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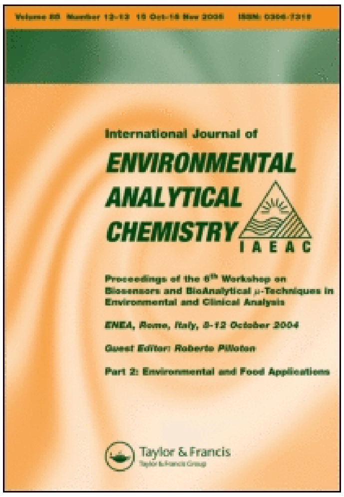

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# DETERMINATION OF FLUORIDE IN ATMOSPHERIC SAMPLES USING MACROCYCLE-BASED ION CHROMATOGRAPHY

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The analysis of fluoride in atmospheric samples poses challenges to current available methods. Ion chromatographic methods often suffer from interferences due to elution of the fluoride peak in the water dip and coelution of weakly retained organic acid anions. A separation system using a macrocycle-based ion chromatographic column provides a fast, effective method for the separation of fluoride in complex matrices. The macrocycle-based system shows better resolution of fluoride than traditional ion chromatographic methods, separating fluoride from both the water dip and the organic acid anions. Isocratic elution with a hydroxide eluent allows for a detection limit of 0.15 μM with a linear response between 0.4 and 150 μM. Results compare favorably with known values and those obtained by ion selective electrode analysis.

**KEY WORDS:** Fluoride analysis, ion chromatography, macrocycles, environmental tracers.

## INTRODUCTION

In the past 10 years there has been a noticeable increase in studies related to air quality and visibility in the southwestern United States as a result of the creation of Class I visibility regions by changes in the U.S. Clean Air Act. This has included an increase in studies to identify sources of airborne sulfate in these protected regions. This has led to a search for useful tracers for coal-fired power plants, smelters and other sources of sulfur oxides to determine the sources of the pollutants responsible for visibility impairment. Fluoride has been used as an endemic tracer for source apportionment studies. The composition of fluoride in emissions from different sources of sulfur oxides is specific to the source type. Fluoride in these emissions is detectable from great distances, up to 250 km in some instances[1,2] and can be used in combination with other endemic tracers in a chemical mass balance source apportionment analysis[2].

In our studies, fluoride is collected by three different sampling methods. Particulate phase fluoride is collected on acid washed quartz or teflon filters and gas phase fluoride is collected on either $NaHCO_3$-glycerol coated paper filters or on $NaHCO_3$-glycerol coated annular denuders. The fluoride extracted from the filters can be analyzed by either ion chromatography or by fluoride selective electrodes. The ion selective electrodes which have been used for fluoride determination suffer from poor detection limits, the need for frequent calibration, and interferences from aluminum and iron[3]. Nonchromatographic methods for the separation of fluoride from interfering species have also been developed, but these require time consuming sample preparation[4].

Ion chromatography with a carbonate-bicarbonate eluent is useful in the determination of nitrate and sulfate from atmospheric samples. The analysis of fluoride by this method is complicated by two different interferences: elution of fluoride near the water dip and coelution of organic acids. Fluoride is the shortest retained species in ion chromatography, eluting at the trailing edge of the water dip. This water dip is associated with the sample solvent and along with any unretained species, such as hydroxide, interferes with quantitation. Anions of organic acids, such as acetate and formate, are also weakly retained and have retention times similar to fluoride. The resulting coelution makes quantitation of fluoride difficult or impossible with isocratic elution methods. Interference from organic acids is especially a problem for the analysis of HF if collected on $NaHCO_3$-glycerol coated surfaces, as some organic acids are created by oxidation of the glycerine during sampling. Gradient elution schemes have been devised to improve the separation of fluoride from the organic acid anions[5] and do improve the separation, but baseline shifts decrease detection limits and analysis time is increased significantly.

Ion chromatography columns containing macrocyclic ligands have been used for the separation of both anions and cations. Cations are separated by their ability to complex with the macrocycle. Those cations that most closely fit into the macrocyclic cavity are often bound most strongly and hence are retained longest[6,7]. Most macrocycles are uncharged, and an anion must be associated with the macrocycle-cation complex on the column in order to maintain electrical neutrality. Different anions with a common cation can be separated with macrocycle-based columns by the ability of some anions to allow closer interaction between the cation and macrocycle, resulting in a more stable complex and greater anion retention[6].

