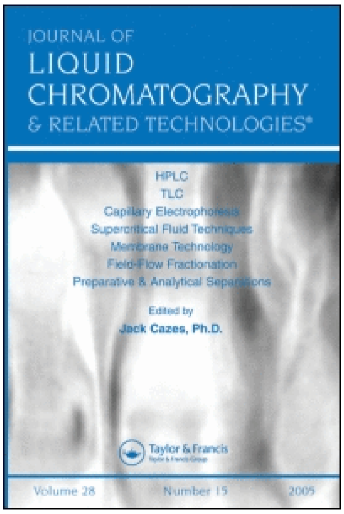

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DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM, AND CALCIUM IN SEAWATER BY CAPILLARY ELECTROPHORESIS WITH INDIRECT PHOTOMETRIC DETECTION

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ABSTRACT

Determination of Na^+, K^+, Mg^{2+}, and Ca^{2+} in seawater is currently performed by using either laborious wet chemical methods or physical ones requiring complicated and expensive instruments. The present study assessed the feasibility of using capillary electrophoresis (CE) as an alternative method for analysis of these metal ions in seawater samples and the robustness of CE in determination of the metal ions in samples of complex matrices. Imidazole was added in various electrophoretic media to provide UV absorbing background for indirect detection and 18-crown-6 was utilized to manipulate selectivity through complexation. Na^+, Mg^{2+}, and Ca^{2+} in seawater samples could be determined in an electrophoretic medium of 40 mM 18-crown-6 and 10 mM imidazole at pH 4.5 with an internal standard of Li^+, but quantitative determination of K^+ had to be carried out in another separate run by using an electrophoretic medium of relatively low concentration of 18-crown-6 to improve the precision of the quantitative results. It was demonstrated that CE could be a fast, simple and low cost means for the determination of Na^+, K^+, Mg^{2+} and Ca^{2+} in seawater with fairly good robustness.

INTRODUCTION

Sodium, potassium, magnesium, and calcium are abundant elements on the earth. Determination of Na^+, K^+, Mg^{2+}, and Ca^{2+} are frequently carried out in various analytical laboratories for diverse samples for different purposes. For example, determination of the metal ions is required to examine overall quality of surface water in an environmental laboratory. The determination of the metal ions is made to study some foodstuffs for their nutriment in a laboratory of food quality control. The determination is also performed to provide valuable information on a patient's electrolyte balance and response to therapy in a clinical laboratory.

Techniques available for the determination of Na^+, K^+, Mg^{2+}, and Ca^{2+} generally include the following:

1. Wet chemical methods, e.g., titration and gravimetry.

2. Electroanalytical methods, e.g., potentiometry with ion selective electrode and voltammetry.

3. Spectrometric methods, e.g., atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and neutron activation analysis (NAA).

4. Separation-base methods, e.g., ion chromatography (IC) and capillary electrophoresis (CE).

Wet chemical methods are known to be insensitive, laborious, and time consuming. One chemical method is usually valid for only one of the metal components. Potentiometry with an ion-selective electrode is generally considered not to be a technique for multielement determination. Voltammetry has difficulties in determination of the electropositive element. AAS is a widely used technique for the determination of single metal elements. It is of relative simplicity, low cost, high sensitivity, and good robustness, but less useful in simultaneous multielement determination of the metal ions. ICP-AES, ICP-MS, XRF, and NAA are sophisticated techniques capable of simultaneous multielement determination, but high cost and low availability are their disadvantages. A well trained personnel is needed for the operation of each of these instruments. IC and CE are techniques capable of simultaneous determination of the metal ions. Advantages of CE over IC are generally in aspects of speed, efficiency, reagent consumption, and flexibility. For complex samples, disadvantages of IC compared with CE may include the need for special cation exchangers, column switching, and/or gradient elution.

