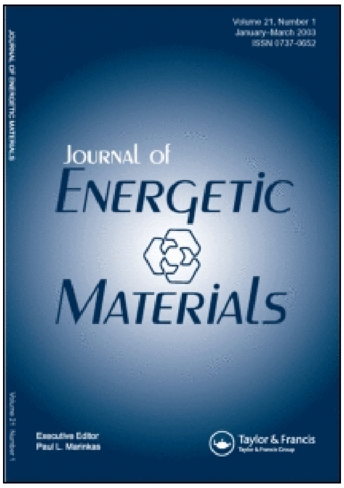

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Analysis of cationic ingredients and degradation products in liquid propellants by capillary ion electrophoresis (CIE)*

Stuart A. Oehrle[a]
[a] Waters Corporation, Milford, MA

To cite this Article Oehrle, Stuart A.(1994) 'Analysis of cationic ingredients and degradation products in liquid propellants by capillary ion electrophoresis (CIE)*', Journal of Energetic Materials, 12: 4, 197 — 209
To link to this Article: DOI: 10.1080/07370659408018650
URL: http://dx.doi.org/10.1080/07370659408018650

ANALYSIS OF CATIONIC INGREDIENTS AND DEGRADATION PRODUCTS IN LIQUID PROPELLANTS BY CAPILLARY ION ELECTROPHORESIS (CIE)*

Stuart A. Oehrle
Waters Corporation
34 Maple Street
Milford, MA 01757

ABSTRACT

Liquid propellants (LP) have received interest as a potential replacement for various solid propellants used in military guns. Analysis of these liquid propellants for both compositional and long-term stability and storage is necessary. Capillary ion electrophoresis (CIE) offers a means of rapidly analyzing for these components. CIE is a capillary electrophoretic technique which has been developed for the rapid analysis of low-molecular weight inorganic and organic ions. Cation analysis of liquid gun propellant samples was done. Analysis of hydroxylammonium nitrate (HAN), triethanolammonium nitrate (TEAN), and diethanolammonium nitrate (DEAN), a degradation product, were accomplished with analysis time of less than 6 minutes.

*Presented at the Sixth International Gun Propellant Symposium, November 14-17, 1994, Parsipanny, NJ.

Journal of Energetic Materials Vol. 12, 197-209 (1994)
Published in 1994 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Over the past few years liquid propellants (LP) have received attention as a possible replacement for various solid propellants currently used in the military. LP's have several advantages over currently used solid propellants in that they are very insensitive. This factor as well several others has led to an extensive surveillance program of these propellants.(1-4) In order to meet ballistic requirements the integrity, stability and safety of these propellants after long periods of storage is required.

The liquid propellant (LP) currently under investigation is a stoichiometric mixture of 61% HAN and 19% TEAN in 20% water. The liquid propellant composition LP1846 is currently one of the candidates under consideration.(3) Analysis of the LP for hydroxylammonium nitrate (HAN), and triethanolammonium nitrate (TEAN) as well as degradation products from long term storage is required for stability measurements as well as shelf-life. Diethanolammonium nitrate (DEAN), is a decomposition product found during long term and short term, high temperature storage. Various analytical methods have been developed for the analysis of the individual constituents and degradation products found in liquid propellants. Many of these techniques have had varying degrees of success. Most have several constraints on detection levels, analysis times, and ease of use. Capillary ion electrophoresis (CIE) has been applied to the analysis of these liquid propellants. Capillary ion electrophoresis (CIE) can analyze liquid propellant samples for cationic ingredients (HAN and TEAN) as well as contaminants (i.e. Na^+) and decomposition products (DEAN) in less than six minutes. CIE also offers the ability to be easily moved around since the injection, detection, and sample compartment are all contained in one box.

Capillary ion electrophoresis (CIE) is a capillary electrophoretic technique which has been optimized for the detection of ions.(5) Figure 1 shows the basic components of a CIE instrument. Since most ions do not absorb UV light, detection is done by adding a UV absorbing chemical to the electrolytic buffer. As the non-absorbing ions pass by the cell the loss of absorbance is measured. The resulting data of absorbance versus time is called an electropherogram. Separation is accomplished by using a fused silica capillary and an appropriate electrolyte buffer which allows for the ions of interest to migrate. A high voltage (typically around 20 kV) is applied and the ions migrate toward the oppositely charged electrode. Sample introduction is done by raising the sample a fixed height for a short period of time. This injection technique is known as hydrostatic injection; volumes injected using this technique are typically in the low nL range. Hydrostatic injection is typically done for high ng/L (ppb) to mg/L (ppm) level analysis. Another injection technique used is called electromigration. In this technique a low voltage is applied to the sample and the ions migrate and concentrate on the head of the capillary. This technique is typically used as a preconcentration step and is applicable for low to mid ng/L (ppb) analysis. Figure 2 is an example electropherogram of a typical cation analysis.

