94-0150

Inorganic Cation Separations by CIA: A Study of Controlled Selectivity Using Various Complexing Agents

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Definition of Capillary Ion Analysis

- Capillary Ion Analysis (CIA), a subset of capillary electrophoresis, is optimized for low molecular weight inorganic and organic ions.

- Indirect UV detection is predominately used since the majority of the analytes lack specific chromophores

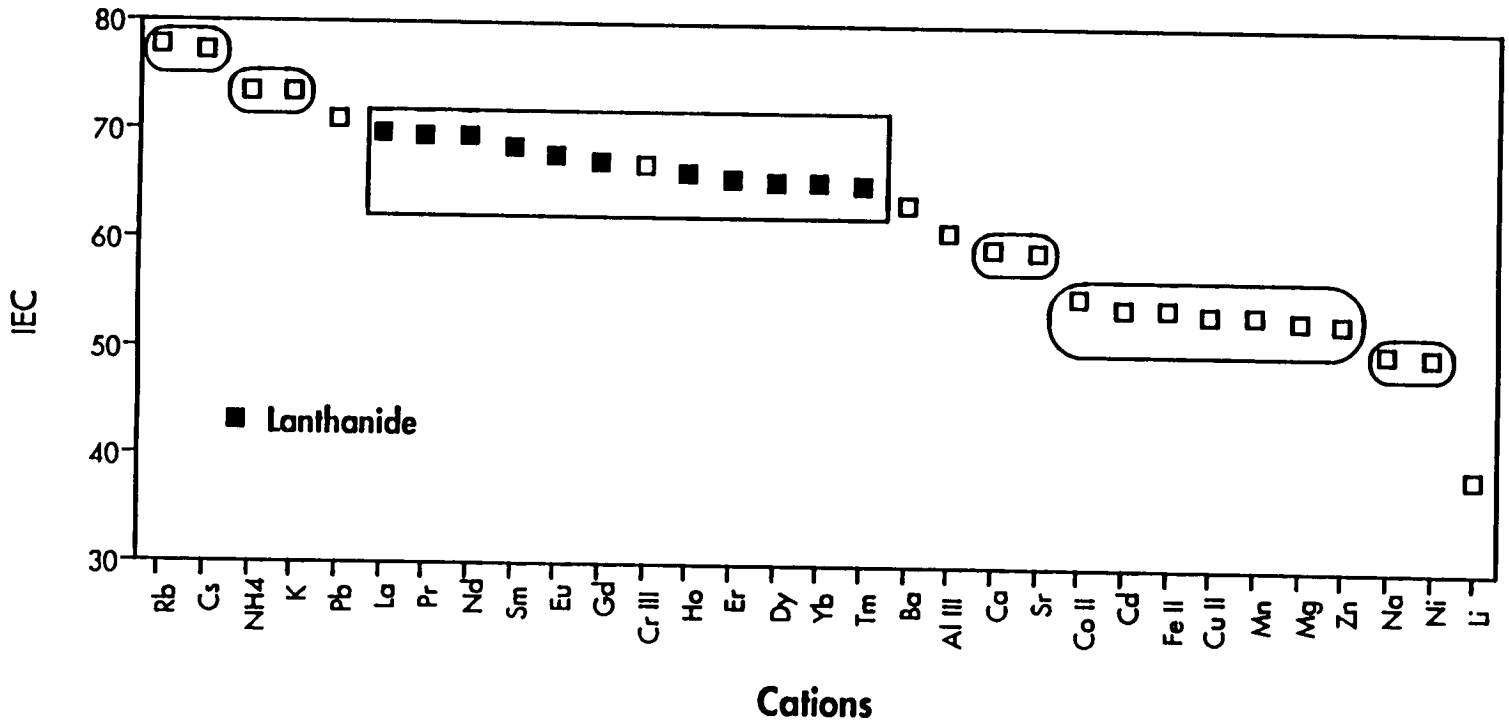
- Rapid analysis times are achieved using the Co-Electroosmotic Principle (Go with the Flow!)

Outline

- Definitions
- Selectivity vs IEC
- HIBA
- Tropolone
- Crown ethers
- pH
- Temperature
- Conclusion

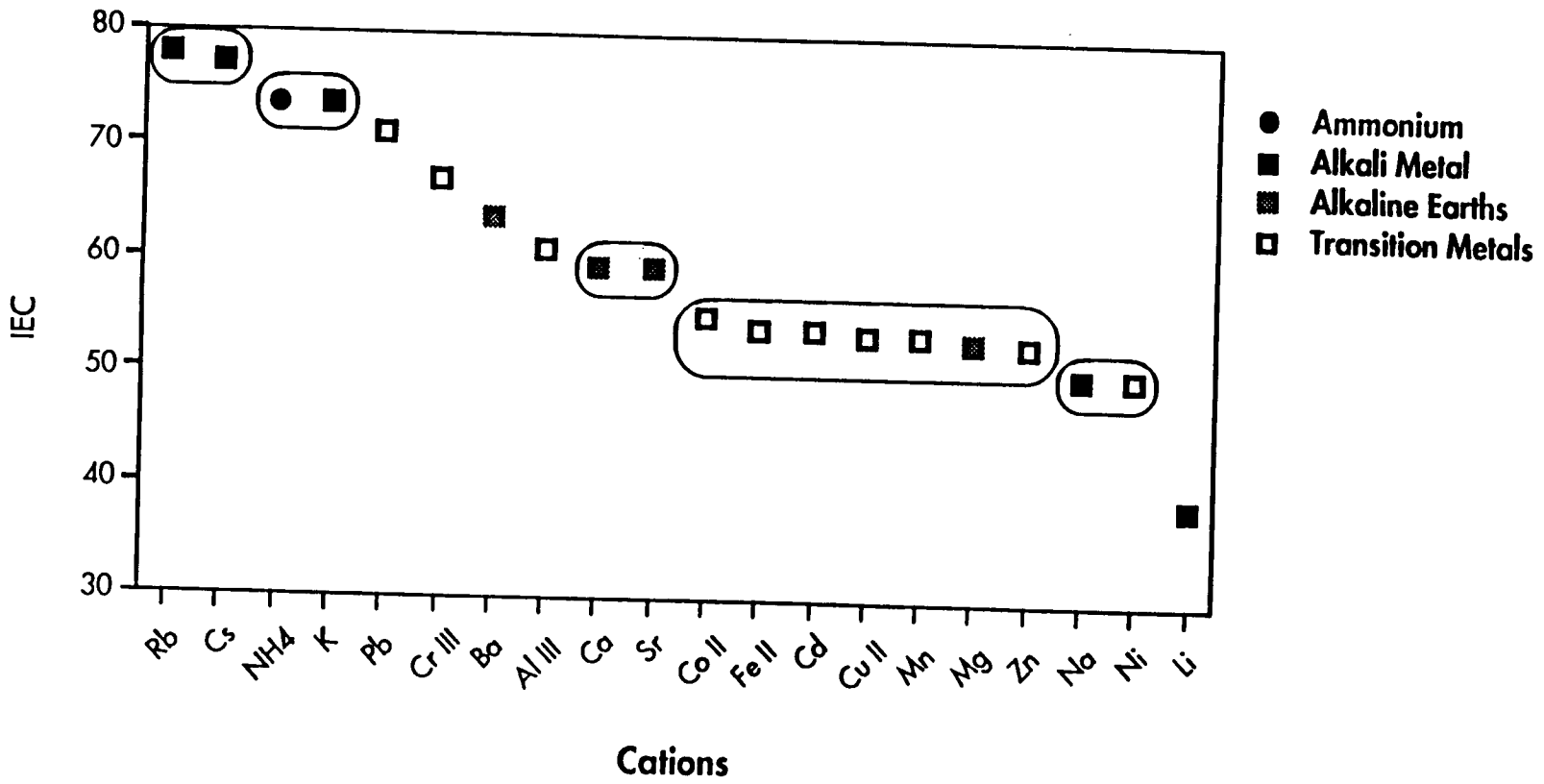
Inorganic Cations vs Ionic Equivalent Conductance