CE has been of growing interest in the determination of metal ions since its merits of simplicity, selectivity, short analysis time, and low operational cost became evident in the early 1990s.[1-6] Additional advantages exist when CE is applied to the determination of Na^+, K^+, Mg^{2+}, and Ca^{2+}. The hydrated cations of these metals show no or little tendency to hydrolyze to form precipitation in the most useful pH range in CE. This fact results in easiness and flexibility in electrophoresis buffer selection. High mobilities of the hydrated Na^+, K^+, Mg^{2+}, and Ca^{2+} lead to short analysis time and simple sample preparation. The analytes of interest migrate through a capillary from the injection end to the detection end at greater velocity and leave slow migrating cations, neutral compounds, and anions in sample matrixes behind without interferences. In fact, it works like a coupled inherent on-line sample clean-up procedure. Therefore, many of the applications of CE so far reported for the determination of metal cations in real samples were concerned with the determination of Na^+, K^+, Mg^{2+}, and Ca^{2+}.[6-14]

Seawater is well known for the complexity of its chemical composition. Analysis of Na^+, K^+, Mg^{2+}, and Ca^{2+} is a common procedure within the frame work of determining the chemical composition of seawater. These ions of similar chemical properties are present at considerably varied concentrations and in complex matrices of high salinity in seawater samples.[15] Determination of Na^+, K^+, Mg^{2+}, and Ca^{2+} in seawater were performed by using either chemical methods or physical ones.[16] Kim et al. reported the use of ICP-AES for the determination of Na^+, Mg^{2+}, and Ca^{2+}, and AAS for K^+ in seawater.[17] Betti, et al. developed an IC method for the determination of alkali and alkaline-earth elements in seawater samples.[18] They completed the determination by the use of eluent step change and column switching with analysis time of 50 min and 25 min, respectively. Pantsar-Kallio and Manninen found CE superior to IC in terms of speed and efficiency and inferior to IC in terms of sensitivity and reproducibility after comparing the results obtained by the two techniques for waste waters and spring, lake and well waters.[19]

This paper presents the results of the determination of Na^+, K^+, Mg^{2+}, and Ca^{2+} in seawater samples by CE. The results provide some information for assessing the value of CE as an analytical technique for determining the metal ions in samples of complex matrices.

EXPERIMENTAL

Materials and Apparatus

Chemicals used in this work were of analytical grade. Standard solutions of Na^+, K^+, Mg^{2+}, Ca^{2+}, and Li^+ metal ions were purchased from BDH (Poole, UK). A standard solution of NH_4^+ was prepared from NH_4NO_3 (BDH). Water used throughout the experiments had resistivity greater than 18 MΩ. Fused silica capillary was of 57 cm in total length and 45 cm in effective length and of 50 μm I.D. (Polymicro Technologies, AZ, USA).

Detector and power supply were the same as those described in one of our previous papers.[20] AAS measurements were performed with an AA-670 Atomic Absorption/Flame Emission Spectrophotometer (Shimadzu Co., Kyoto, Japan) and ICP-AES with an IRIS/AP Plasma Spectrometer (Thermo Jarrell Ash Co., Franklin, MA, USA). Seawater samples were obtained at the harbor around the World Trade Center of Singapore.

CE Procedure

The CE method used in this work was adopted from the one reported by Francois et al.[21] with little modification. Preconditioning of a new capillary included 2 min. rinse with water, 5 min. with 0.1 M NaOH, 2 min. with water and finally 5 min. with buffer. Between two consecutive runs the capillary was rinsed with only buffer for 2 min. Voltage of 18 kV was applied to the capillary for separation. Sample injection was made in hydrodynamic mode by lifting the injection end of the capillary to 4.0 cm relative to the detection end of the capillary for 20 s. Detection was made at 214 nm.

Seawater samples were filtered through a 0.45 μm syringe filter, acidified at about pH 2 and diluted appropriately with water. 0.2% lanthanum chloride was added to standards and diluted seawater samples when calcium in the seawater samples was determined by using AAS.

RESULTS AND DISCUSSION

There are two problems to be solved to successfully determine alkali and alkaline-earth metal ions by CE with a common ultraviolet-visible (UV-VIS) detector. One is low selectivity due to insufficient differences in their mobilities as a result of similar charge to mass ratio of the corresponding hydrated metal ions. The other is poor detectability as these ions typically have little, if any, absorbance in the UV-VIS range due to the lack of chromophores. Common and simple solutions to the above problems are to introduce complexing agents to the electrophoretic media to enlarge the differences in effective mobilities of the ions through complexation and to provide co-ions of strong UV-VIS absorption in the electrophoretic media to make use of indirect photometric detection.[1,4-6,20-24]