EXPERIMENTAL

Instrumentation:

The capillary electrophoresis (CE) system employed was the Quanta™ 4000E Capillary Ion Analyzer (Waters Corporation, Milford, MA, U.S.A.). A Hg lamp was used for indirect UV detection at 185nm for cation analysis. AccuSep™ polyimide fused silica capillaries of dimension 75 m I.D. X 60cm were used throughout. Data acquisition was carried out with a Waters

Millennium^{TM} 2010 Chromatography Manager with a SAT/IN module connecting the CIE to the data station with the signal polarity inverted from the CIE.

Preparation of electrolytes:

High purity water (Milli-Q^{TM}) was used to prepare all solutions (Millipore, Bedford, MA, U.S.A.). The working electrolyte for cation analysis was a solution of 1.2 mM UV Cat-2 (Waters) and 3.0 mM Tropolone (Aldrich Chemical, Milwaukee, WI, U.S.A.). All working electrolytes were prepared fresh daily and degassed prior to use.

Chemicals:

Hydroxylammonium nitrate (HAN), triethanolammonium nitrate (TEAN), standard LP mixtures and aged samples were obtained from Mr. Stan Griff of the Geo-Centers (Lake Hopatcong, NJ) and were used as received. All other cation standards were prepared from their salts and were of ACS grade or better.

RESULTS

Figures 3 and 4 are electropherograms of a standard of HAN. Sodium ion (Na^+) was found to be present in the HAN standard. This was expected since the samples and standards had been stored in glass containers. To verify the presence of sodium, a small amount of sodium (0.4 mg/L) was added to the sample and it was rerun, figure 4. As can be seen the peak at 3.82 minutes increased. Figure 5 is an electropherogram of a HAN and TEAN standard; total analysis time for this was under 6 minutes. Next a sample of liquid propellant was analyzed before and after accelerated aging for 296 days at 65 degrees celcius. The separation process in CIE is based on both the size and charge of the ion. DEAN, a decomposition product in LP, was expected to migrate, if present, somewhere between HAN and TEAN. This was confirmed by CIE as shown in figures 6 and 7. Figures 6 and 7 are electropherograms of a liquid propellant before (figure 6) and after (figure 7) aging. As seen in figure 7 a peak at 5.06 minutes is present suggesting the formation of DEAN. This peak was later confirmed to be DEAN by spiking in a solution of pure DEAN.

CONCLUSIONS

Capillary ion electrophoresis offers the capability to analyze liquid propellants rapidly with little, if any, sample preparation required. HAN, TEAN and DEAN could be easily analyzed for in less than 6 minutes by CIE. CIE further offers the capability to be portable for direct on-site analysis in a mobile laboratory environment.

ACKNOWLEDGMENTS

The author wishes to thank Mr. Stan Griff and Mr. Gerald Doyle of Geo-Centers for providing the liquid propellant samples and reference materials.