In our laboratory, macrocycle columns have also been employed in an ion exchange mode rather than a ligand exchange mode for anion separations by the incorporation of an alkali metal hydroxide into the eluent[8–12]. The eluent cation complexes with the neutral macrocycle, forming a positively charged anion exchange site. The hydroxide ion serves to elute the analyte anions from the column. The column anion exchange capacity is determined by the number of cation-macrocycle complexes formed. Capacity gradient anion separations have been developed based on this principle[8,9]. Column stability is good, with no loss of cryptand from the column even after six months of use.

In this work we report the isocratic separation of fluoride using a macrocycle-based ion chromatography column. The fluoride is separated from the water dip and is also resolved from the organic acid anions, providing an excellent method for the analysis of atmospheric samples.

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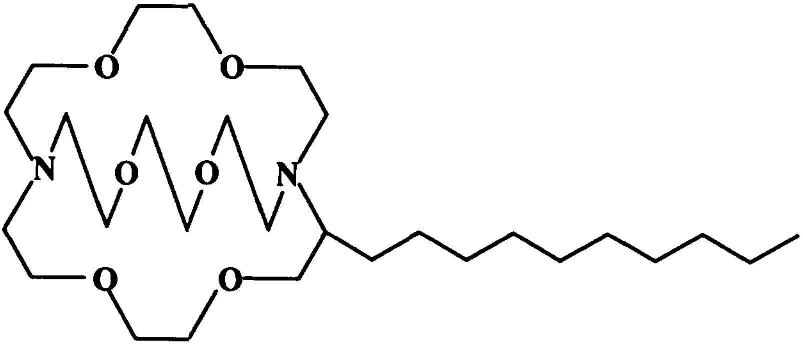

**Figure 1** Structure of the cryptand D-2.2.2

## EXPERIMENTAL

### *Materials*

Reagent grade cryptand Kryptofix 222D (D-2.2.2), pictured in Figure 1, was obtained from EM Science (Gibbstown NJ). Reagent grade compounds were used in making standards and eluents. All water used in making standards and eluents was purified to 18 MΩ resistivity with a Milli-Q water purification system (Millipore) and eluents were degassed by sparging with helium.

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### *Apparatus*

All chromatography was performed on a Dionex 4000i series ion chromatograph. A Dionex anion micromembrane suppressor (AMMS) was used for eluent suppression prior to conductivity detection with a Dionex conductivity detector. Suppressant was 12.5 mM $H_2SO_4$ flowing at 3–5 ml/min. Columns used were a Dionex AS4A ion exchange column with a 1.7 mM $NaHCO_3$–1.8 mM $Na_2CO_3$ eluent at 2.0 ml/min and a Dionex NS-1 MPIC-based macrocycle column (10 μm particle size) with a 30 mM NaOH eluent at 1.5 ml/min. The macrocycle-based column was prepared as previously described[8] by circulating a solution of 150 μmoles of D-2.2.2 dissolved in 25 mls of a 60:40 methanol:water solution through the MPIC column for 12 hours at 1.0 ml/min. The chromatography was controlled by and data collected on a personal computer with Dionex AI400 software.

Fluoride selective electrode measurements were made with a Corning model 250 Ion Analyzer in conjunction with an Orion model 96-09 fluoride combination electrode.

### *Sample preparation*

Environmental air samples were collected on either $NaHCO_3$-glycerol coated paper filters or $NaHCO_3$-glycerine coated annular denuders. Samples were prepared by sonication of the filters in 4–20 mls (depending on the filter size) of water for 20 minutes. Samples were diluted 1:1 (v:v) with TSAB with CDTA (1,2-cyclohexylene dinitrilotetraacetic acid) from Orion (Cambridge, MA) before measurement by the fluoride selective electrode.

## RESULTS AND DISCUSSION

One unique feature of macrocycle-based ion chromatography columns is the different selectivity for fluoride. The separation of an anion standard on both the AS4A and macrocycle-based columns is shown in Figure 2. With traditional IC columns the fluoride

