mM). Therefore, a creatinine concentration of 8.0 mM was used to obtain a calibration curve for H_3O^+.

Figure 9 is the calibration curve of H_3O^+ in a creatinine buffer of 8.0 mM. A linear dependence of the peak areas on the amount injected with a range of 0.03 - 0.70 nanomoles for the H_3O^+ is evident. At a concentration higher than 0.70 nanomoles, the H_3O^+ peak was unsymmetrical with severe

fronting. As a result, the calibration curve for the H_3O^+ peak plateaus out. The limit of quantification is about 0.03 nanomoles. The limit of detection is much lower than 0.03 nanomoles because deionized water gives a notable signal. Using linear regression statistical analysis, a correlation coefficient of 0.998 was noted for the linear plot. The reproducibility was checked by multiple measurements (n=3) and the average of R.S.D. values was about 2.4 % in the linear plot of H_3O^+.

CONCLUSION

Lanthanides in acidic solution can be baseline separated and resolved from H_3O^+ by addition of acetate due to the acid-base equilibrium of H_3O^+ and Ac^- in the electrolyte. The linear calibration curve of H_3O^+ suggests that H_3O^+ concentration can be quantified.

ACKNOWLEDGEMENTS

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office o f Energy Research, US Department of Energy (Grant DE-FG05-93ER14219). The authors also acknowledge the Ministry of Education and Science of Spain (MSP) and the Howard Hughes Medical Institute (ST) for their financial support. The authors are grateful to Mr. Eugene J. Billiot for his technical assistance.

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Received March 6, 1996
Accepted April 24, 1996
Manuscript 4106