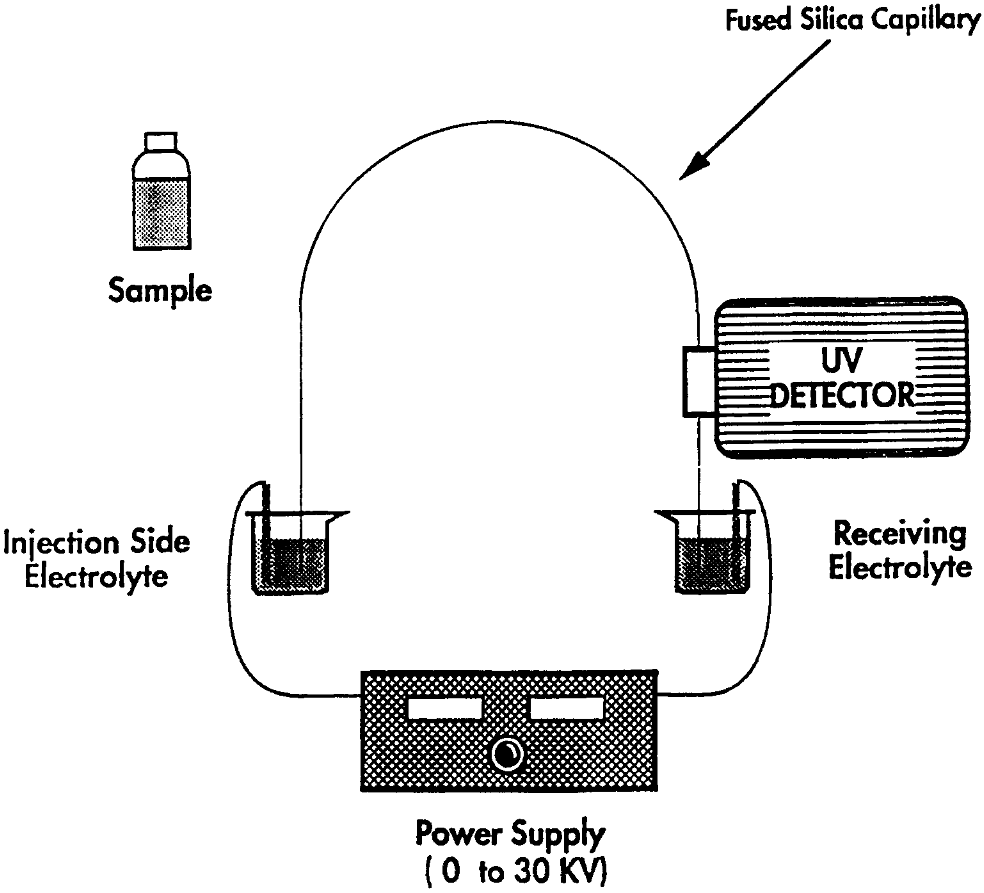

Figure 1: Basic diagram of a capillary electrophoresis system.

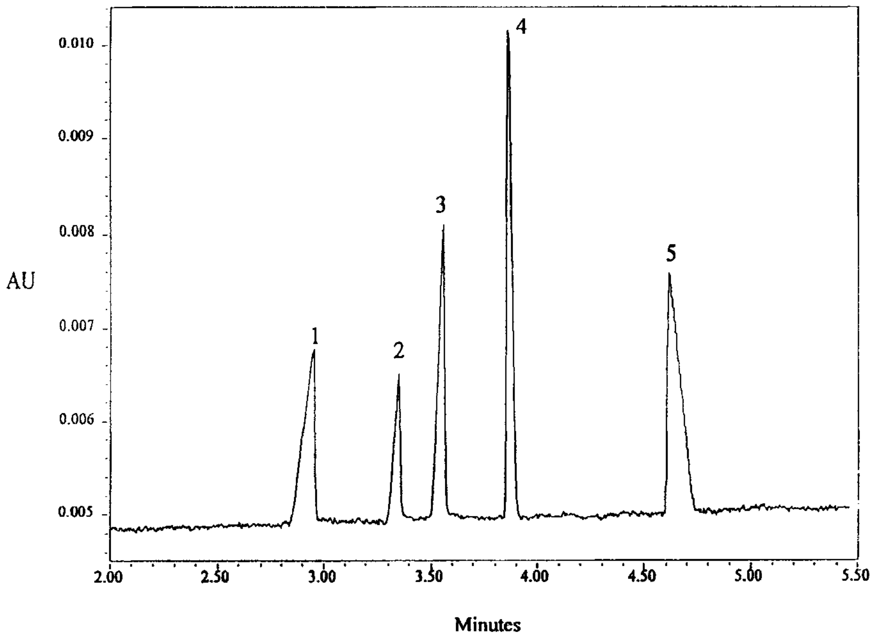

Figure 2: Electropherogram of a cation standard. Conditions as stated in experimental section. Peaks: **1**: NH_4^+; **2**: Ba^+; **3**: Ca^+; **4**: Na^+; and **5**: Li^+.