Hjerten was the first one to separate metal ions by CE and to introduce indirect detection to CE.[25] Beck and Engelhardt carried out early studies on the separation and detection of alkali and alkaline-earth metal ions in imidazole-based electrophoretic media.[6] As UV absorbing electrolyte to indirectly detect metal cations, imidazole was recommended to be used in a pH range of 3 to 5.[22] Two approaches were known to be effective in separation of K^+ from NH_4^+. In one approach, basic electrophoresis buffer was employed to reduce the mobility of NH_4^{+5}. This approach is not applicable to the imidazole-based electrophoretic media. In the other crown ethers, such as 18-crown-16, were introduced to the electrophoresis buffer.[22,26] It is known that crown ethers complex most strongly those metal ions whose ionic crystal radii best match the radius of the cavity formed by the ring upon complexation.[27,28] K^+ forms a more stable complex with 18-crown-16 than NH_4^+, Na^+, Mg^{2+}, and Ca^{2+} do. The effective mobility of a metal ion in electrophoretic media containing 18-crown-6 is the weighted sum of mobilities of the hydrated metal ion and the metal-8-crown-6 complex. The more stable is the metal-8-crown-6 complex, the larger is the fraction of the metal-8-crown-6 complex in a given concentration of 8-crown-6. Consequently, the effective mobility of the metal ions decreases to a greater extent. So, the selectivity of the CE separation of the metal ions can be adjusted by simply changing the concentration of 18-crown-6.

Francois et al. recently made detailed studies on the migration behavior of ammonium, alkali, and alkaline-earth metal ions in electrophoretic media containing imidazole as a UV chromophore and 18-crown-6 as a complexing agent.[21] Their results showed that the electrophoretic media consisting of imidazole and 18-crown-6 had advantages of simple composition and good flexibility in adjusting selectivity. We employed this type of electrophoretic media to separate Na^+, K^+, Mg^{2+}, Ca^{2+}, in seawater in this work.

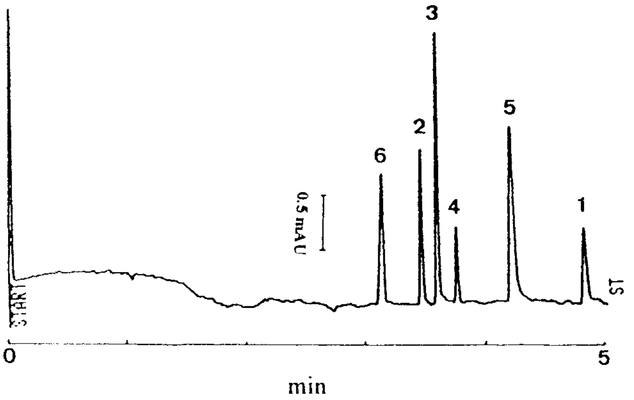

Figure 1. Electropherogram of a standard mixture of ammonium, lithium, sodium, potassium, magnesium, and calcium. Electrophoresis buffer: 10 mM imidazole and 40 mM 18-crown-6 at pH 4.5. Concentrations of Na^+ and Li^+ were 5 ppm each and concentrations of the other cations 10 ppm each. Peaks: 1. K^+, 2. Ca^{2+}, 3. Mg^{2+} 4. Na^+, 5. Li^+ 6, NH_4^+. For other experimental conditions, see text in the experimental section.

Table 1

Mobilities of Some Inorganic Cations and EOF in Different Electrophoresis Buffers

Electrophoresis Buffers	Mobilities of Cations ($x10^{-4}$ cm^2/Vs)						EOF ($x10^{-4}$ cm^2/Vs)
	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Li^+	
10 mM imidazole and 40 mM 19-crown-6-at pH 4.5	5.62	4.38	2.97	4.83	4.64	3.69	1.90
10 mM imidazole and 4 mM 18-crown-6 at pH 4.5	7.35	5.05	6.04	5.41	4.87	3.88	1.85

