HPLC '95

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Ion Determination Using CIA(Capillary Ion Analysis) Application to difficult samples

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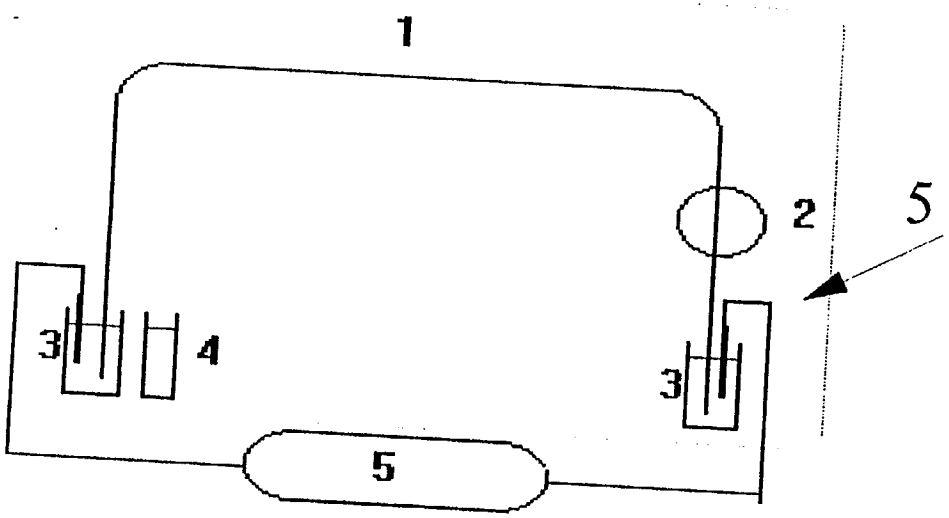
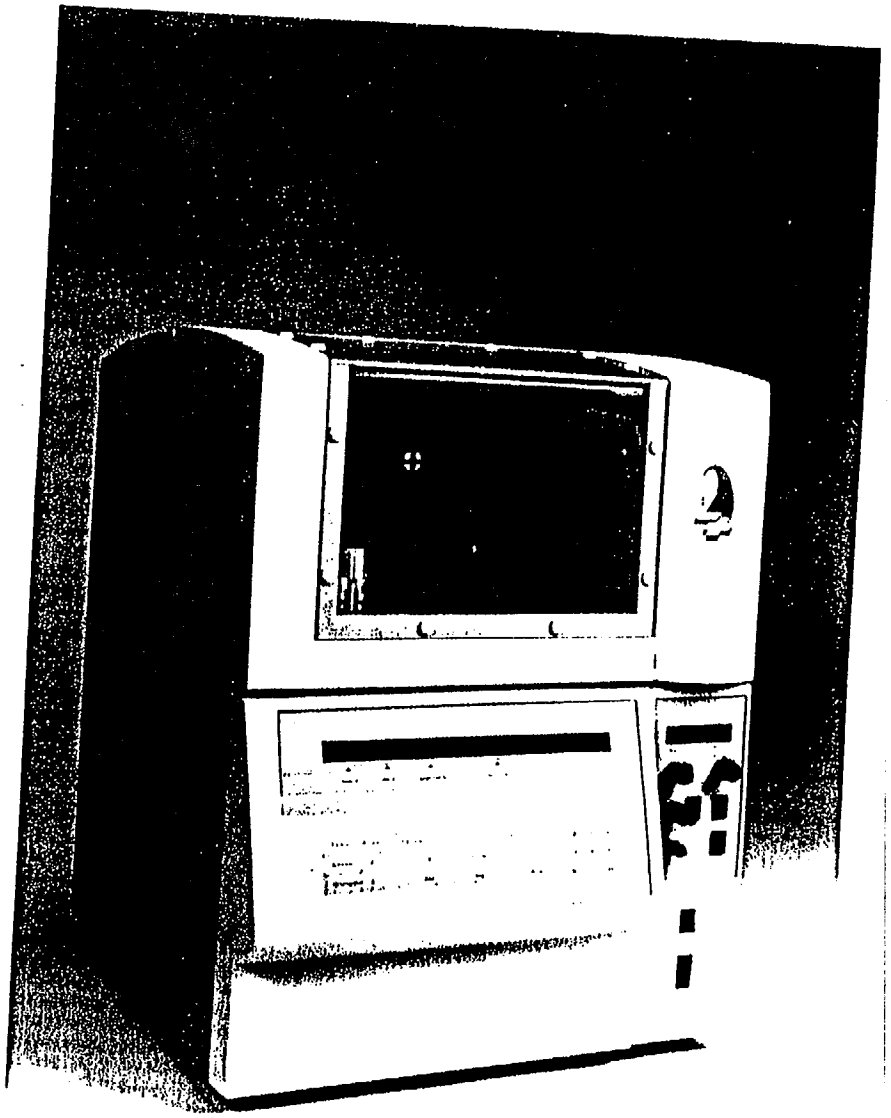
CIA Equipment





1) Bare silica capillary, 50 to 100 µm i.d.
2) UV detector:for simplicity and low cost of use, the detection cell is simply created by removing the protective polymeric coating. High energy lamps for sensitive indirect or direct UV detection. Wavelengths from 185 nm.
3) Large electrolyte vials, for migration time stability
4) Sample vials, 500 µl capacity for ppm analysis or 4 ml capacity for ion determination at trace level
5) Complete temperature control for migration times stability

Conditions for obtaining reproducible migration times and correct determinations

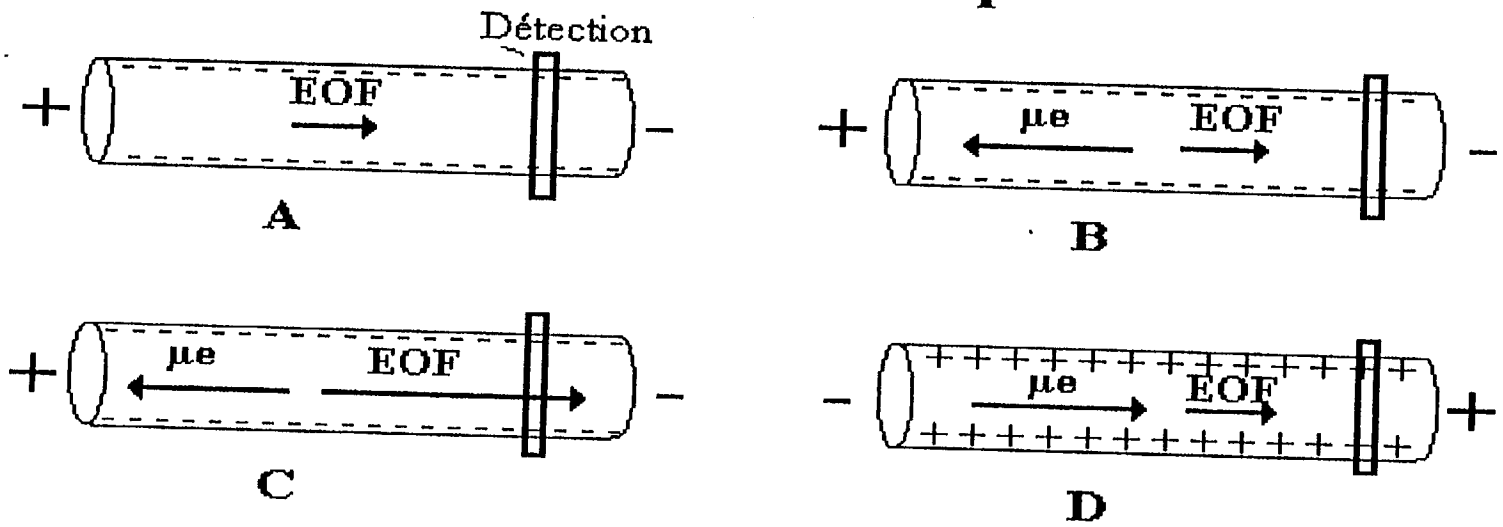
Constant osmotic flow, obtained by

- wall interactions control
  - electrolyte composition
  - rinse routine for difficult samples
- stable pH of the electrolyte
  - composition, buffering capacity
  - large electrolyte vials
  - purge effluents going to a separate vial
- control of the temperature of both electrolyte and capillary

" High capacity" electrolyte, allowing large differences of concentation without loosing the resolution.

Large linear range, related to electrolyte composition, and detector design

Electroosmotic flow (EOF) control for anion separation



For most of the applications, it is suitable to get the fast inorganic species (i.e. Chloride) migrating first, followed by the organic anions.

This is achieved by detecting the anions at the anode and by reversing the osmotic flow by addition of a cationic surfactant in the electrolyte

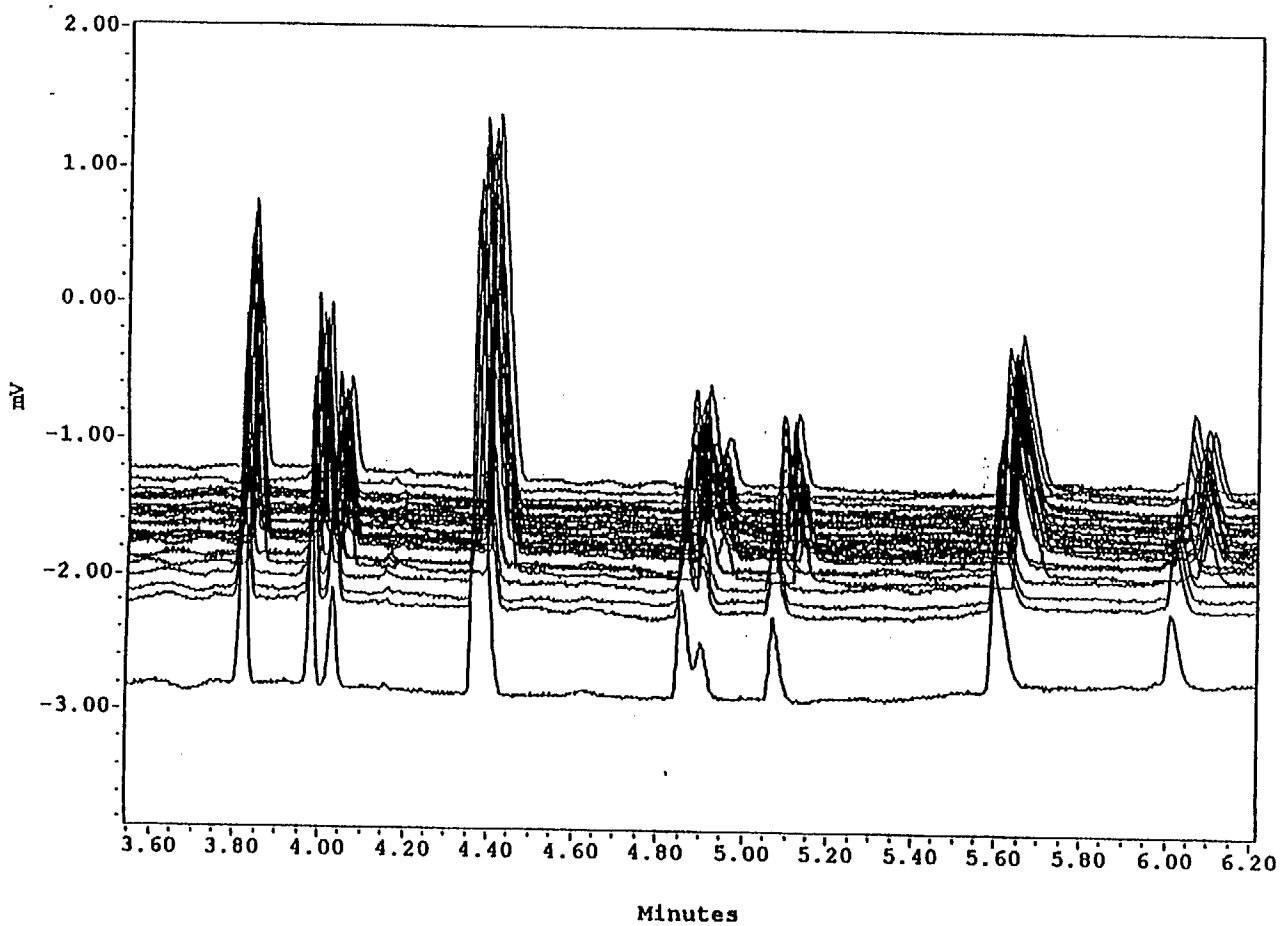
A: EOF in its normal direction.