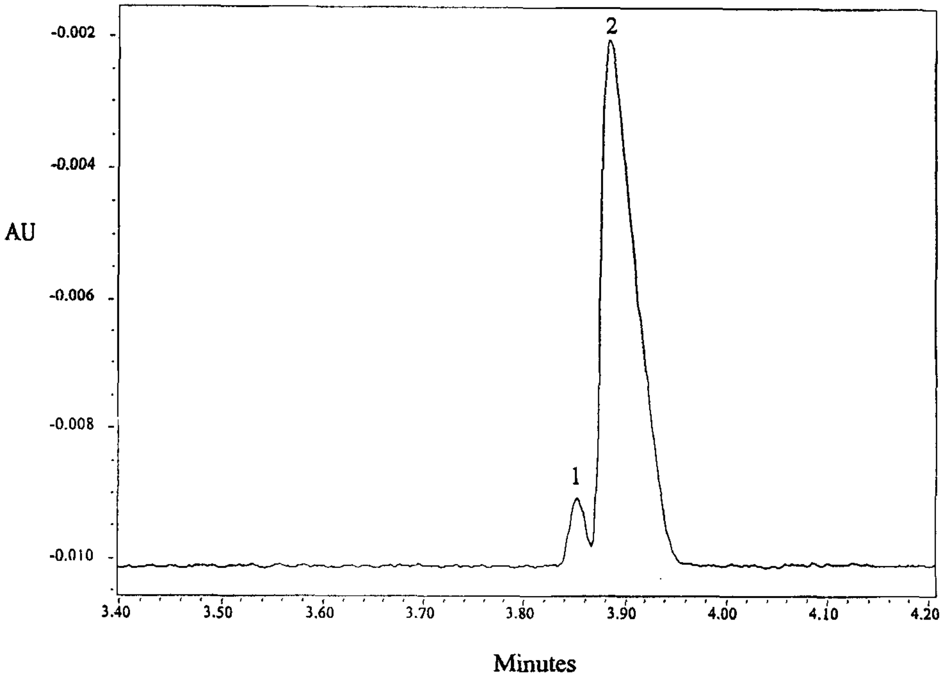

Figure 3: HAN standard showing sodium (Na^+) and hydroxylammonium (HA^+) peaks. Diluted 0.2 mL-10 mL. Peaks: **1**: Na^+, and **2**: HA^+.

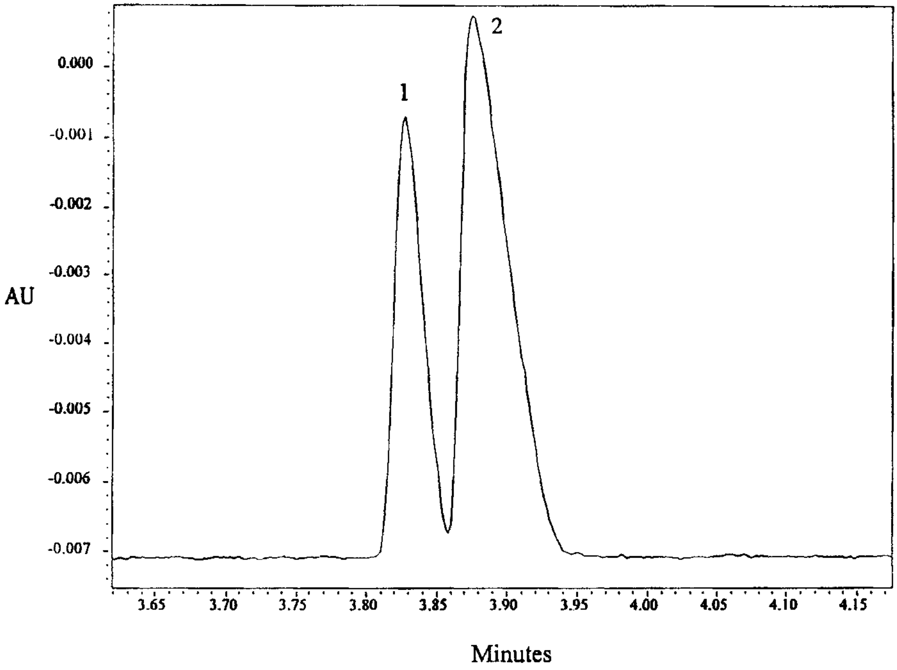

Figure 4: HAN standard after spiking in approximately 0.4 mg/L of sodium (Na^+) to solution in figure 3. Peaks: **1**: Na^+, and **2**: HA^+.