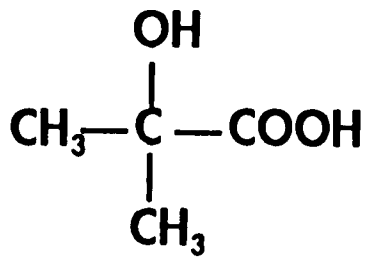
Inclusion of Lanthanides



Inorganic Cations vs Ionic Equivalent Conductance

Cations Placed in Decending Order





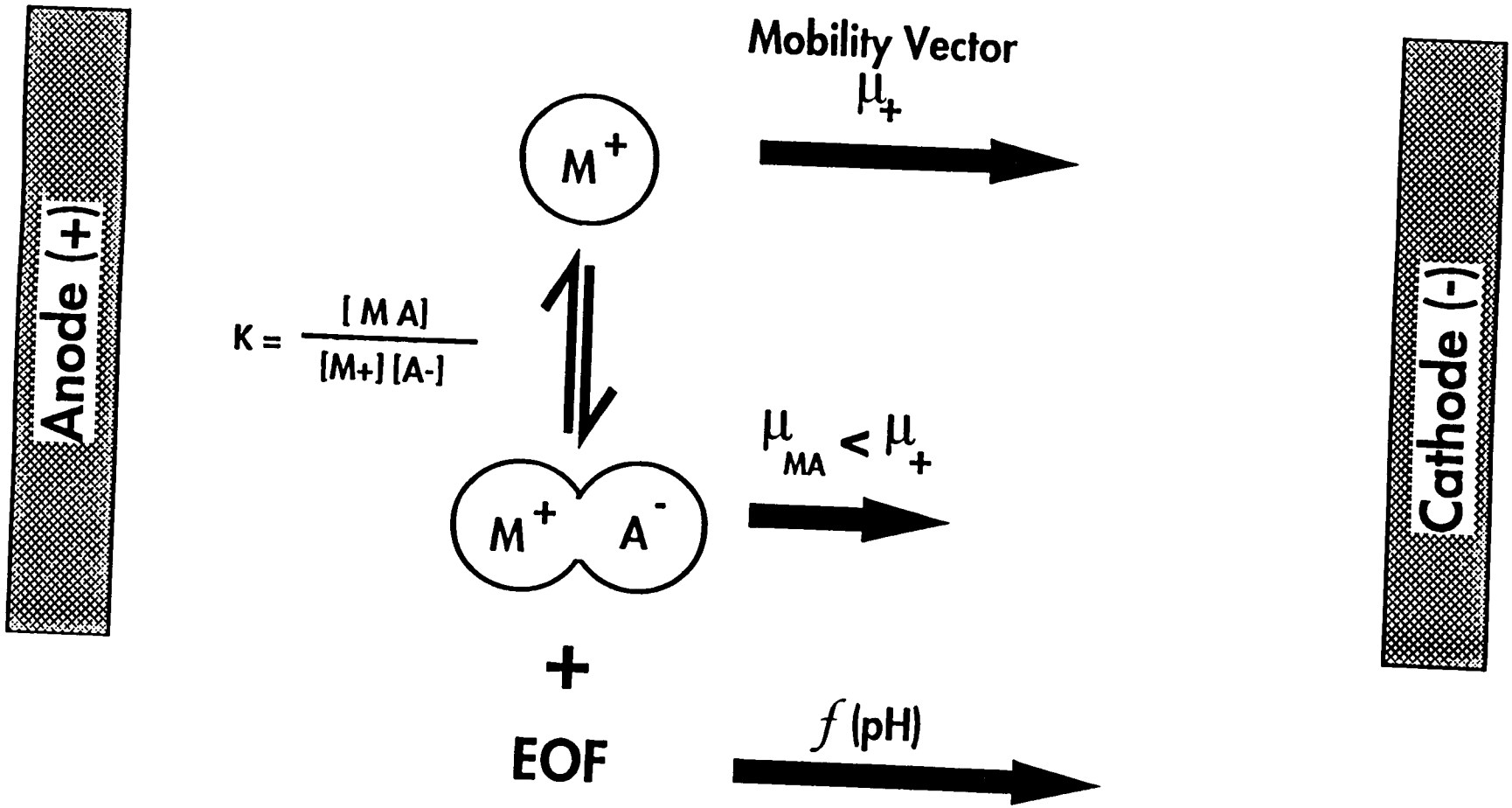
HIBA

α-hydroxyisobutyrate