B: Anions displacement

C: accelerated EOF. The anions can be detected at the cathode, but low mobility species are coming first. This configuration is sometimes difficult to maintain when dealing with real samples.

D: reversed EOF, by addition of a cationic surfactant. Stable situation.

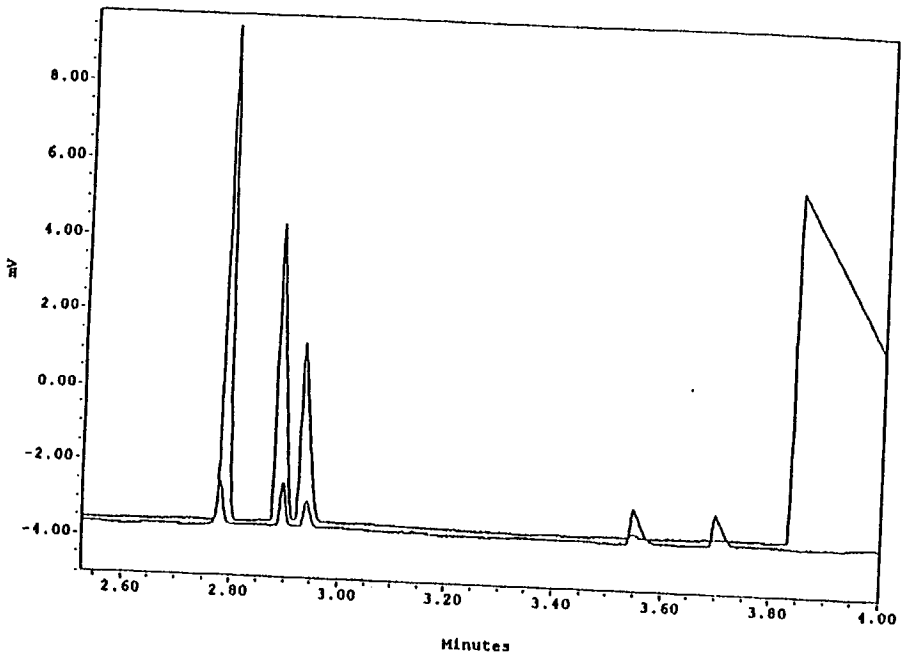
Migration times reproducibility



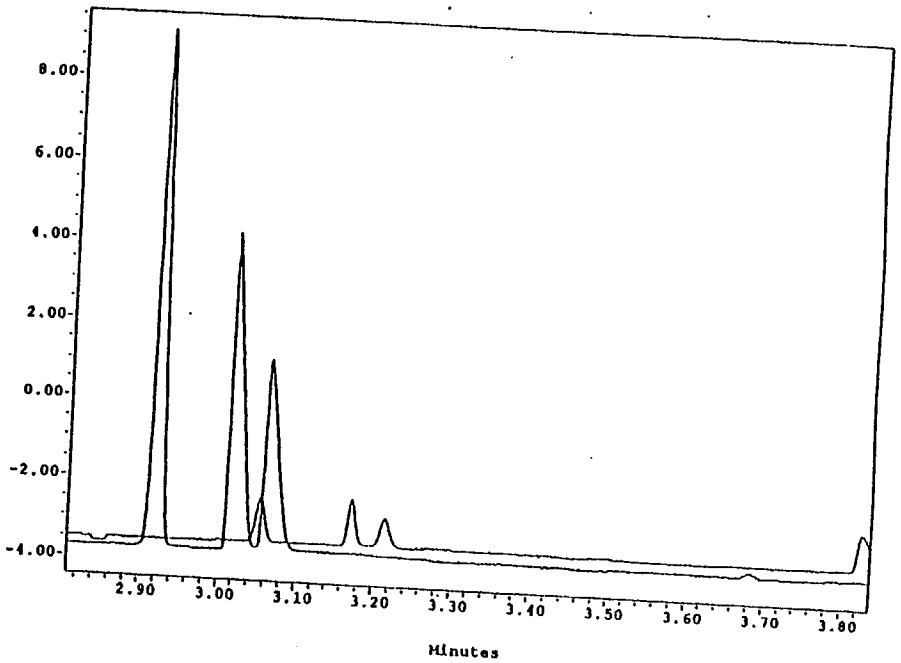
	% rsd
Chloride:	0.34
Sulfate:	0.36
Nitrate:	0.36
Chlorate:	0.39
Fluoride:	0.41
Formate:	0.40
Phosphate:	0.45
Carbonate:	0.34

Trace (5 ppb) anions in dionised water

Isomigration technique for compensating conductivity differences



With isomigration



Without isomigration

Overlay of a 1 ppm standard solution and a drinking water sample

Detection

Sensitive detection is achieved using UV detection, most of the time in the indirect mode.

The detection cell is created directly on the capillary by removing the polyimide protective coating

UV detection is compatible with osmotic flow modifiers and can be used for both anions and cations determination.

Non UV absorbing compounds are detected in the indirect mode.

Adequate detector design allows detection at very low wavelength(185 nm), providing a very sensitive detection of cations and organic acid.

Selectivity

The migration order depends on the mobility of the analyte into the electrolyte.

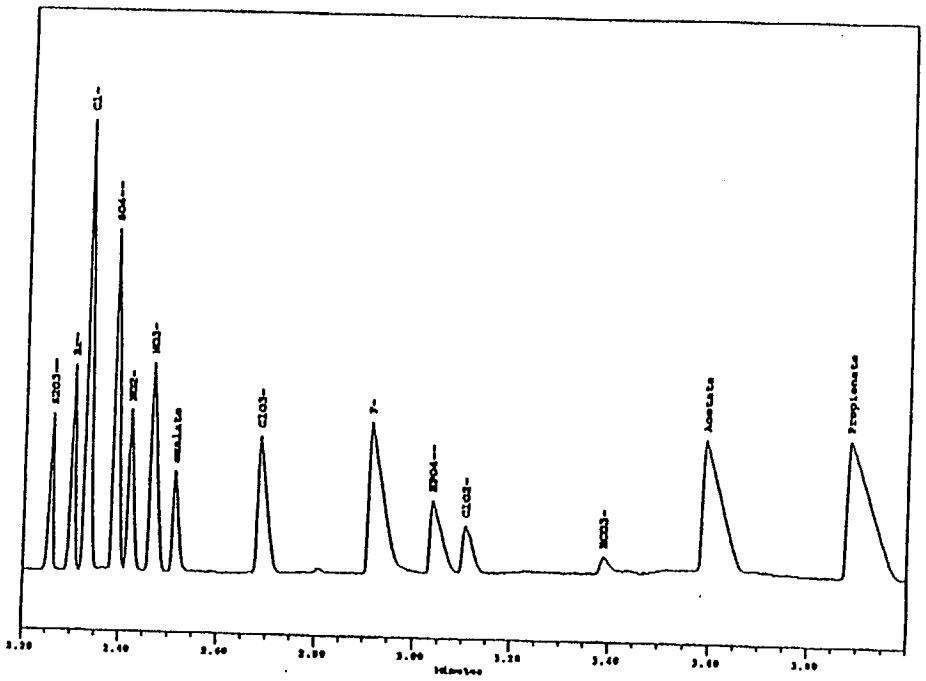
The mobility is affected by:

- the presence, nature and concentration of an osmotic flow modifier
- induced complexation or precipitation reactions
- the pH of the electrolyte (weak acids separation)

The peak shape depends on the ratio electrolyte mobility / analyte mobility

Consequently, it is possible to adapt the composition of the electrolyte for specific needs

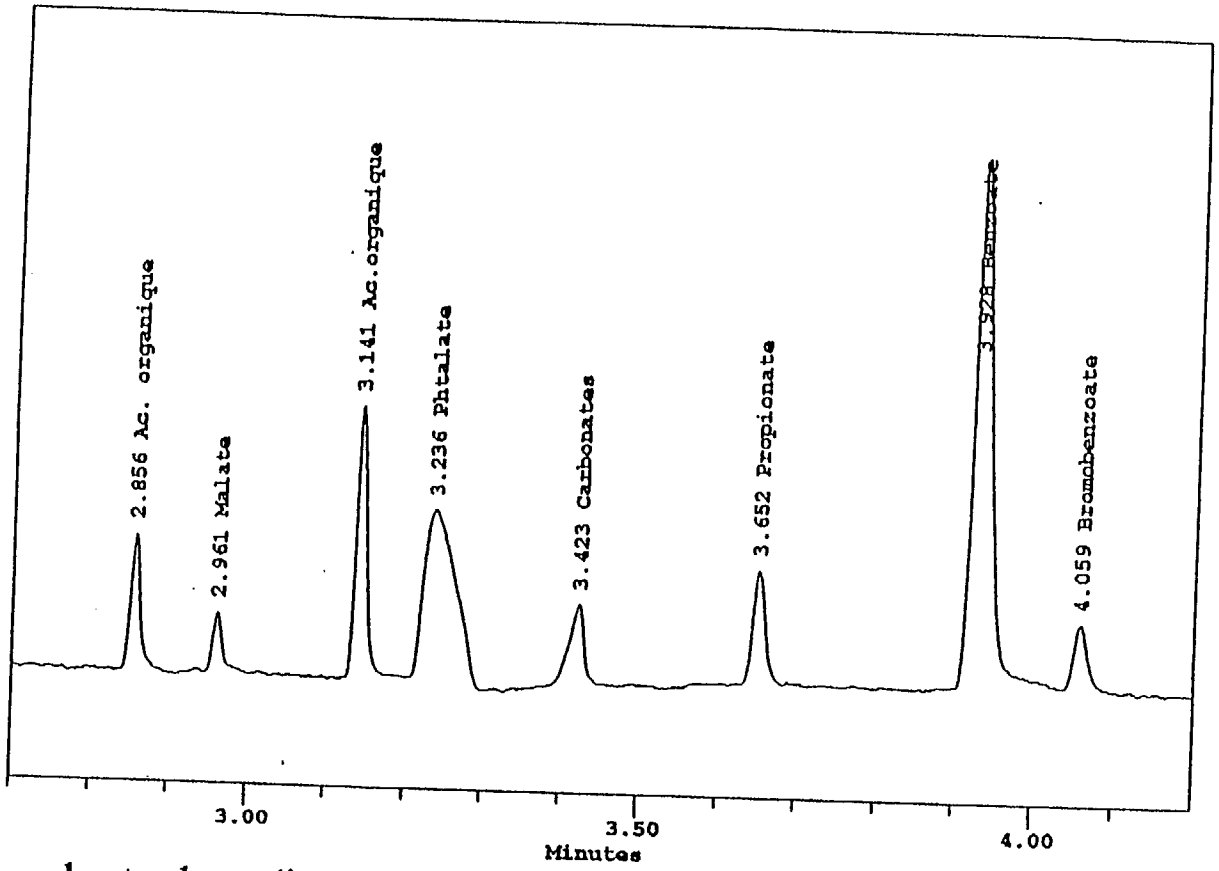
Selectivity for anions separation



From this separation, it is possible for instance:

- to displace the oxalate peak by adding calcium to the electrolyte
- to improve the separation Cl-SO4 by increasing the chromate concentration
- to position the sulfate peak after the nitrate by changing the osmotic flow modifier

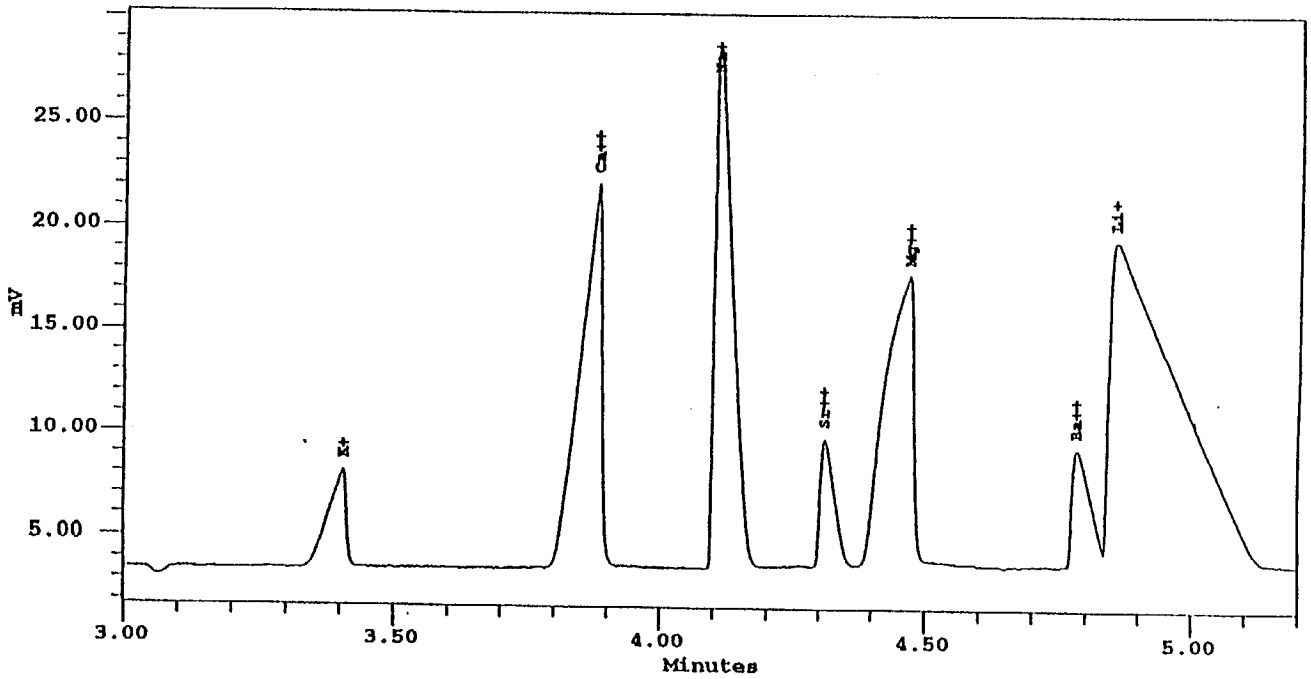
Separation optimized for organic acids



By choosing a slow electrolyte (i.e. phosphate), symmetrical peaks are obtained for organic acids.

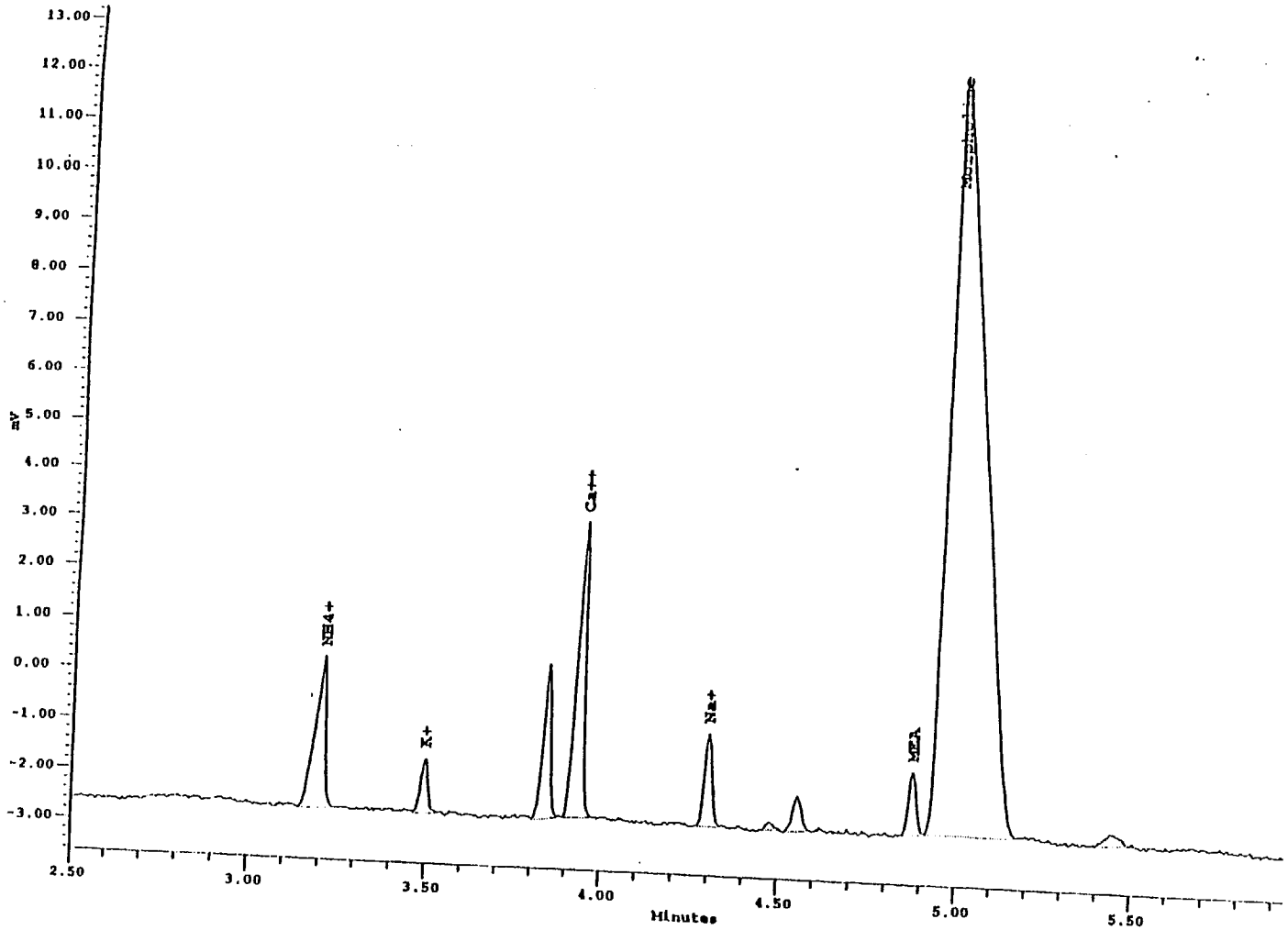
Direct UV detection at 185 nm

Selectivity for cations separation



The tropolone acts as a complexant for changing the apparent mobility of divalent cations.
Separation of alkaline earths is impossible without the addition of a complexant.
The 18-Crown-6 allows the separation NH4/K, which have very close mobilities.
In these conditions, detection must be achieved at 185 nm.

Selectivity for cations separation: amines separation



The separation of both inorganic and organic cations can be achieved in one injection.
Longer chain amines can be analyzed using optimized conditions

Selectivity of the separations

The CIA separations show

- Very high efficiency
- No water peak
- No cation peak when determining anions, and reverse
- Organic species clearly separated from inorganic species
- No interference from organic molecules