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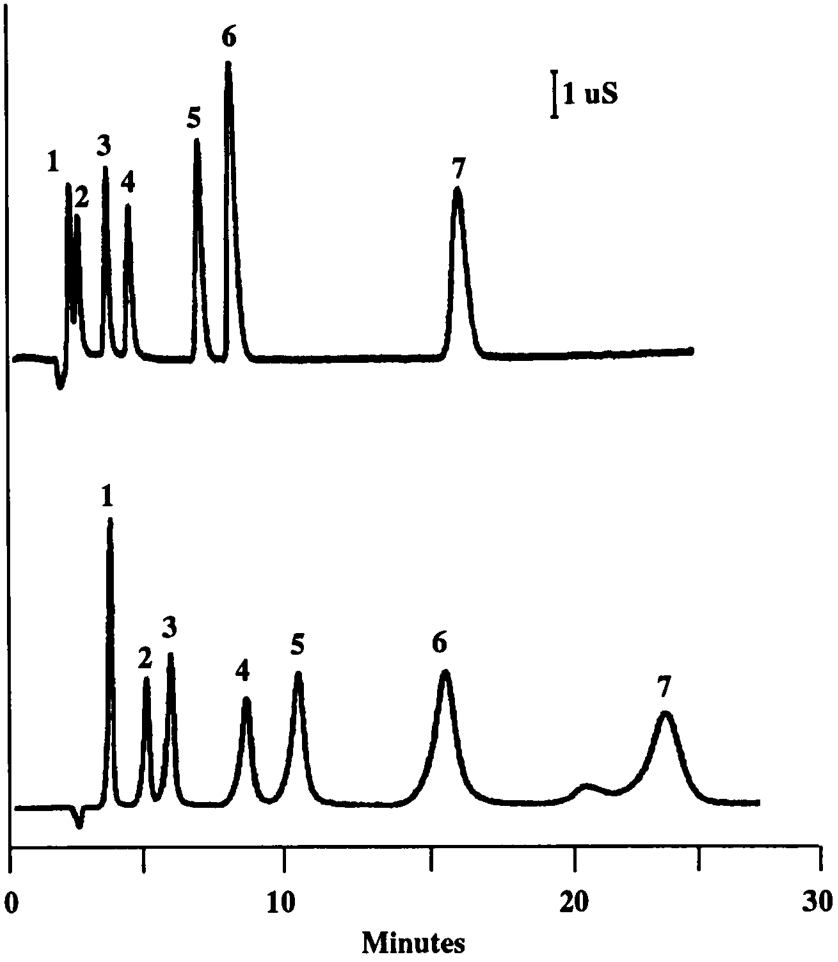

**Figure 2** Separation of an anion standard solution on: top) Dionex AS4A column, eluent is 1.7 mM $NaHCO_3$-1.8 mM $Na_2CO_3$ at 1.5 ml/min; and bottom) D-2.2.2 column. Eluent: 30 mM NaOH at 1.5 ml/min. Peaks: 1=fluoride; 2=acetate, formate; 3= chloride; 4=nitrite; 5=bromide; 6=nitrate; 7=sulfate.

elutes near the trailing edge of the water dip, as shown in the top chromatogram in Figure 2. On the macrocycle-based column, shown in the bottom chromatogram, fluoride is retained longer, moving it out of the water dip. This results in better quantitation since the fluoride peak appears after the baseline has returned to normal following the water dip. Since the macrocycle column includes features of a reversed phase column, the anions of organic acids are also retained slightly longer than on normal IC columns, resulting in the separation of formate and acetate from the fluoride peak. This eliminates the other major source of interference in atmospheric samples, namely the coelution of the organic anions present in the environment and created from the sample collection system.

The macrocycle-based IC separation of a typical sample collected on a Schleicher and Schuell fast flow filter coated with a 1% carbonate-1% glycerol solution in a study of tracers from coal fired power generation plants in the Southwestern United States is shown in the top chromatogram in Figure 3. The fluoride is well separated from the hydroxide peak eluting in the void volume, the elution volume corresponding to an unretained species, due to the hydroxide used to extract the sample from the filter. Resolution from the other weakly retained species in the sample is also accomplished. The separation of the same sample spiked with a fluoride standard, bottom chromatogram in Figure 3, confirms that the peak at 3.2 minutes is the fluoride peak.

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Figure 4 compares the isocratic separation of fluoride in an atmospheric sample collected on a denuder coated with a 1% carbonate-1% glycerol solution (top) on the AS4A system used for the analysis of nitrate and sulfate by traditional IC and (bottom) on the macrocycle-based IC. The macrocycle-based system achieves separation from all other matrix interferences, while fluoride is difficult to identify in the separation on the AS4A column. While anion retention times of fluoride on the AS4A column is shorter, resulting in a quicker separation of nitrate and sulfate, it is difficult to identify and quantitate the fluoride peak. The macrocycle-based column, on the other hand, shows good separation of the fluoride from both the species eluting in the water dip and from organic acids present in the sample, resulting in much more reliable identification and quantitation of fluoride.