Figure 1 shows an electropherogram obtained with a standard mixture of Na^+, K^+, Mg^{2+}, Ca^{2+}, and Li^+ metal ions, and NH_4^+ ions in an electrophoresis medium of 10 mM imidazole and 40 mM 18-crown-6 at pH 4.5. This medium was chosen due to a few reasons. All the cations in the standard mixture were separated with high resolution. The peak of Na^+, which was usually of the highest concentration of the metal ions in seawater samples, migrated behind very closely adjacent peaks of Ca^{2+} and Mg^{2+}. If the order of the peaks were reversed, it would have made the resolution and quantification of those metal ions difficult. Nearly symmetric peaks were obtained for Ca^{2+}, Mg^{2+}, and Na^+ as a result of a good match of their effective mobilities with that of the UV chromophore. Imidazolium was determined to have mobility of 4.4 cm^2/Vs in 10 mM sodium acetate at pH 4.5.[21] The mobilities of the cations in the standard mixture were determined and given in Table 1. Symmetric peaks would extend linearity of calibration curve in CE separation with indirect photometric detection.[29] As concentrations of Na^+, K^+, Mg^{2+}, and Ca^{2+} differed significantly in the seawater samples, symmetric peak shape was needed to obtain a wide linearity range which might permit quantitative determination of all those metal ions in one run with good precision. The peak of Na^+ started to merge with the peak of Mg^{2+} when the concentration of 18-crown-6 slightly decreased. The peak shape of K^+ became severely deteriorated when the concentration of 18-crown-6 increased in the range of 40 to 60 mM.

Figure 2 shows an electropherogram obtained in the above electrophoretic medium with a seawater sample diluted 100 times. To improve precision in quantification of the metal ions, an internal standard of 5 ppm Li^+ was added to the sample. All the peaks were baseline separated in the above electropherogram. The quantitative results of the metal ions obtained by CE are presented in Table 2 with precision in terms of the relative standard deviation (RSD). The results of those metal ions in the same sample obtained by other instrumental techniques, such as ICP-AES or AAS, are also given in Table 2 for the purpose of comparison. Response functions for Na^+, Mg^{2+}, and Ca^{2+} were as follows:

Na^+ $Y = 0.0552\,X + 5.432$ $R^2 = 0.999$
Mg^{2+} $Y = 0.0980\,X + 1.111$ $R^2 = 0.998$
Ca^{2+} $Y = 0.0597\,X + 0.212$ $R^2 = 0.995$

The linearity range was valid up to 200 ppm for all the three metal ions. The results of K^+ in Table 2 was not obtained in the electrophoretic media of 10 mM imidazole and 40 mM 18-crown-6 at pH 4.5, but in another electrophoretic media of relatively low concentration of 18-crown-6. The precision of the results for K^+ was very poor when analysis was performed in the electrophoretic media of 10 mM imidazole and 40 mM 18-crown-6 at pH 4.5. The RSD of the results for K^+ was about 10%. The irreproducible results for K^+ might be due to its poor peak shape.

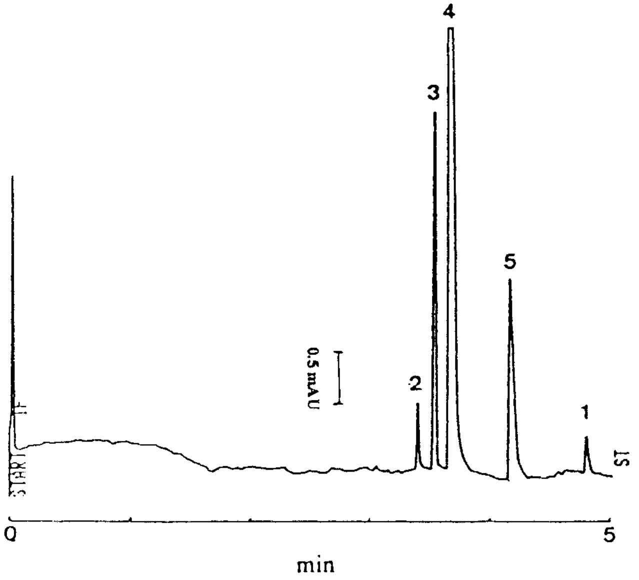

Figure 2. Electropherogram of a diluted (1:100 v/v) seawater sample containing Li^+ (5 ppm) as an internal standard. For other experimental conditions and peak identities, see Figure 1.

Table 2

Results of Sodium, Potassium, Magnesium and Calcium in the Seawater Samples Determined by Different Instrumental Techniques

	CE[a]	ICP-AES[a]	AAS[a]
Sodium (ppm)	9.11×10^3 (1.3)[b]	8.87×10^3 (0.1)[b]	9.13×10^3 (1.2)[b]
Magnesium (ppm)	1.13×10^3 (1.7)[b]	1.26×10^3 (1.0)[b]	1.07×10^3 (0.9)[b]
Calcium (ppm)	3.62×10^2 (3.9)[b]	3.71×10^2 (0.6)[b]	3.62×10^2 (1.0)[b]
Potassium (ppm)	3.90×10^2 (5.4)[b]	----[c]	3.59×10^2 (1.6)[b]

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[a] Mean value of triplicate measurements.