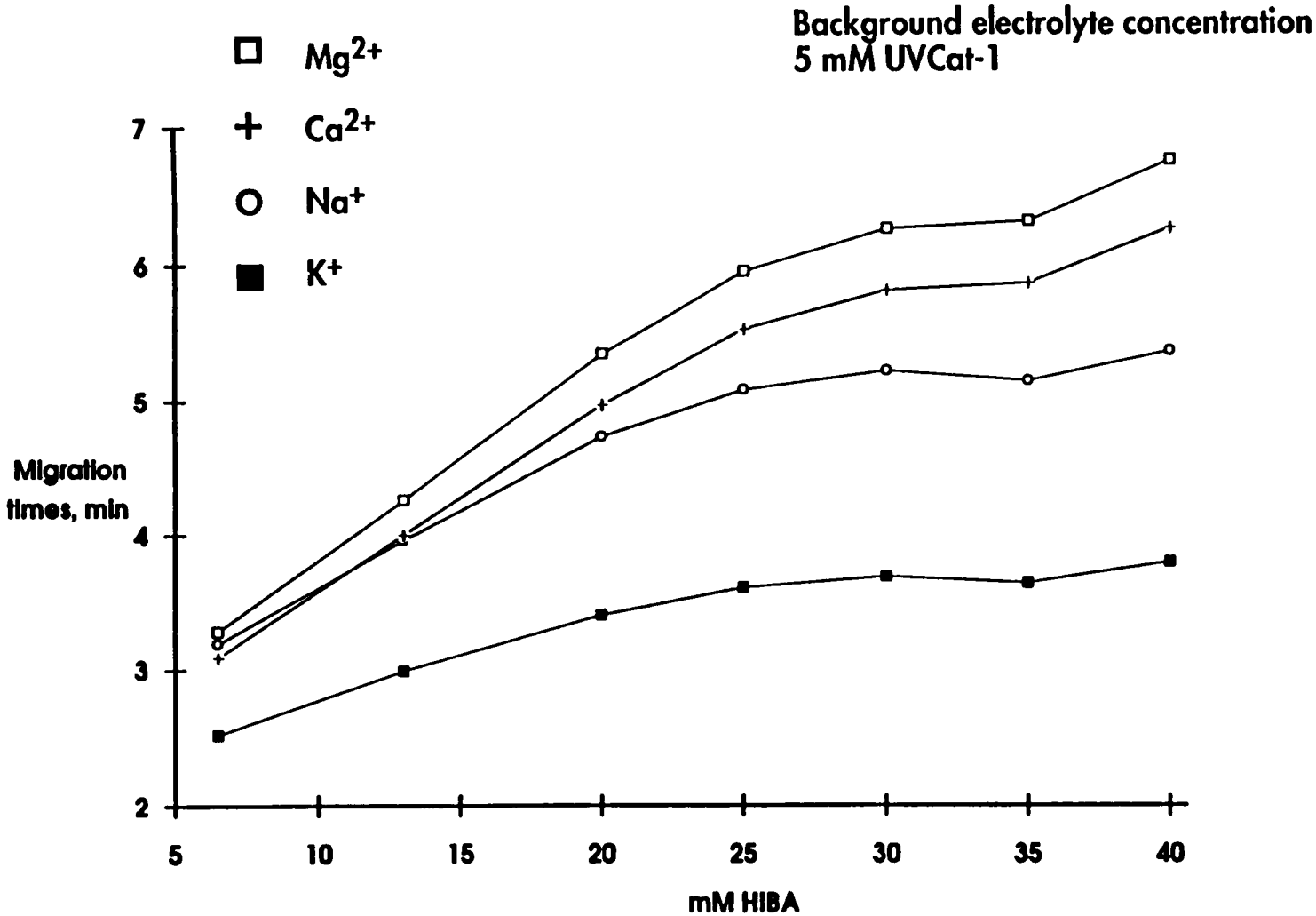
(2-methyllactate)

	Log K
Ba	0.36
Mg	0.81
Ca	0.92
Mn	0.96
Zn	1.71
Cu	2.74

Mobility of Cations in the Capillary



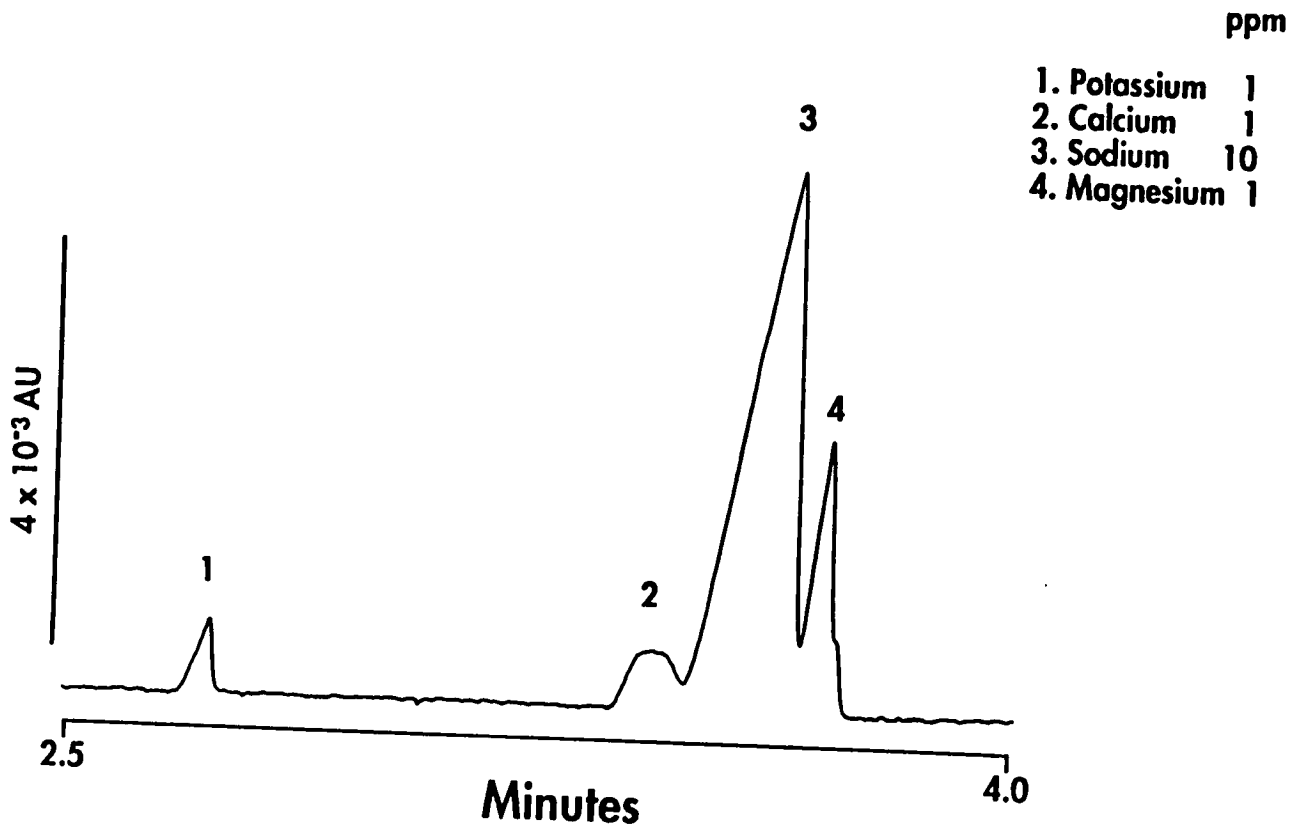
Effect of HIBA Concentration on Selectivity of Calcium