A calibration curve generated by the macrocycle-based analysis of fluoride standards ranging from 0.38 μM to 150 μM showed a linear response with an $r^2$ value of 0.999 with a slope of 5.28 ± 0.06 and an intercept of 0.27 ± 0.03. Calibration curves generated by the standard addition method to an atmospheric sample showed similar linearity. The use of hydroxide eluents with the macrocycle-based system results in lower background conductivity than the carbonate-bicarbonate eluent used with the AS4A system, improving the limit of detection. The detection limit of 0.1 μM corresponds to three times the baseline noise. This compares to a detection limit of 0.5 μM for gradient elution methods and 0.5 μM for ion selective electrodes. In order to check the accuracy of the macrocycle-based separation, the method was used to quantify the fluoride in a NIST certified simulated rain water standard. The fluoride concentration provided by NIST was 3.0 μM. With the macrocycle-based separation system we measured the fluoride concentration to be 3.20 ± 0.11 μM, based on 7 repetitions. This compares to a value of 5.7 μM ± 0.2 by the fluoride selective electrode. The retention time was also quite reproducible, with a retention time of 3.18 ± 0.03 minutes.

The ability of the macrocycle-based system to quantitate fluoride in real atmospheric samples was evaluated by comparing measured fluoride concentrations in several types of

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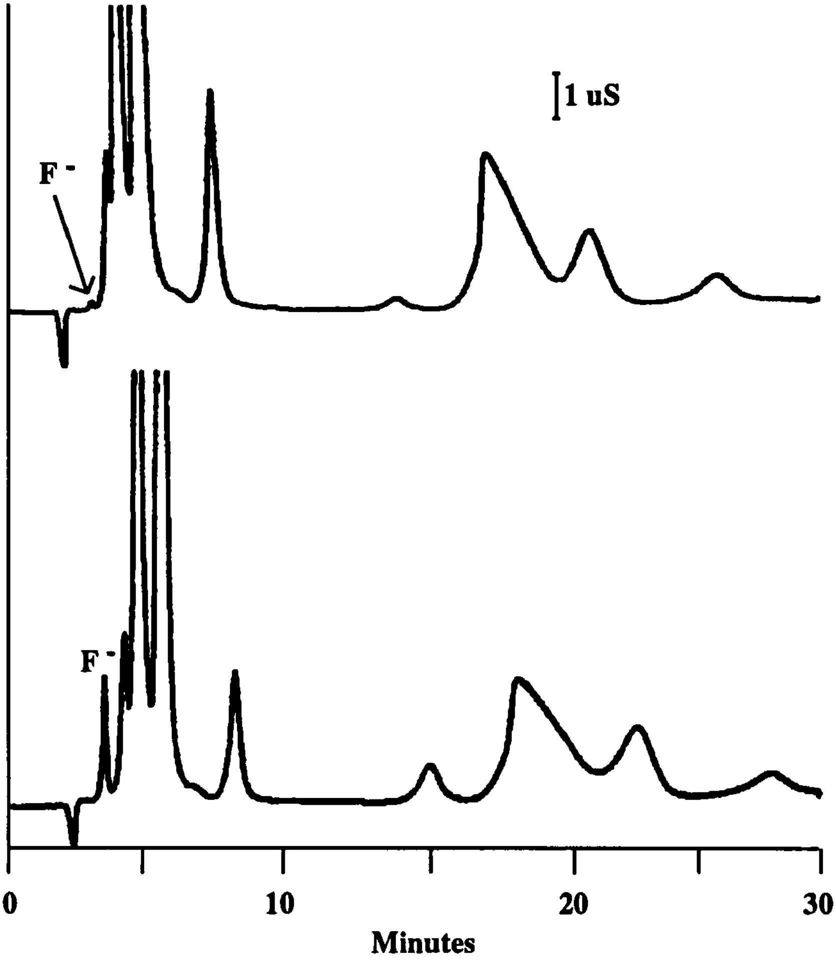

**Figure 3** top) Separation of an atmospheric sample collected on 1% $Na_2CO_3$-1% glycerol (w/w) coated filter on D-2.2.2 column. bottom) Same sample spiked with 15 μM $F^-$. Conditions and identified peaks are the same as in Figure 2.