[b] Relative standard deviation of triplicate measurements

[c] Not determined.

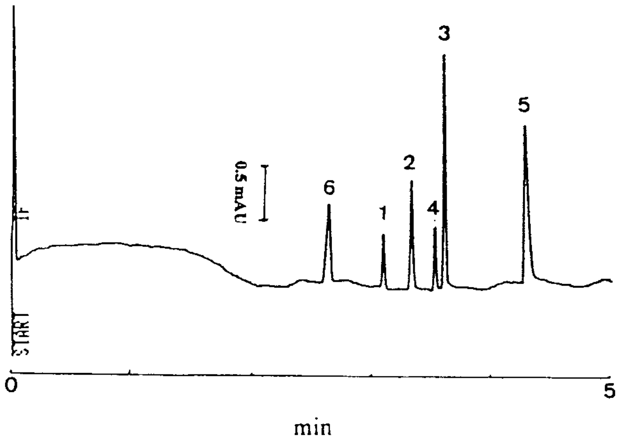

Figure 3. Electropherogram of a standard mixture of ammonium, lithium, sodium, potassium, magnesium, and calcium. Electrophoresis buffer: 10 mM imidazole and 4 mM 18-crown-6 at pH 4.5. For other experimental conditions and peak identities, see Figure 1.

To improve the precision of the results of K^+ we reduced concentration of 18-crown-6 in the electrophoresis buffer and used less diluted samples. Figure 3 shows an electropherogram obtained with a standard mixture of the cations in an electrophoretic medium of 10 mM imidazole and 4 mM 18-crown-6 at pH 4.5.

The migration order of the cations in Figure 3 was different from that in Figure 1. K^+ migrated very much faster than it did under the experimental conditions for Figure 1. Effective mobility of K^+ ions increased most significantly (see Table 1) as concentration of 18-crown-6 decreased. It is attributed to the fact that ionic crystal radius of K^+ matches best with cavity size of 18-crown-6 and complex of K^+ with 18-crown-6 is most stable comparing with the other metal ions.[26,-28,]

Similarly, an explanation can be made for reverse order between peaks of Ca^{2+} and Mg^{2+} in Figure 3. It implies that complex of Ca^{2+} with 18-crown-6 is more stable than the one of Mg^{2+} under the experimental conditions.

Figure 4 shows an electrpherogram obtained with a less diluted seawater sample (25 times) in the electrophoretic medium of 10 mM imidazole and 4 mM 18-crown-6 at pH 4.5. The internal standard of Li^+ (5 ppm) was also added for the same reason to improve the precision of the quantitative results.

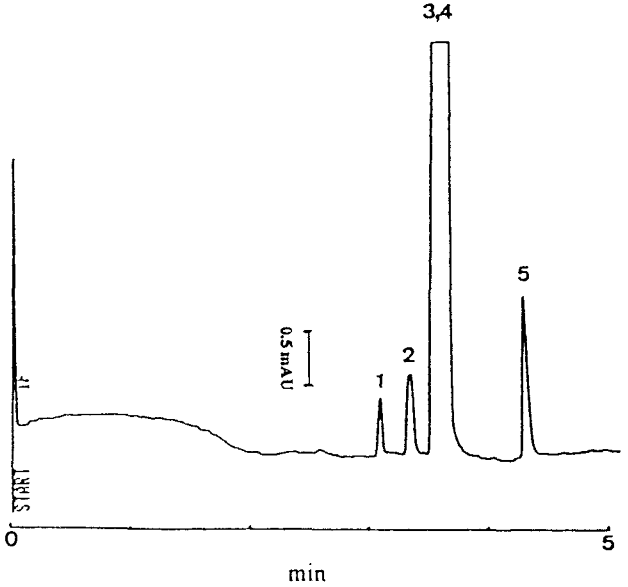

Figure 4. Electropherogram of a diluted (1:25 v/v) seawater sample containing Li^+ (5 ppm) as an internal standard. Electrophoresis buffer: 10 mM imidazole and 4 mM 18-crown-6 at pH 4.5. For other experimental conditions and peak identities, see Figure 1.