M. Koberda, M. Konkowski, P. Youngberg, W. R. Jones, A. Weston, *J. Chromatogr.*, 602 (1992) 235.

Sodium Interference with Calcium Determination

Electrolyte: 5 mM UVCat-1, 6.5 mM HIBA, pH 4.4



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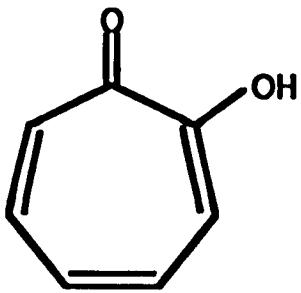


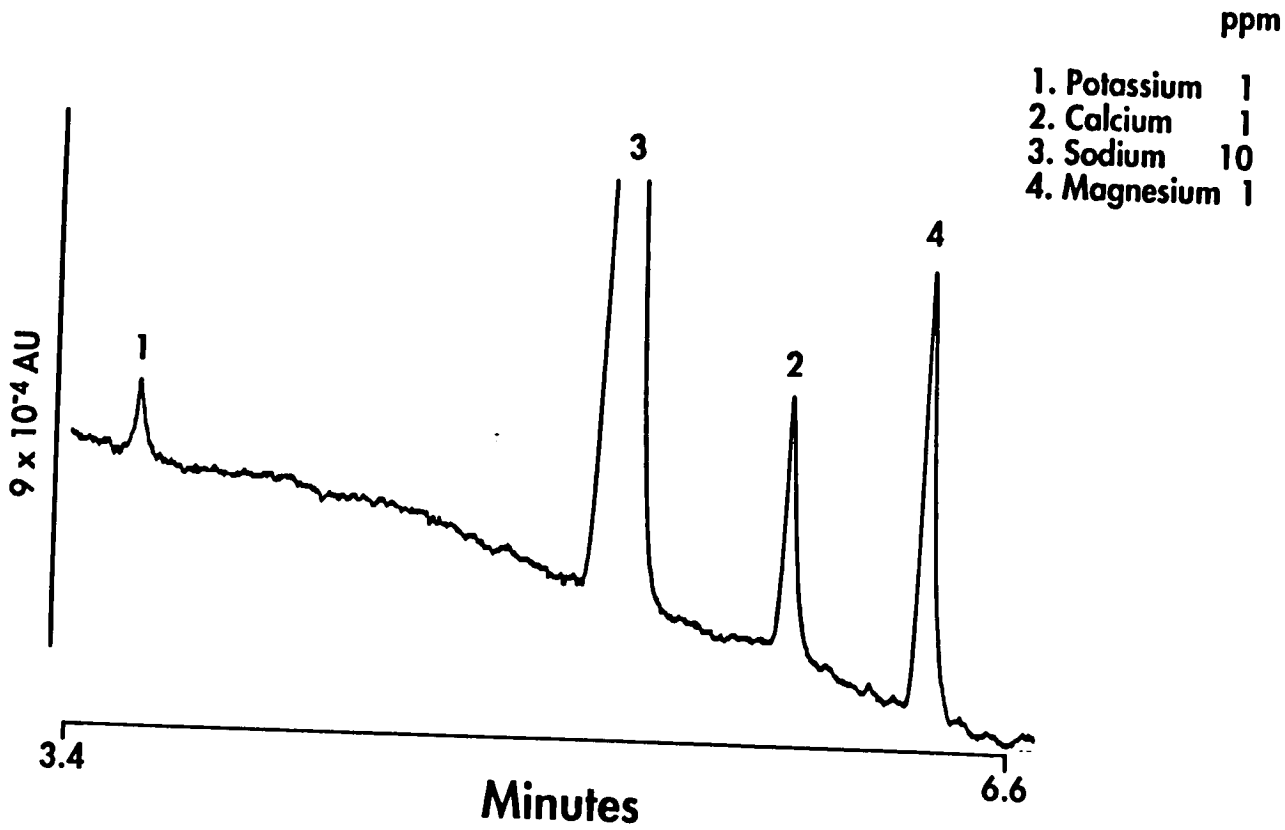
Tropolone

	ionic radius (Å)	log K_1
Be (II)	0.27	7.40
Cu (II)	0.57	9.23
Pb (II)	1.18	7.54

* Personal communications from
A. E. Martell, Texas A&M University

Sodium Interference with Calcium Eliminated

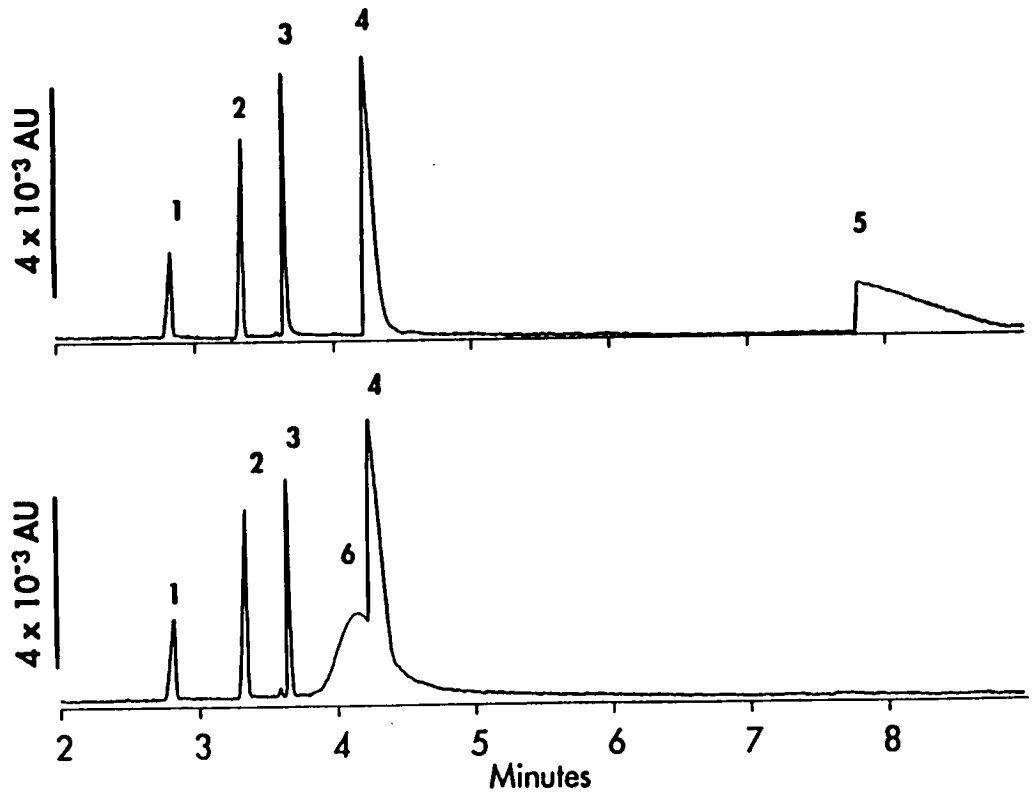
Electrolyte: 5 mM UVCat-1, 30 mM HIBA, pH 4.4