samples to those obtained by the fluoride selective electrode. The results of the comparison are given in Table 1. For the impinger and quartz filter type samples there was good agreement between the two methods. For the bicarbonate filters, however, the results obtained by macrocycle-based chromatography gave significantly lower fluoride concentrations than the electrode. In the analysis of more than 20 different bicarbonate filter samples there was not consistent agreement between the two methods of analysis. The bicarbonate filter samples differ in that the filters are coated with a solution that contains glycerine, and the products from the oxidation of the glycerine may cause interferences. In order to discover the cause of the discrepancy in fluoride concentration by the two methods with the

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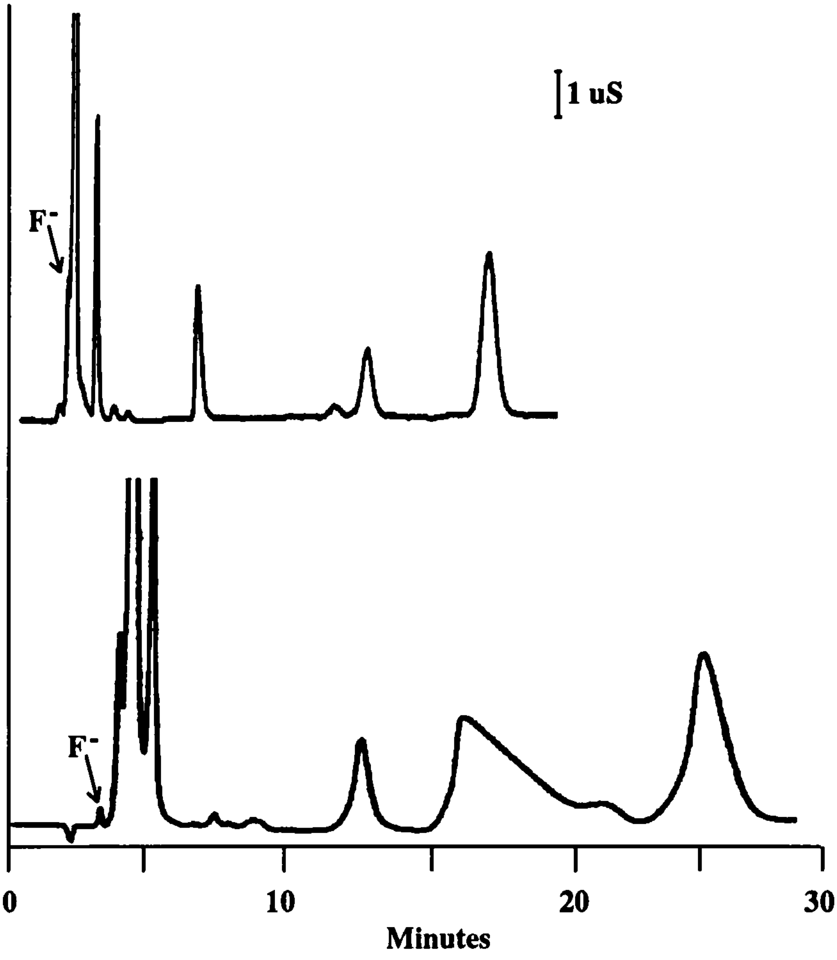

Figure 4 Comparison of separation of an atmospheric sample collected by a diffusion denuder coated with $Na_2CO_3$-1% glycerol (w/w) solution on top) Dionex AS4A column with 2.7 mM $NaHCO_3$– 2.8 mM $Na_2CO_3$ eluent and bottom) D-2.2.2 column with 30 mM NaOH eluent.

bicarbonate filters, a simulated bicarbonate filter sample containing 1% glycerol-1% $NaHCO_3$ was prepared with a known fluoride concentration. The fluoride concentration of this sample was measured by the two methods. The sample was prepared containing 1.0 μM $F^-$. The macrocycle-based IC yielded a F concentration of 1.09 μM (± 0.02). The fluoride selective electrode gave a $F^-$ concentration of 2.28 μM (± 0.25). This results indicates interference with fluoride measurements made with the fluoride selective electrode by some matrix element. While many interferences with fluoride selective electrodes can be eliminated by sample pretreatment, the purpose of this research was to compare the two methods with no sample treatment.