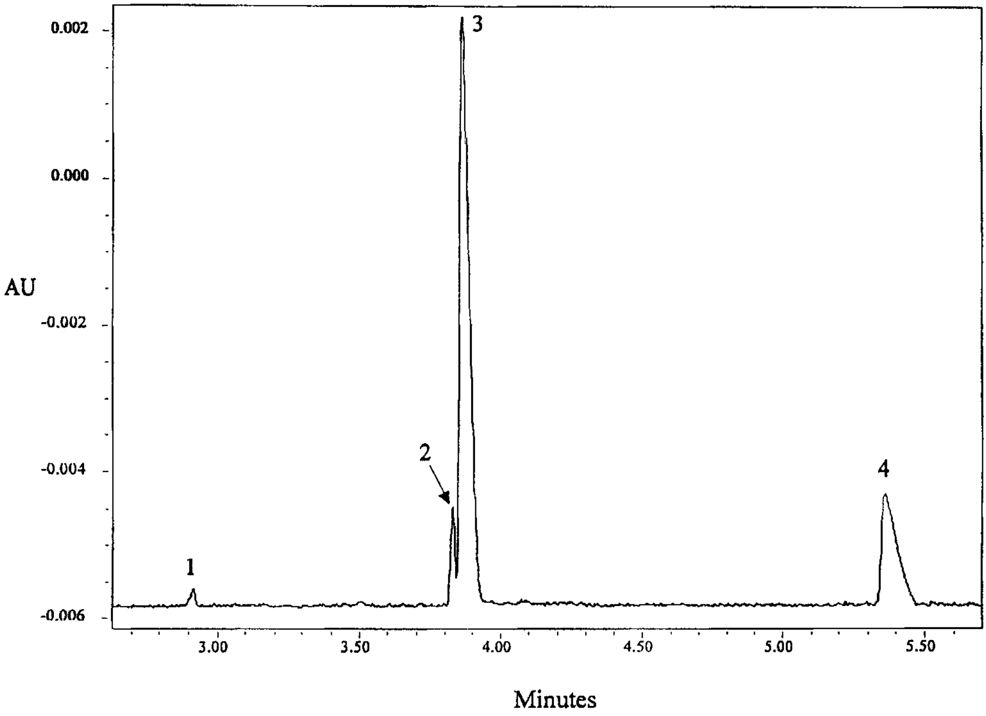

Figure 5: Liquid propellant (LP) standard. Diluted 0.2 mL-10 mL. Peaks: **1**: NH_4^+; **2**: Na^+; **3**: hydroxylammonium (HA^+); and **4**: triethanolammonium (TEA^+).

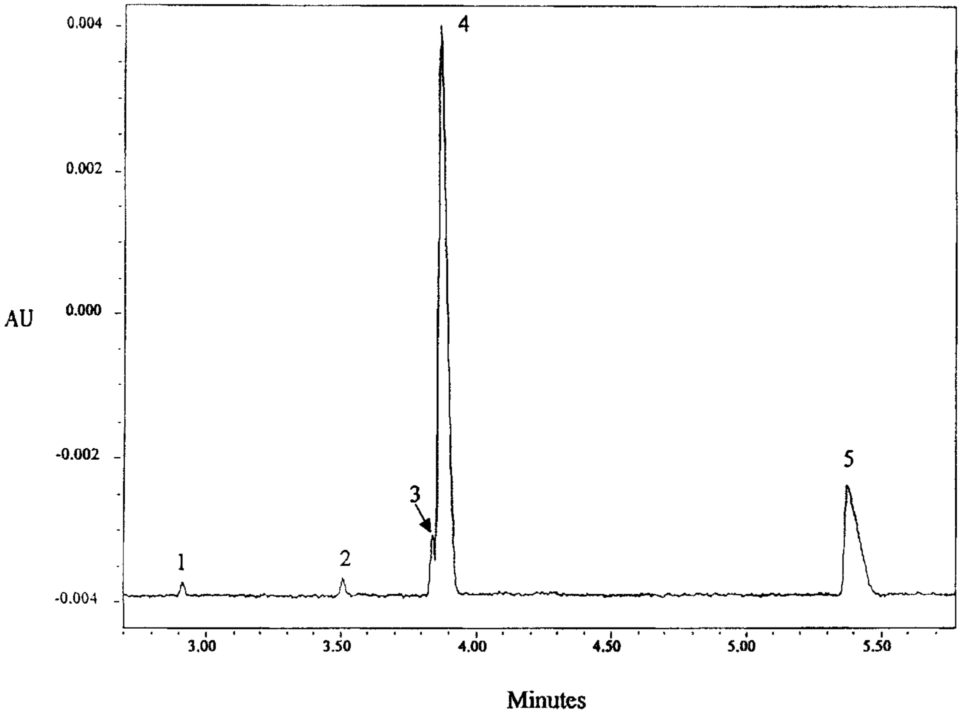

Figure 6: LP sample prior to aging. Diluted 0.1 mL-5 mL. Peaks: **1**: NH_4^+; 2: Ca^+; **3**: Na^+; **4**: hydroxylammonium (HA^+); and **5**: triethanolammonium (TEA^+).