Consequence

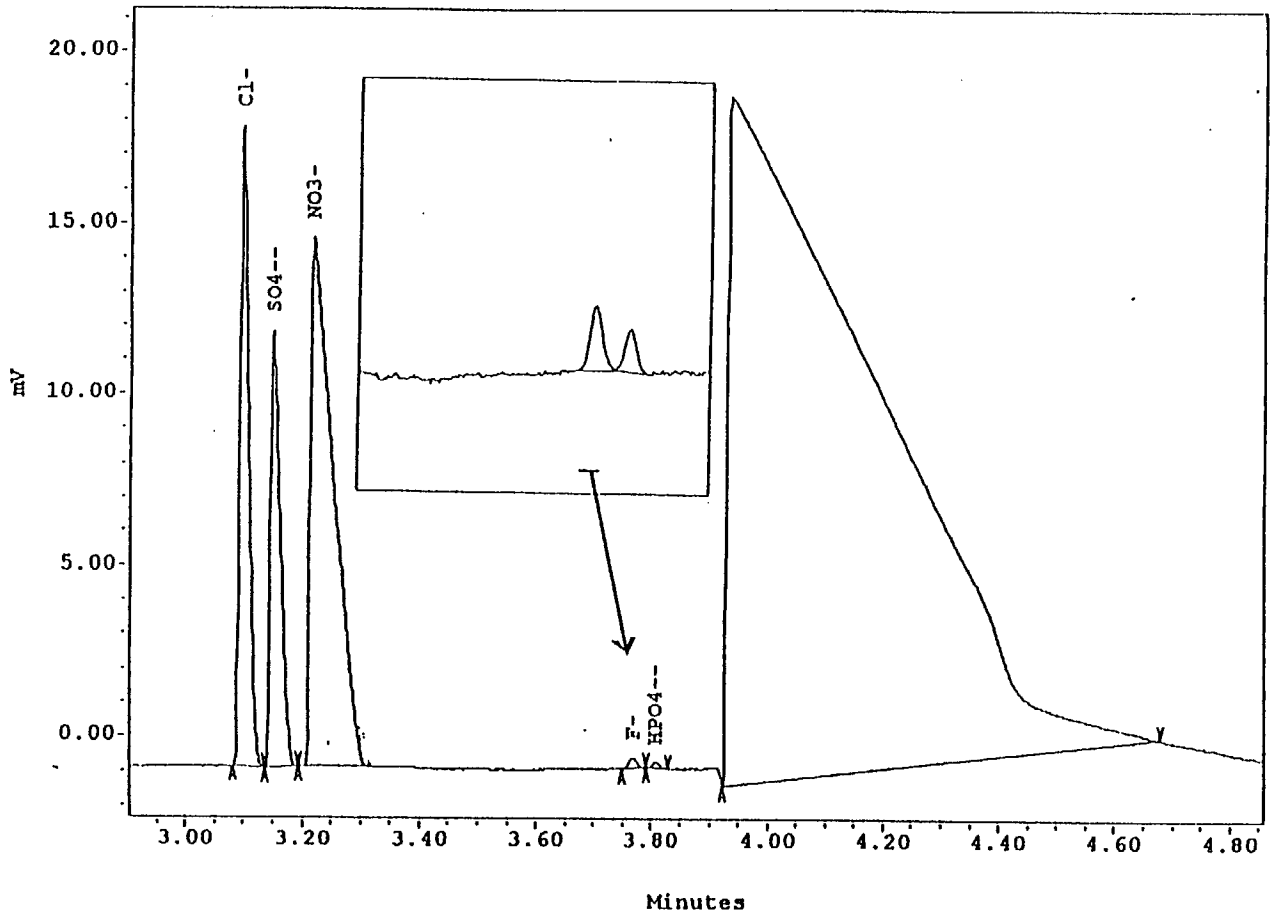
- Simplified sample preparation

Applications

Capillary electrophoresis is routinely used for:

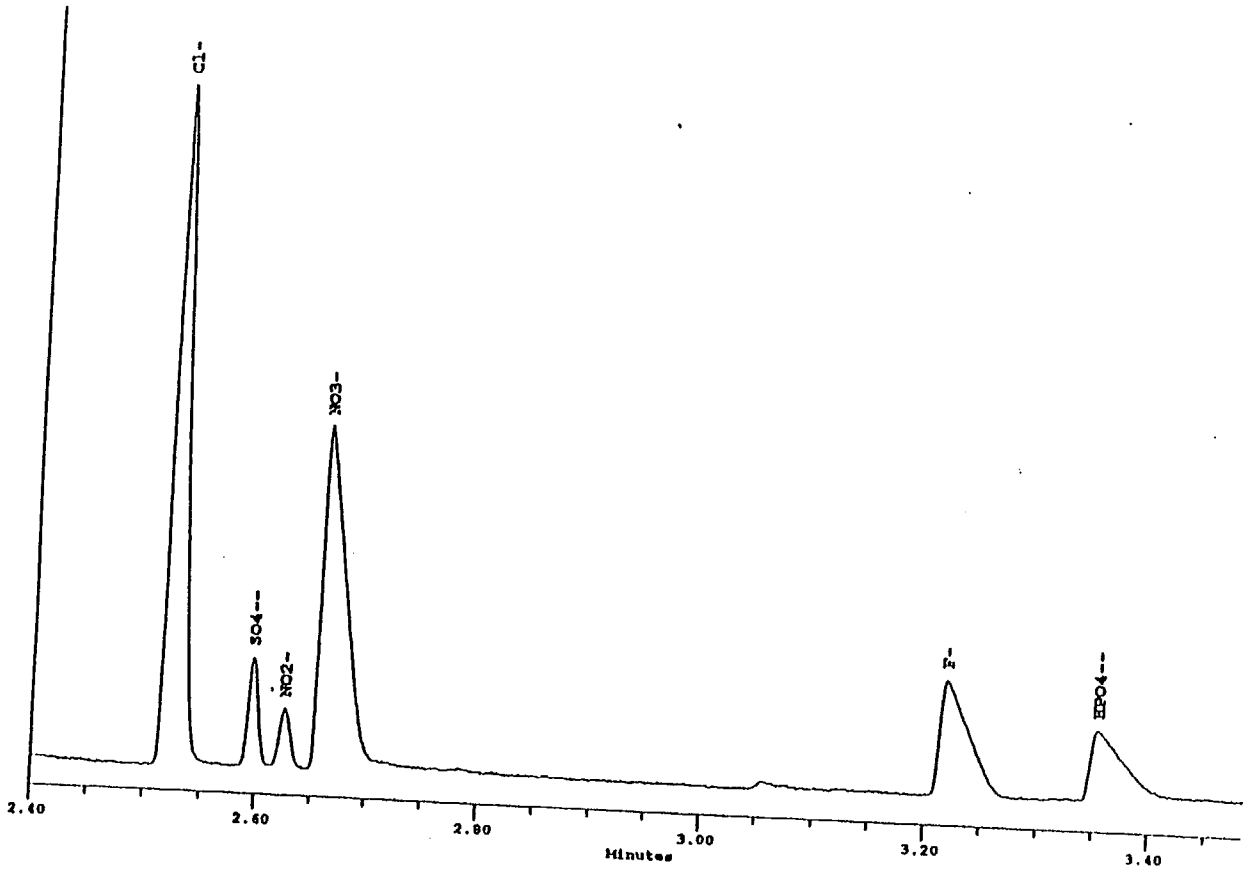
- Environmental control
- Monitoring of industrial processes
- Quality control of industrial products
- Ion determination at trace level for nuclear and fossile fuel power plants
- Ion determination at trace level for electronic industry industry
- anion determination in food or beverage
- research

Applications: water analysis



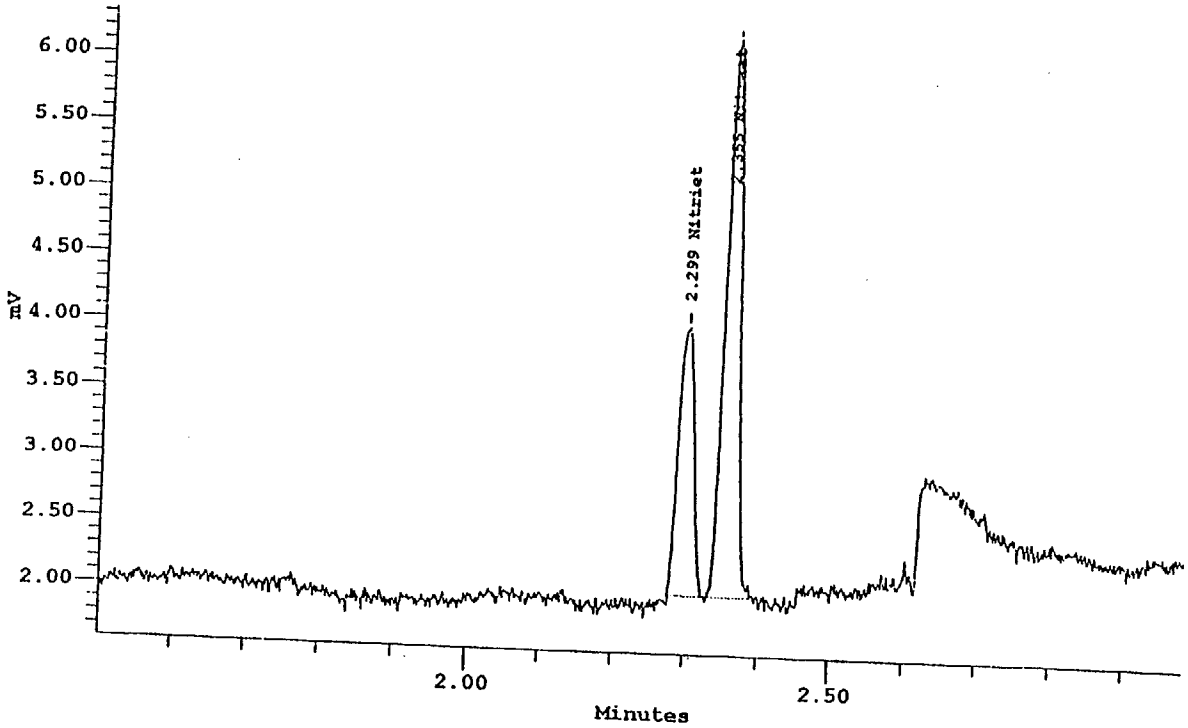
Cl: 7.92 ppm,SO4:16.6 ppm, NO3: 54.8 ppm, F: 0.09ppm, HPO4: 0.15ppm,
HCO3: nq

Applications: waste water analysis



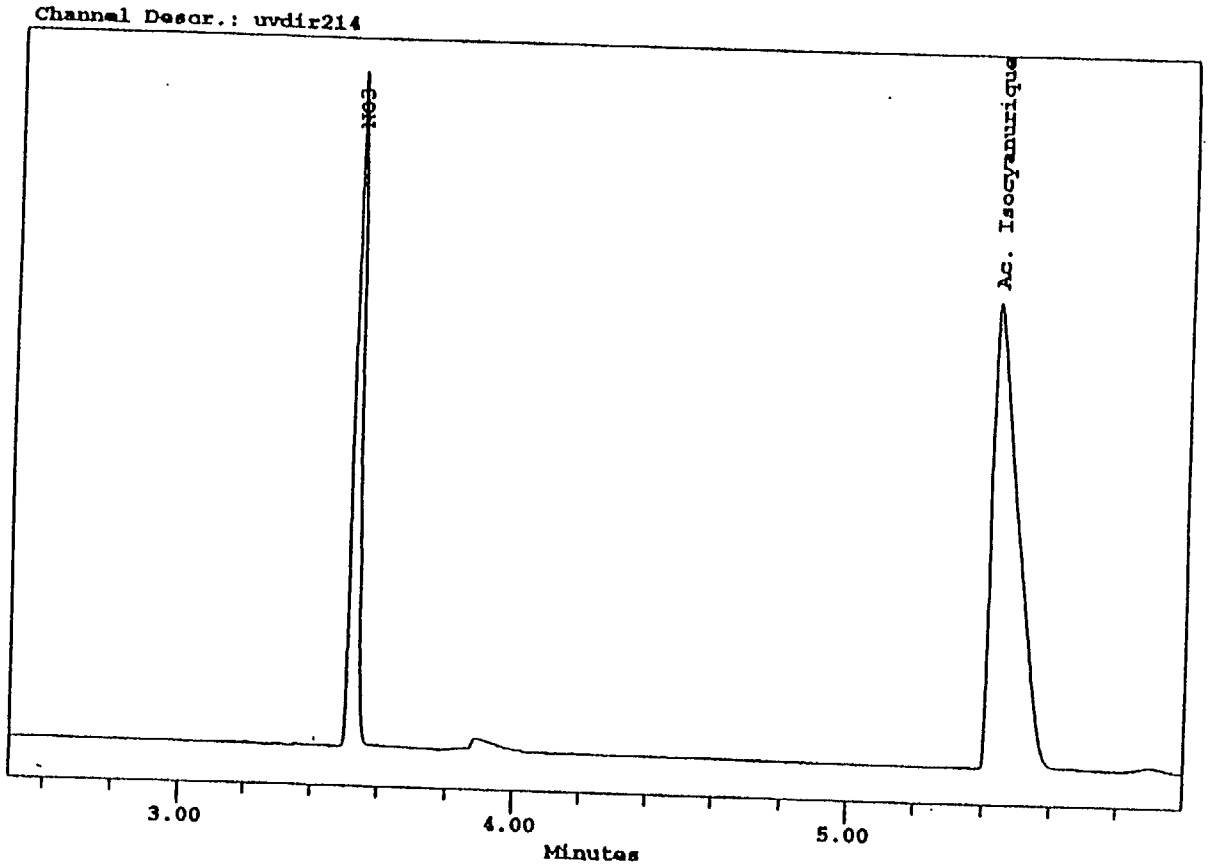
The only sample treatment was a 10 time dilution. No interference of organic compounds.