The quantitative results of K^+ were given in Table 2. The precision of the results for K^+ was significantly improved. The response function of K^+ was:

K^+ $Y = 0.025\,X + 0.0269$ $R^2 = 0.998$

The linearity range was up to 150 ppm.

CONCLUSIONS

This work demonstrated that CE could be an alternative means for the analysis of Na^+, K^+, Mg^{2+}, and Ca^{2+} metal ions in seawater samples of complex matrices with fairly good robustness. The CE method for analysis of the metal ions in samples of complex matrices had advantages of simplicity and low operational cost. To make the CE method more competitive against other instrumental techniques in the analysis of Na^+, K^+, Mg^{2+}, and Ca^{2+} metal ions in samples of complex matrices, experiments to further improve precision should be performed.

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REFERENCES

1. F. Foret, S. Fanali, A. Nardi, P. Bocek, Electrophoresis, **11**, 780-783 (1990).
2. L. Gross, E. S. Yeung, Anal. Chem., **62**, 427-431 (1990).
3. D. F. Swaile, M. J. Sepaniak, Anal. Chem., **63**, 179-184 (1991).
4. P. Jandik, W. R. Jones, A. Weston, P. R. Brown, LC-GC, **9**, 634-641 (1991).
5. A. Weston, P. R. Brown, P. Jandik, W. R. Jones, A. L. Heckenberg, J. Chromatogr., **593**, 289-295 (1992).
6. W. Beck, H. Engelhardt, Chromatographia, **33**, 313-316 (1992).
7. W. Buchberger, K. Winna, M. Turner, J. Chromatogr. A., **671**, 375-282 (1994).
8. Y. Qing, M. Jimidar, T. P. Hamoir, J. Smeyers-Verbeke, D. L. Massart, J. Chromatogr. A., **673**, 275-285 (1994).
9. S. A. Oehrle, R. D. Blanchard, C. L. Stumpf, D. L. Wulfeck, J. Chromatogr. A., **680**, 654-652 (1994).
10. H. L. Shi, R. L. Zhang, G. Chandrasekher, Y. F. Ma, J. Chromatogr. A., **680**, 653-658 (1994).
11. E. Dabek-Zlotorzynska, J. F. Dlouhy, J. Chromatogr. A., **706**, 527-534 (1995).
12. E. L. Pretswell, B. A. McGaw, R. Morrisson, Talanta, **42**, 283-289 (1995).

13. T.-I. Lin, Y.-C. Chen, Y.-H, Lee, J.-T. Kao, Clin. Chem., **41**, S157 (1995).

14. J. Havel, P. Janos, P. Jandik, J. Chromatogr. A., **745**, 127-134 (1996).

15. R. Bond, C. Straub (Editors), **Handbook of Environmental Control**, CRC Press, Cleveland, OH, 1973, pp. 109-110.

16. T. R. Crompton, **Analysis of Seawater**, Butterworths, London, 1989, pp. 74-81.

17. J. P. Kim, M. R. Reid, R. G. Cunninghame, K. A. Hunter, Mar. Freshwat. Res., **47**, 919-928 (1996).

18. M. Betti, G. Giovannoni, M. Onor, J. Chromatogr., **546**, 259-271 (1991).

19. M. Pantsar-Kallio, K. G. Manninen, Anal. Chim. Acta, **314**, 67-75 (1995).

20. T. Wang, S. F. Y. Li, J. Chromatogr. A, **707**, 343-353 (1995).

21. C. Francois, Ph. Morin, M. Dreux, J. Chromatogr. A, **706**, 535-553 (1995).

22. W. Beck, H. Engelhardt, Fresenius J. Anal. Chem., **346**, 618-621 (1993).

23. M. Chen, R. M. Cassidy, J. Chromatogr., **640**, 425-431 (1994).

24. Y. Shi, J. S. Fritz, J. Chromatogr., **640**, 473-479 (1994).

25. S. Hjerten, Chromatog. Rev., **9**, 122-219 (1967).

26. K. Bachmann, J. Boden, I. Haumann, J. Chromatogr., **626**, 259-265 (1992).

27. C. J. Pedersen, J. Am. Chem. Soc., **89**, 7017- 7036 (1967).

28. R. M. Izatt, K. Pawlak, J. S. Bradshaw, Chem. Rev., **91**, 1721-2085 (1991).

29. G. W. Tindall, D. R. Wilder, J. Chromatogr., **641**, 163-167 (1993).

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