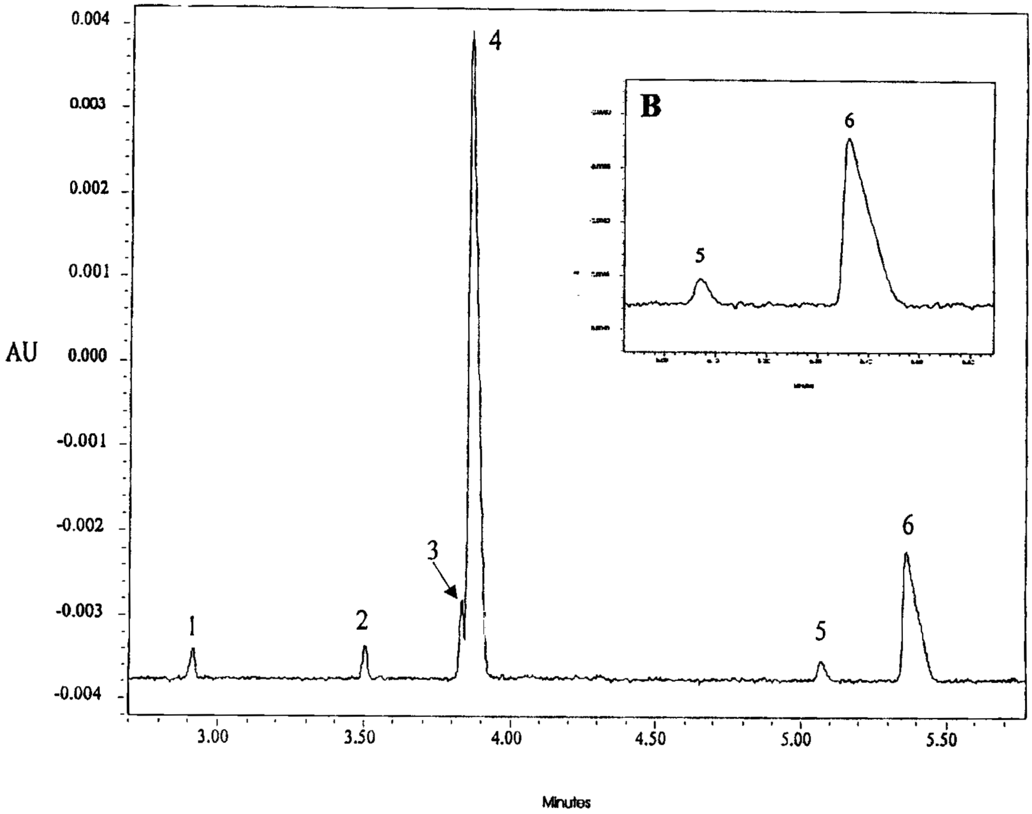

Figure 7: LP sample after aging for 296 days at 65 degrees celcius. Diluted 0.1 mL-5 mL. Peaks: **1**: NH_4^+; **2**: Ca$^+$; **3**: Na$^+$; **4**: hydroxylammonium (HA$^+$); **5**: diethanolammonium (DEA$^+$) and **6**: triethanolammonium (TEA$^+$). Inset B is close up of the DEA and TEA area of the electropherogram.

REFERENCES

1. Griff, S.P.; Doyle, G.; Turngren, E.; Seals, W.O.; and Bracuti, A. Report ARAED-CR-89016; Picatinny Arsenal, February 1990.
2. Griff, S.P.; Doyle, G.; Turngren, E.; and Seals, W.O.; Report ARAED-CR-90011; Picatinny Arsenal, August 1990.
3. Griff, S.P.; Doyle, G.; Turngren, E.; and Seals, W.O.; Report ARAED-CR-90010; Picatinny Arsenal, August 1990.
4. Rathburn, D.W.; and Strong, A.B. ; Preliminary Report, U.S. Army Corps of Engineers Waterways Experiment Station, February 1993.
5. Jandik, P.; Jones, W.R.; Weston, A.; and Brown, P.R.; LC-GC, Vol. 9, No. 9.