Determination of nitrite and nitrate in bacon



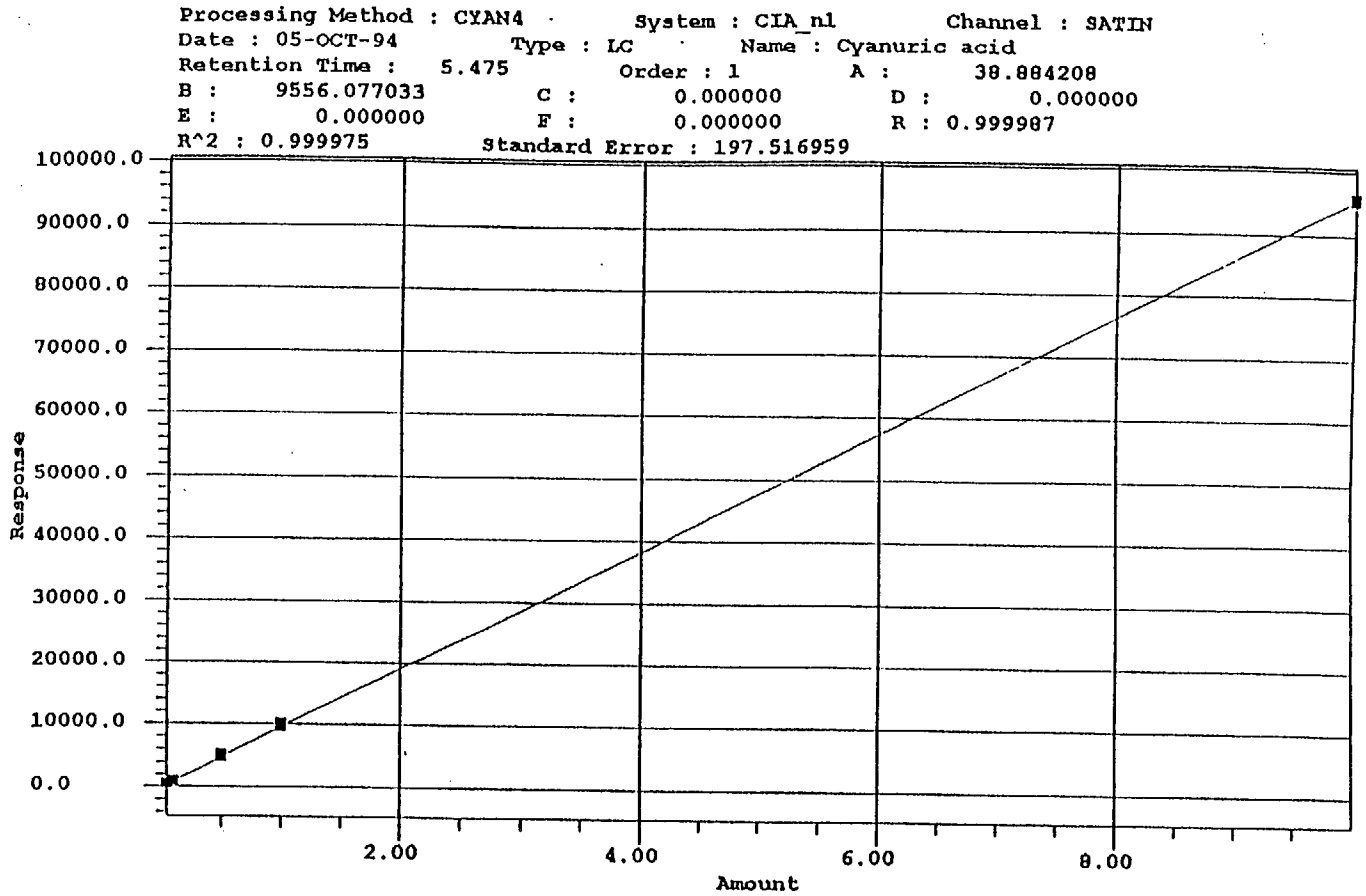
NO2: 6.5 ppm, NO3:12.2 ppm (injected concentrations)
Electrolyte: Sodium chloride + flow modifier
Detection: direct UV, 214 nm
Sample preparation: proteins removal with Carrez 1+2
Courtesy of Waters Holland

Determination of cyanuric acid in swimming pool water



Electrolyte: Sodium sulfate + flow modifier:
Detection: direct UV, 214 nm

Calibration curve for cyanuric acid

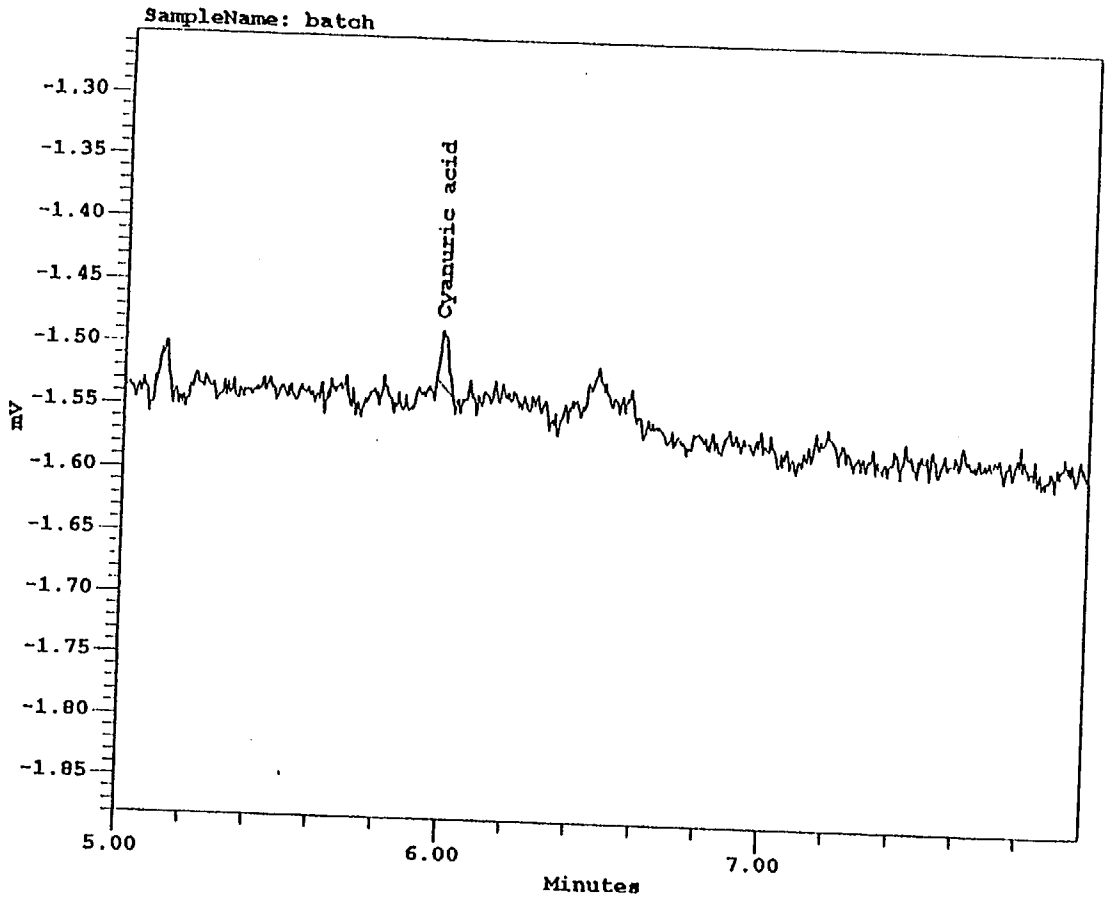


Electrolyte: Sodium sulfate + flow modifier:

Detection: direct UV, 214 nm

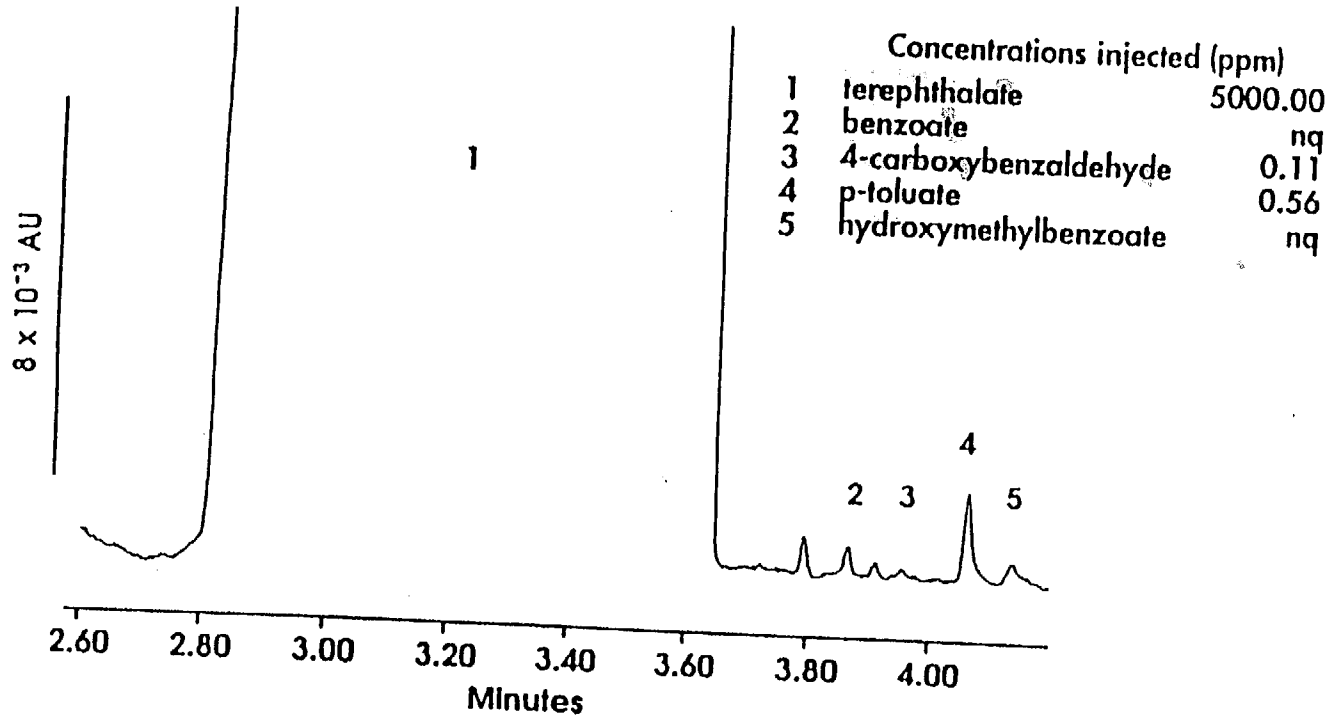
Calibration from 0.05 ppm to 10 ppm

Cyanuric acid detection limit: 5 ppb hydrostatic injection



Electrolyte: Sodium sulfate + flow modifier:
Detection: direct UV, 214 nm

Impurities in terephthalic acid

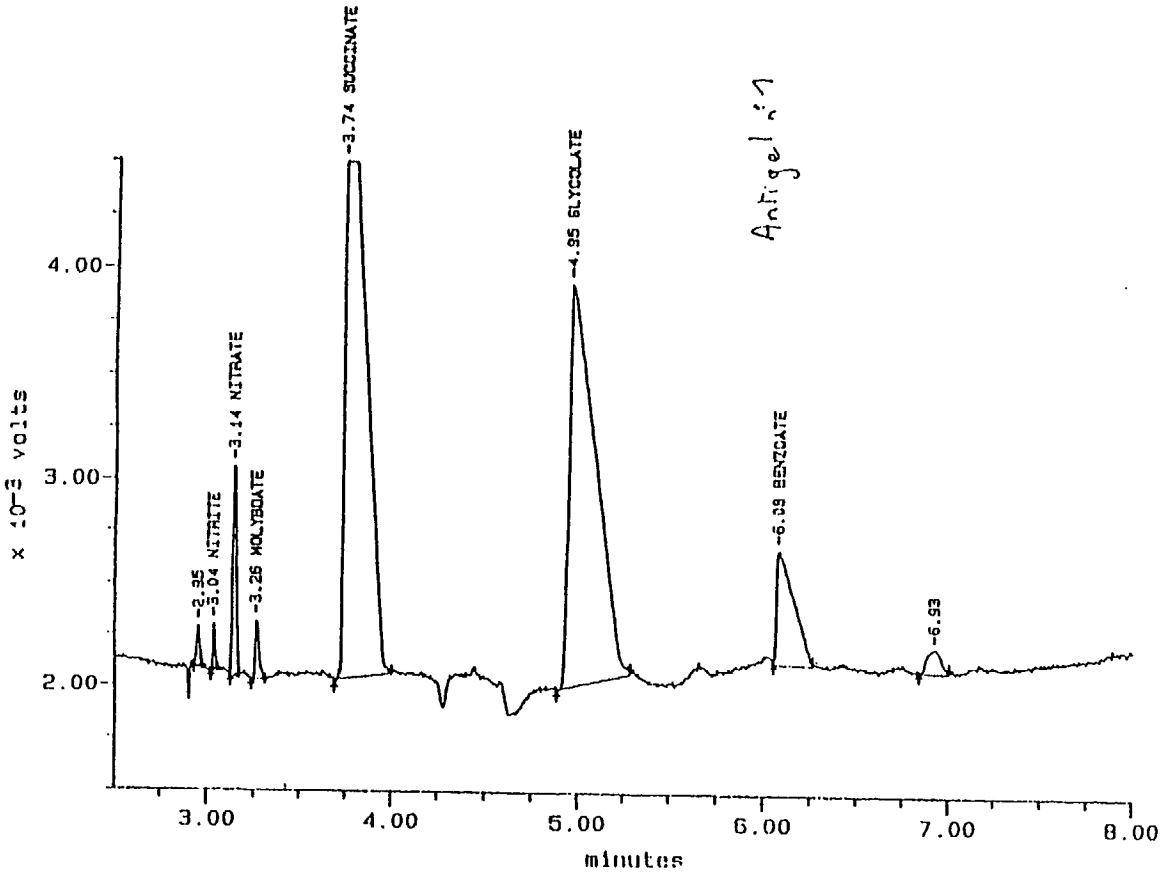


185 nm detection allows the analysis of organic acids with a high sensitivity. The selected conditions gives a fronting terephthalate peak, which allows the easy quantitation of the impurities.

The replaced IC method was taking 40 mn per injection

Waters European Marketing, HPLC 95

Organic acids in antifreeze



This sample containing 30% glycol is simply diluted before injection. The CIA technique is now used for both routine analysis and formulation - deformulation of antifreezes

Impurities in hydrogen peroxyde

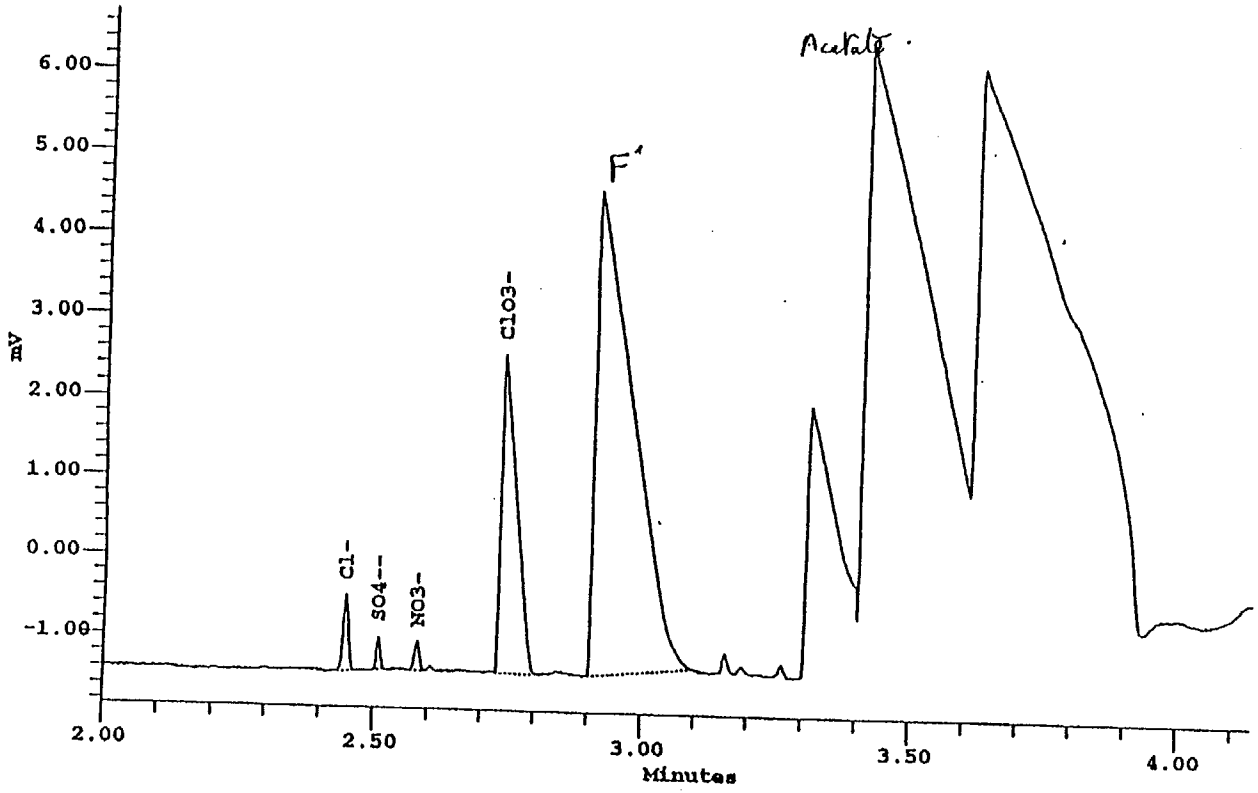
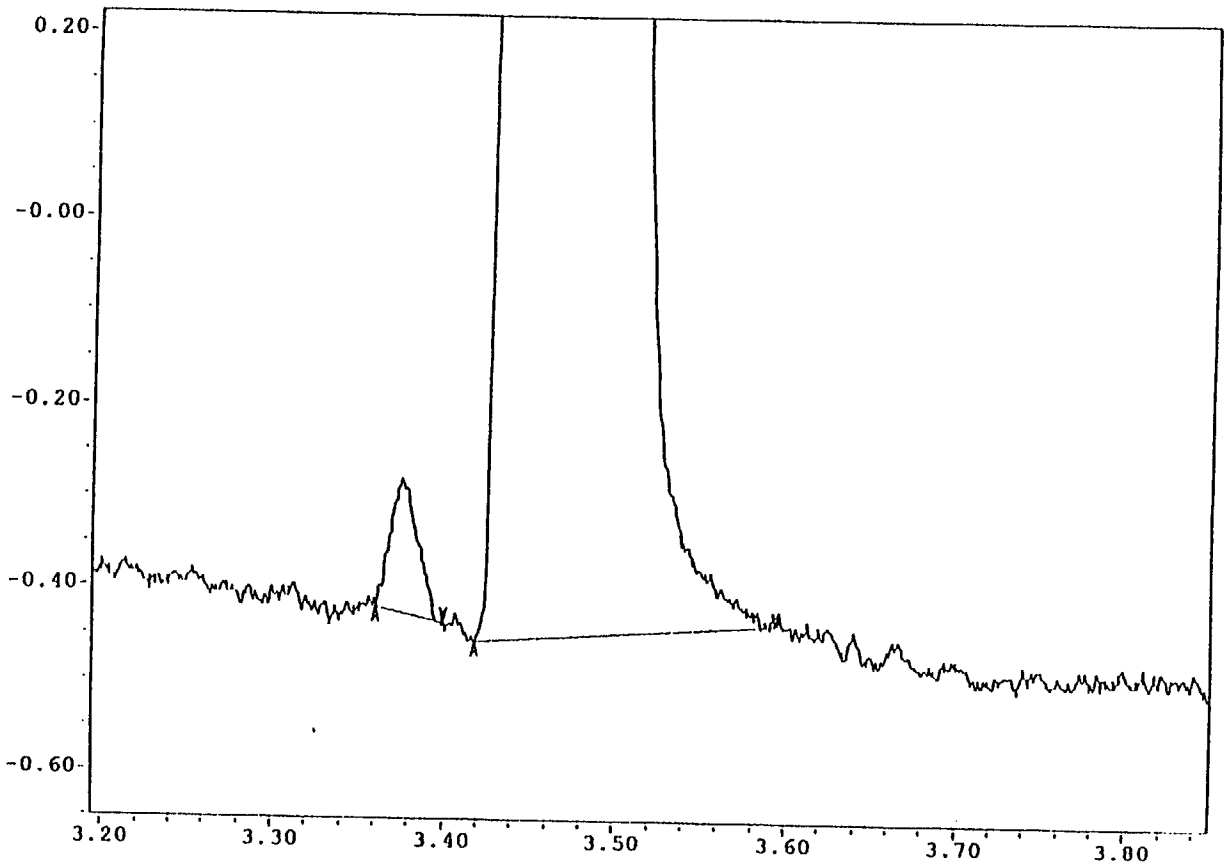