M. Koberda, M. Konkowski, P. Youngberg, W. R. Jones, A. Weston, *J. Chromatogr.*, 602 (1992) 235.

Effect of Low Concentration of Tropolone on Transition Metal Selectivity

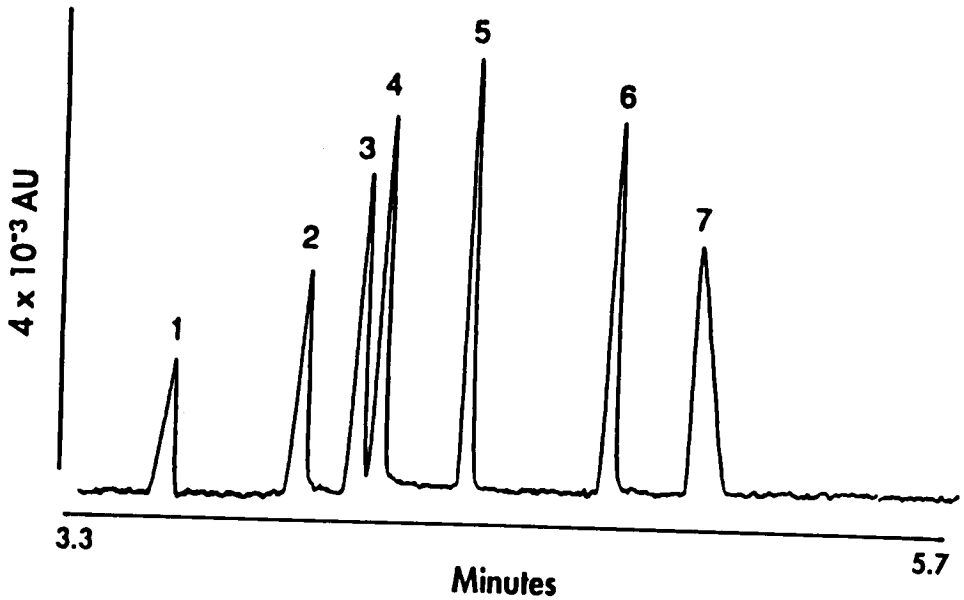
Electrolyte: 1.2 mM UVCat-2, 0.05 mM Tropolone
Capillary: 75 µm x 60 cm fused silica
Detection: 185 nm indirect UV
Injection: 30 s hydrostatic



	ppm
1. Potassium	0.8
2. Calcium	0.7
3. Sodium	0.6
4. Lithium	0.2
5. Copper	5.0
6. Nickel	5.0

Alkali and Alkaline Earth Separation Using Tropolone as a Selectivity Modifier

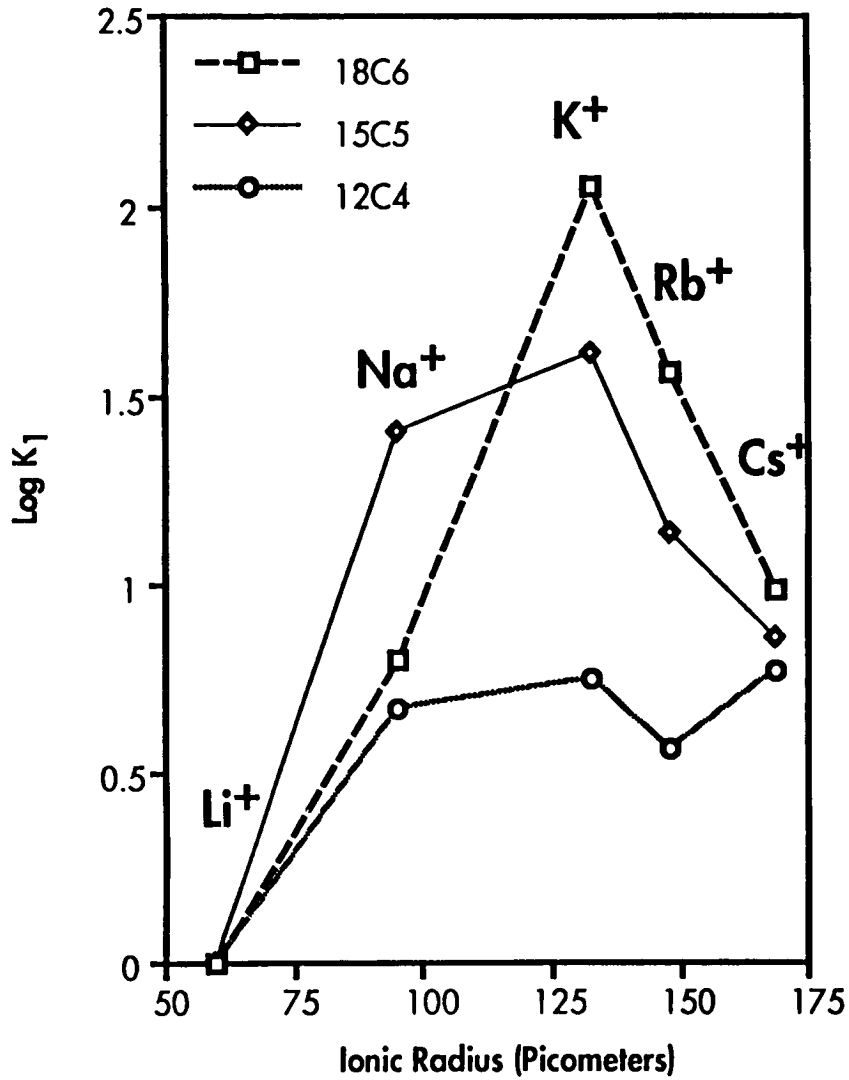
Electrolyte: 1.2 mM UVCat-2, 3 mM Tropolone
Capillary: 75 µm x 60 cm fused silica
Detection: 185 nm indirect UV
Injection: 30 s hydrostatic

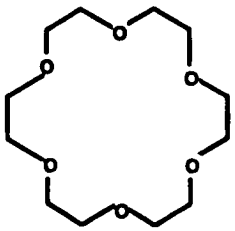


	ppm
1. Potassium	1.0
2. Barium	2.0
3. Strontium	1.5
4. Calcium	0.7
5. Sodium	0.6
6. Magnesium	0.4
7. Lithium	0.2

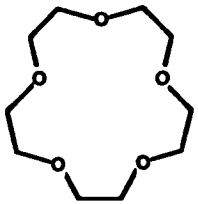
A. Weston, P.R. Brown, P. Jandik, A.L. Heckenberg and W.R. Jones, *J. Chromatogr.*, 608 (1992) 395.