**Table 1** Comparison of fluoride measurements in three types of atmospheric samples by fluoride selective electrode and macrocycle-based ion chromatographic methods.

| | $[F^-]$ (μM) | |
|---|---|---|
| *Sample* | *Macrocycle-Based IC* | *Fluoride Selective Electrode* |
| Impinger Type | | |
| I1[a] | 3.25 ± 0.14 | 3.65 |
| I2[a] | 1.45 ± 0.04 | 1.38 |
| I3[a] | 0.57 ± 0.03 | 0.51 |
| Quartz Filter Type | | |
| Q1[b] | 0.84 ± 0.04 | 0.78 |
| Q2[b] | 4.69 ± 0.27 | 5.12 |
| Q3[b] | 4.12 ± 0.14 | 5.36 |
| Bicarbonate Filter Type | | |
| B1[b] | 0.21 ± 0.01 | 1.10 |
| B2[b] | 0.30 ± 0.02 | 1.0 |
| B3[b] | 0.22 ± 0.01 | 0.85 |
| B4[c] | 0.38 ± 0.01 | 2.03 |
| B5[c] | 0.56 ± 0.03 | 1.48 |

[a] Air samples collected at Bridger Generating Station, Bridger, WY., May, 1992.
[b] Air samples collected at Grand Canyon, AZ, January 1992.
[c] Air samples collected at Sycamore Canyon, Flagstaff, AZ, February 1992

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One possible concern with macrocycle-based ion chromatography with the macrocycle adsorbed onto the column is column stability. We have used the same column for up to 6 months with no loss in anion retention. No column degradation was observed after 50 sample injections during the course of this study. In fact macrocycle-based columns have the advantage that very strongly retained anions can be removed simply by changing the eluent to one containing a cation with little affinity for the macrocycle, reducing column capacity and eluting even strongly retained species such as thiocyanate.

## CONCLUSIONS

Macrocycle-based ion chromatography allows the efficient separation of fluoride from both the water dip and from other weakly retained species in atmospheric samples. The D-2.2.2 column shows better separation of fluoride than commercially available columns, with a lower detection limit. Excellent separations have been shown under isocratic conditions, providing a simple, fast method for the analysis of fluoride in complex matrices. The results obtained here suggest that macrocycle-based ion chromatographic analysis for $HF_{(g)}$ trapped by carbonate/glycerol avoids interferences present in analyses using a fluoride specific electrode.

## Acknowledgements

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## References

1. M. McDannel, D. J. Eatough, N. L. Eatough, S. Houtrow, L. D. Hansen, and R. J. Farber, *Proc. 81th* Ann. Meet. APCA, 88-72.3 (1985).
2. D. J. Eatough, J. R. Bennett, N. Lytle, M. Brutsch, T. Luke, S. Houtrouw, N. F. Mangleson, M. W. Hill, E. A. Lewis, L. D. Hansen, N. L. Eatough and R. J. Farber, *Proc. 79th* Ann. Meet. APCA, 720–735 (1986).
3. A. Yuchi, N. Yanai, H. Wada and G. Nakagawa, *Analyst*, **113,** 1405–1408 (1988).
4. D. R. Taves, *Talanta*, **15,** 969–974 (1968).
5. L. J. Lewis, J. D. Lamb, D. J. Eatough, L. D. Hansen, R. T. Paxton and E. A. Lewis, *J. Chromatogr. Sci.*, **28,** 490–492 (1990).
6. E. Blasius, K. P. Janzen, W. Klein, H. Klotz, V. B. Nguyen, T. Nguyen-Tien, R. Pfieffer, G. Scholten, H. Simon, H. Stockemer and A. Toussaint, *J. Chromatogr.*, **201,** 147-166 (1980).
7. K. Kimura, H. Harino, E. Hayata and T. Shono, *Anal. Chem.*, **58,** 2233–2236 (1986).
8. J. D. Lamb and P. A. Drake, *J. Chromatogr.*, **482,** 367–380 (1989).
9. J. D. Lamb, P. A. Drake and K. Woolley, in *Advances in Ion Chromatography, Vol. 2*, P. Jandik and R. M. Cassidy, (Editors), Century International, Medfield, MA, (1990) pp. 215–231.
10. J. D. Lamb and R. G. Smith. *J. Chromatogr.*, **546,** 73–88 (1991).
11. J. D. Lamb and R. G. Smith, *Talanta*, **39,** 923–930 (1992).
12. J. D. Lamb and R. G. Smith, *J. Chromatgr.*, **640,** 33–40 (1993).

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