Formation Constants for Alkali Metal with Various Crown Ethers

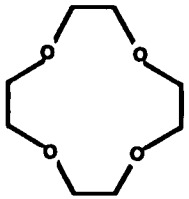




18-Crown-6



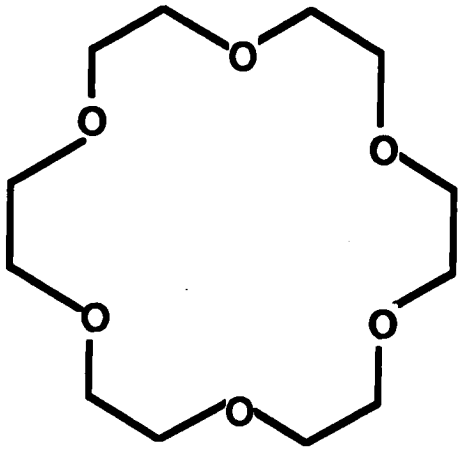
15-Crown-5



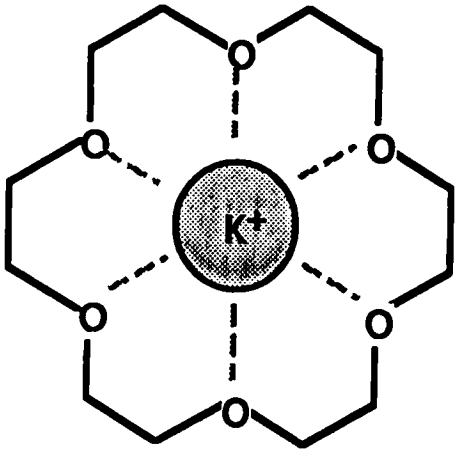
12-Crown-4

Adopted from Personal Communication ,
A.E. Martel, Texas A&M University

Interaction of Potassium with 18-Crown-6

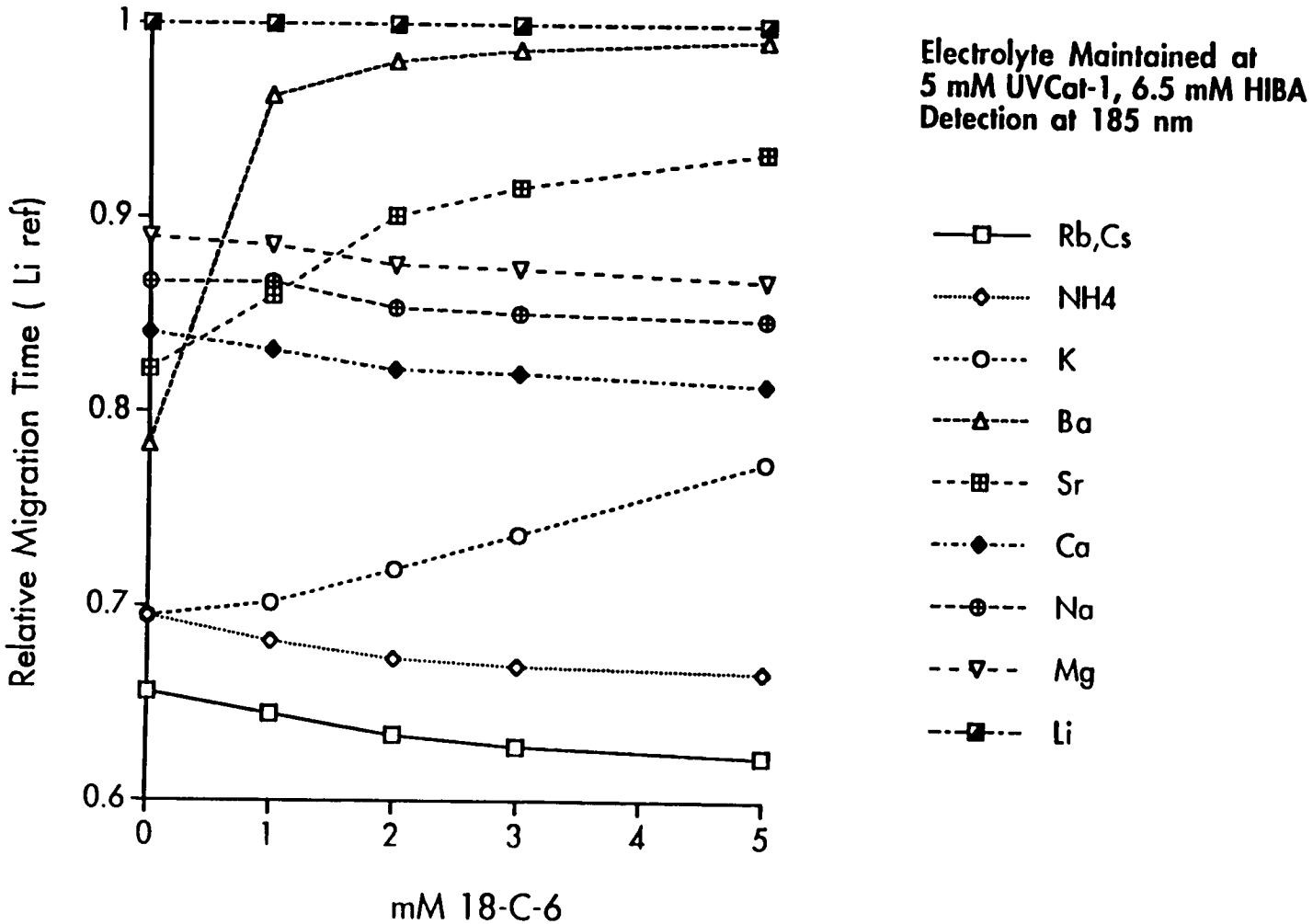


18-Crown-6

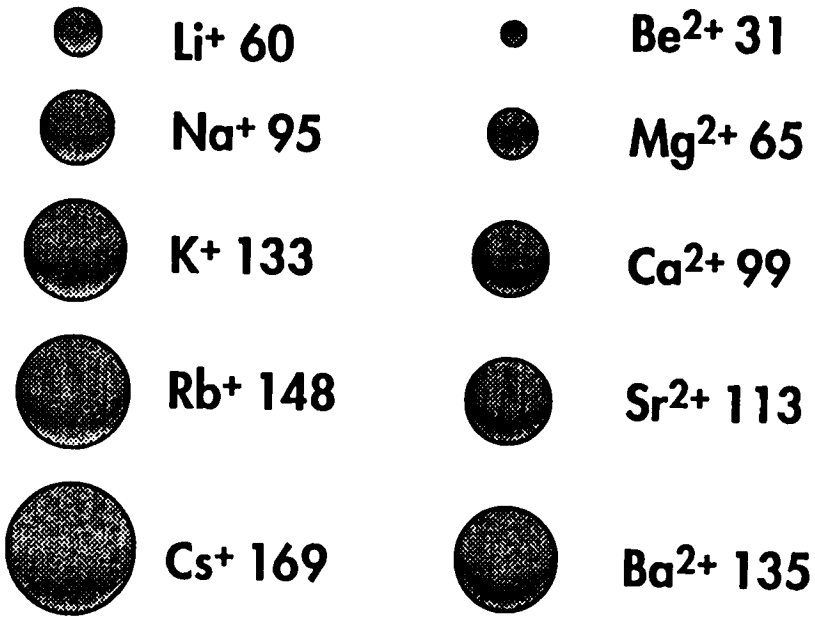


18-Crown-6
with Potassium

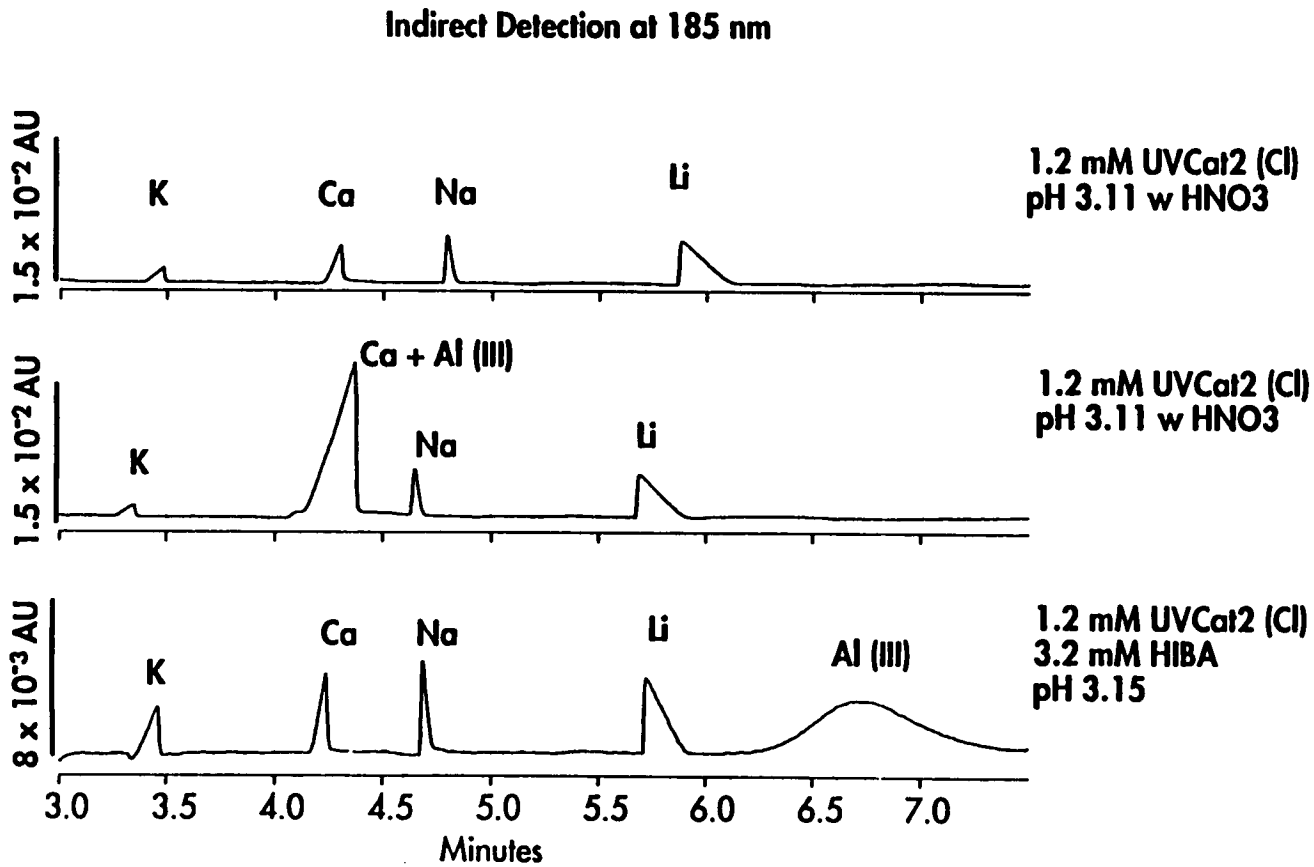
Selectivity Changes Through Addition of 18-Crown-6 to Electrolyte



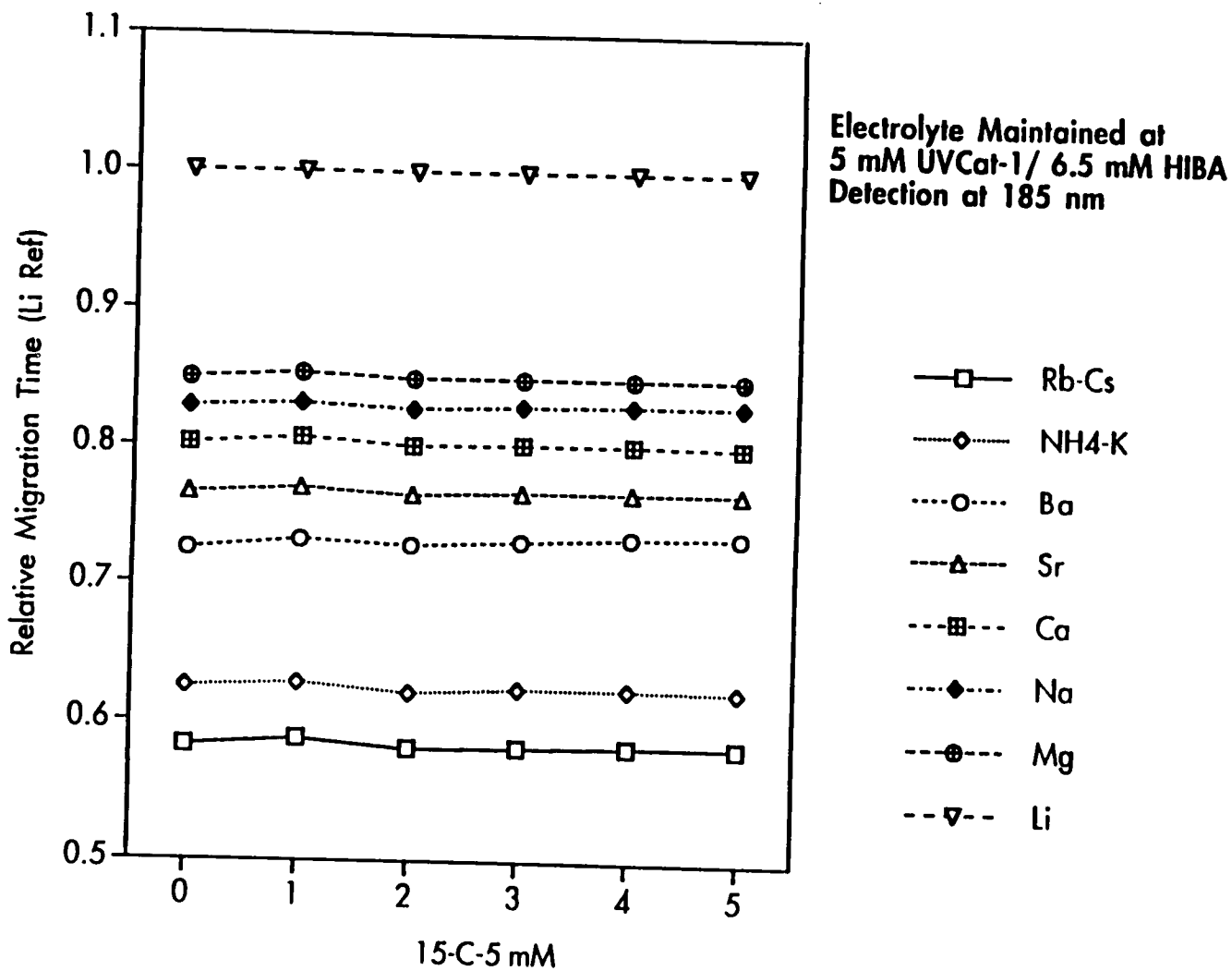
Ionic Radii of Alkali and Alkaline Earths
(in picometers)



Preliminary Work: Free Aluminum Determination



Effect of 15-Crown-5 on Selectivity



Conclusion

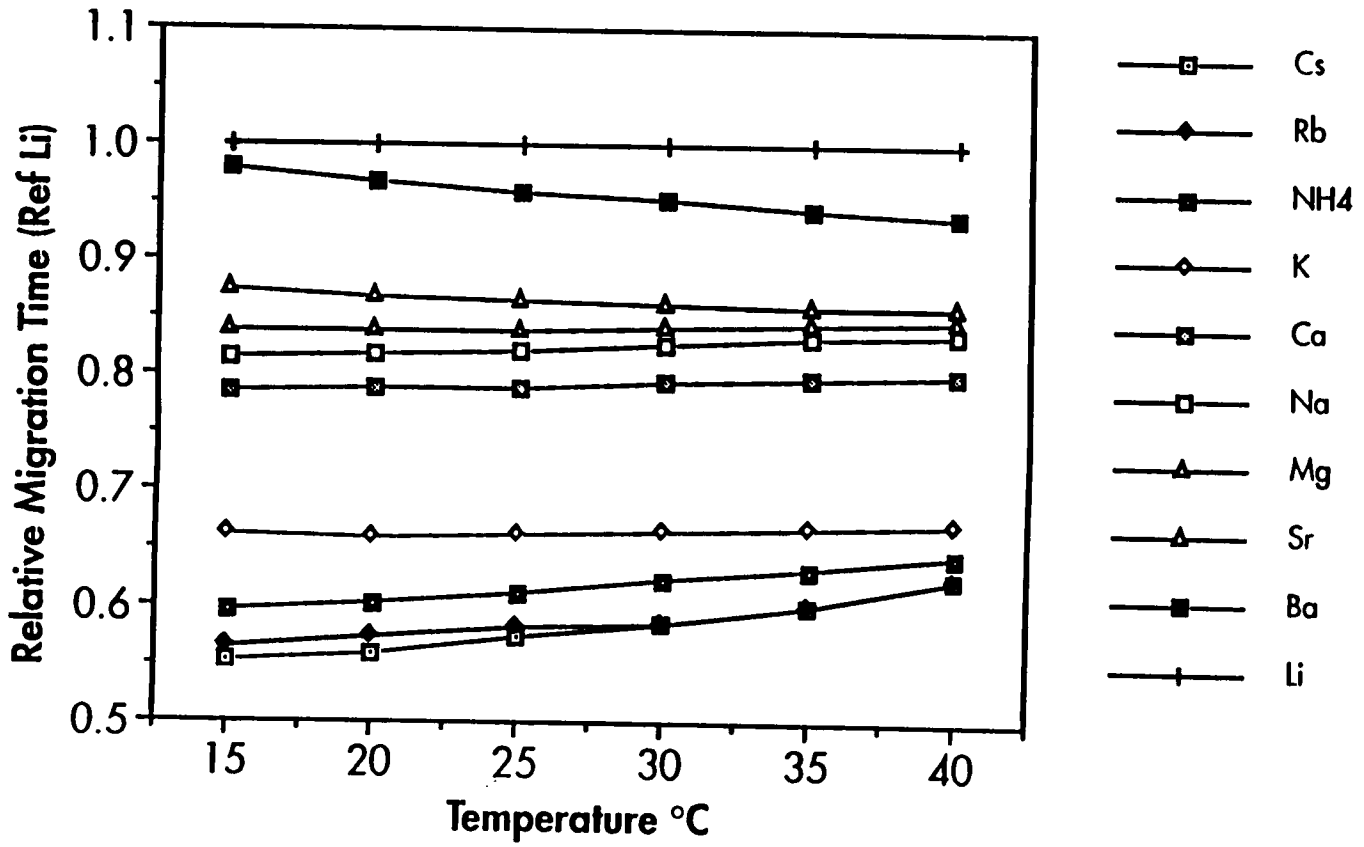
1. Comigration of many cations occurs in CE due to similar mobilities as illustrated with IEC values

2. To achieve multiple cation separations weakly complexing additives are required in the electrolyte

3. Selective use of strongly complexing agents can be utilized as a form of eliminating certain matrix interferences (i.e Tropolone for transition metals)

4. Cations with high degrees of hydration require lower pH electrolytes to fully ionize the species

5. Temperature control offers modest effect on selectivity (Keeping temperature constant is most important for maintaining stable migration times)

Relative Migration as a function of Temperature for Alkali and Alkaline Earths

Electrolyte: 5 mM UVCat-1, 6.5 mM HIBA, 2 mM 18-C-6