Tableau de Résultats

#	nom comp	temps de migr. (min)	reponse	conc. inj. (Ug/l)	conc. orig (Ug/l)
1	Cl-	2.45	0.08390	7.09	28.38
2	SO4--	2.51	0.02686	2.51	10.03
3	NO3-	2.58	0.03141	4.86	19.43
4	ClO3-	2.74	7851.62500	1.00	4.00

Impurities in hydrogen peroxyde can be easily detected using capillary electrophoresis. The sample preparation consists simply in a dilution

Optimized conditions for nitrite determination

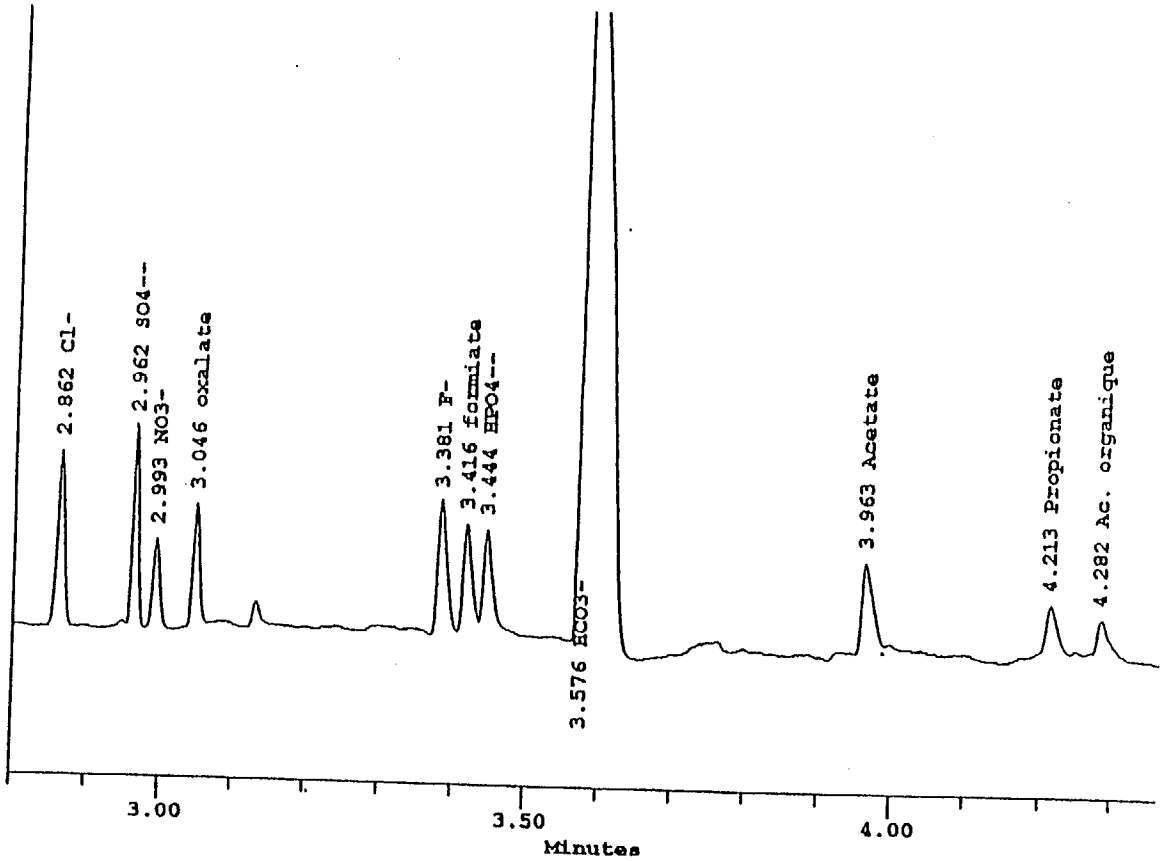


NO2: 20 ppb, NO3: 40 ppm

Electrolyte: Sodium sulfate + flow modifier

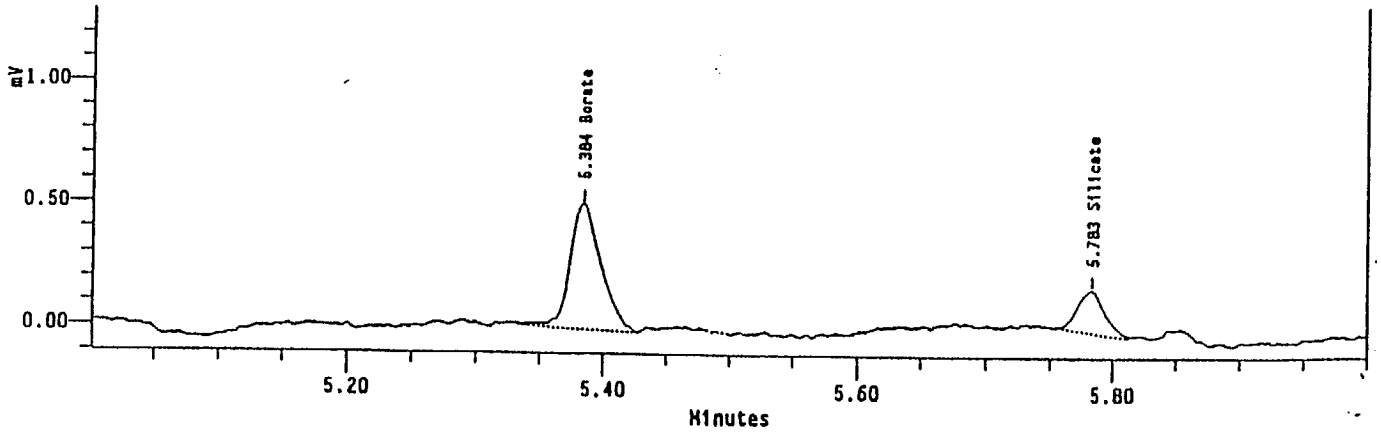
Detection: direct UV, 214 nm

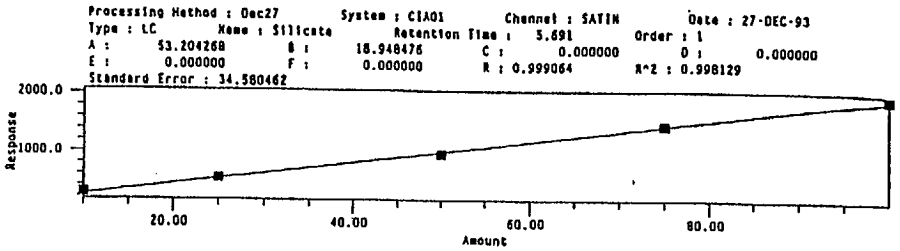
Anions at trace level



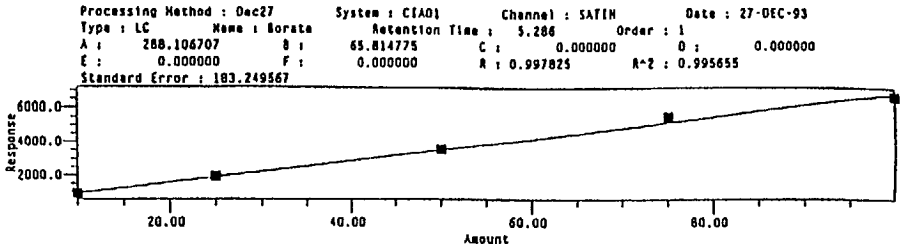
Trace level determination of anions is now achieved routinely for nuclear power plants control. It is applicable for deionised water as well as for primary and secondary circuit waters. Trace analysis is also used in electronic industry.

Determination of silicate and borate at 10 ppb level in dionized water





Calibration silicate: 10 to 100 ppb

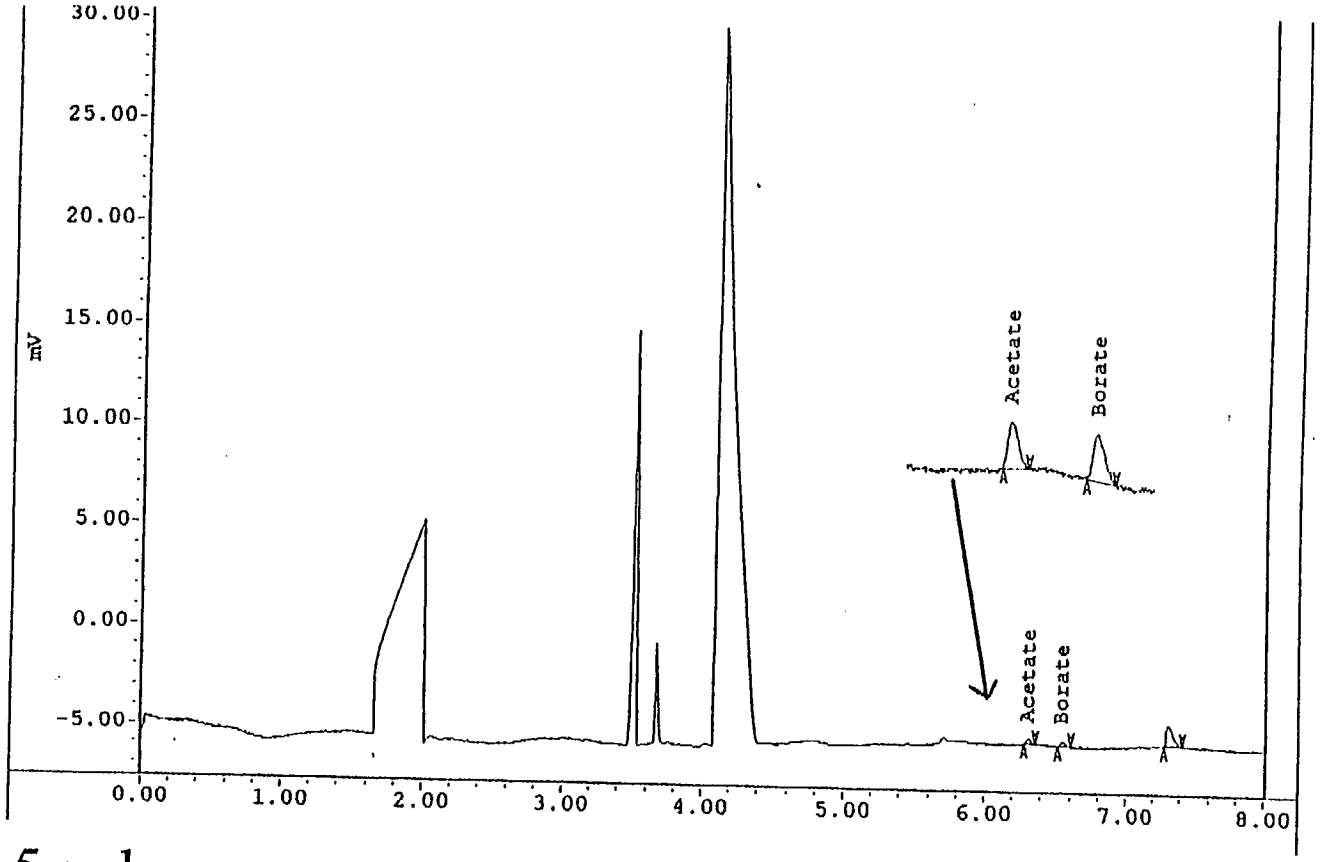


Calibration borate: 10 to 100 ppb

Electrolyte: Sodium chromate + flow modifier:

Detection: indirect UV, 254 nm

Determination of boron at ppb level in heavy water



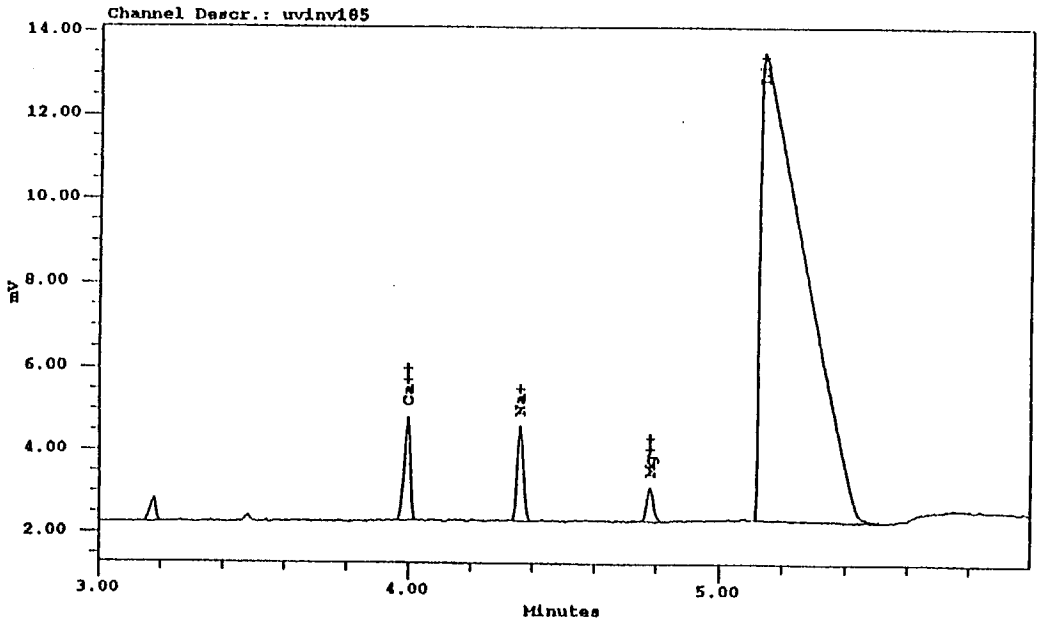
Borate: 9.5 ppb

Electrolyte: Sodium chromate + flow modifier:

Detection: indirect UV, 254 nm

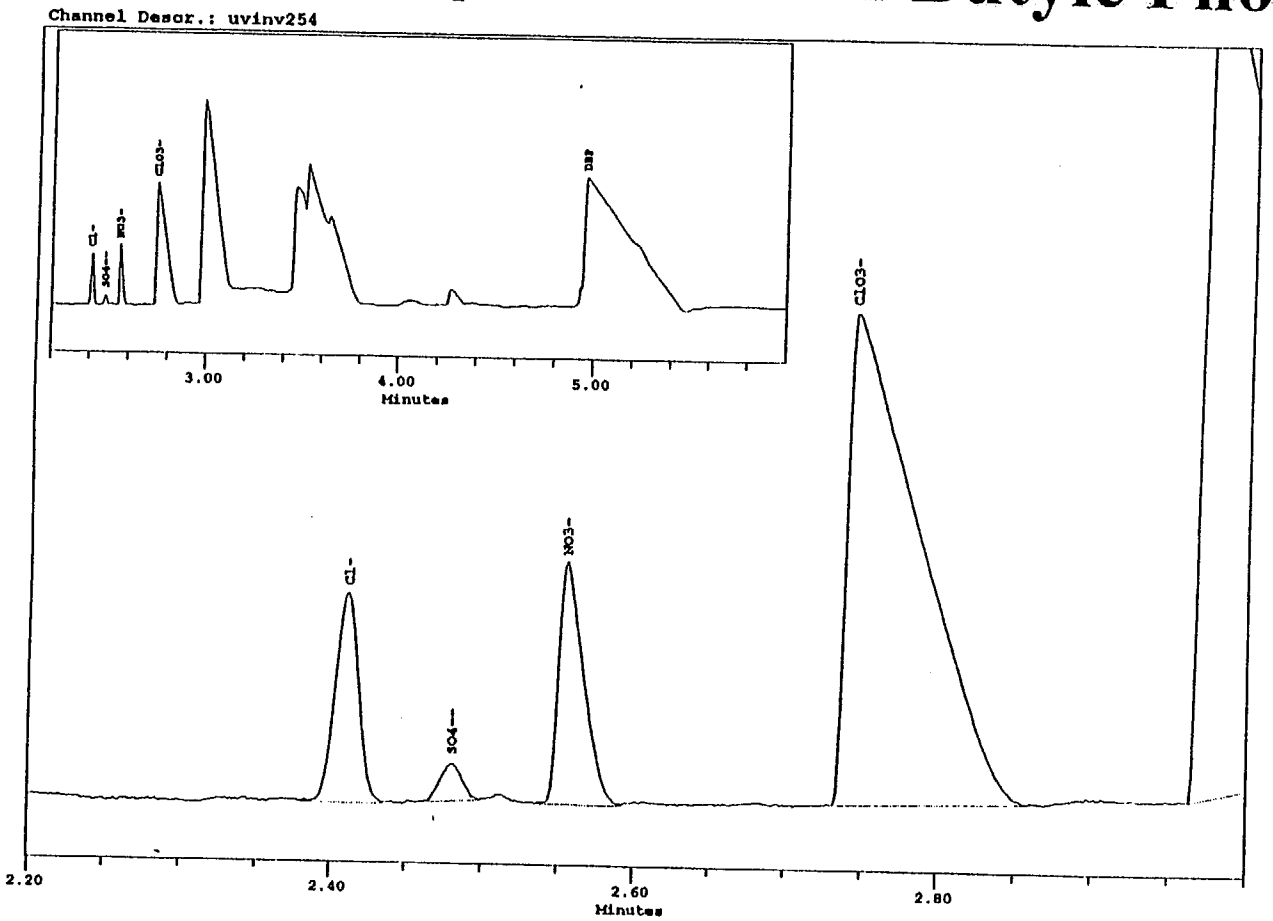
(courtesy of Mr W¢ien, Institutt for energiteknikk, Norway)

Determination of cations at ppb level with 185 nm detection



Electrolyte composition:	**Sample:**
UVCat 2: 30 mg	Potassium: 1 ppb
Tropolone: 60 mg	Calcium: 10 ppb
18-Crown-6: 52 mg	Sodium: 10 ppb
H2O: 100 ml	Magnesium: 2 ppb
Injection: electromigration	Lithium: 100 ppb

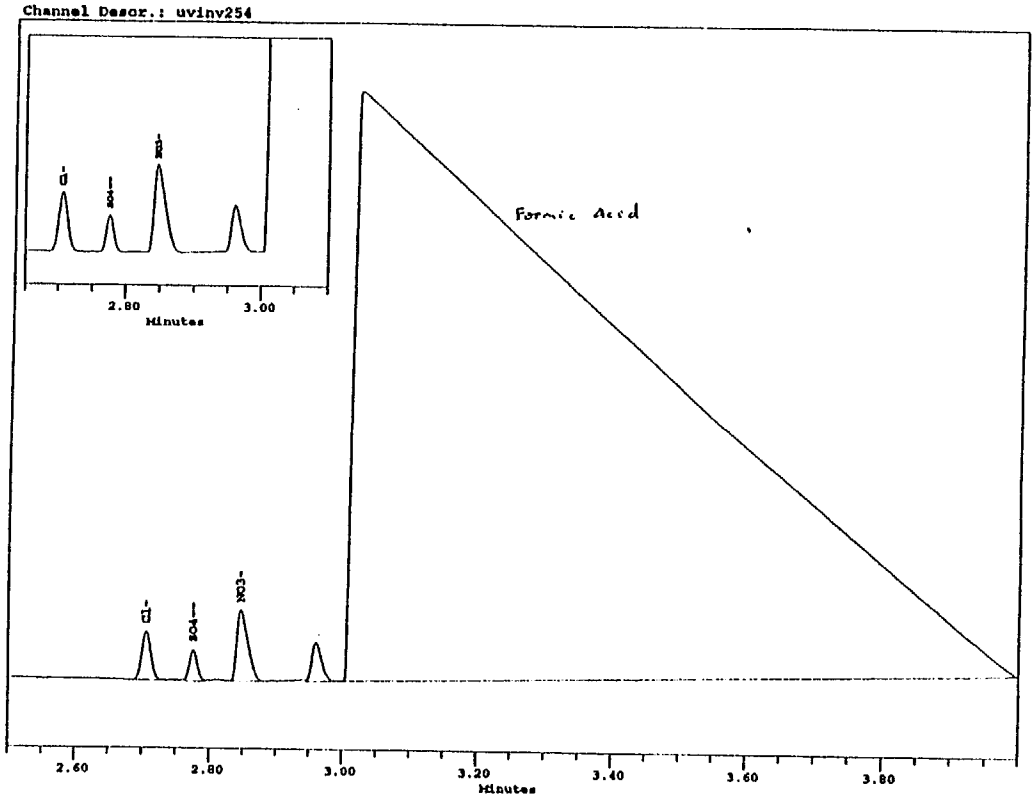
Anionic impurities in tri-Butyle Phosphate



This sample is not water soluble. Selective injection of anions is made using electromigration.

This analysis is important for the nuclear fuel re-treatment industry.

Anionic impurities in Formaldehyde



The pur formaldehyde is analyzed without any sample treatment or dilution.
Selective injection of anions is made using electromigration.

This analysis is important for the nuclear fuel re-treatment industry.

Similar approach is used for impurities determination in organic solvents as used in the electronic industry.

Conclusion

CIA (Capillary Ion Analysis) is now recognized as a valid ion analysis method.

The CIA technique is applicable to a wide variety of samples.

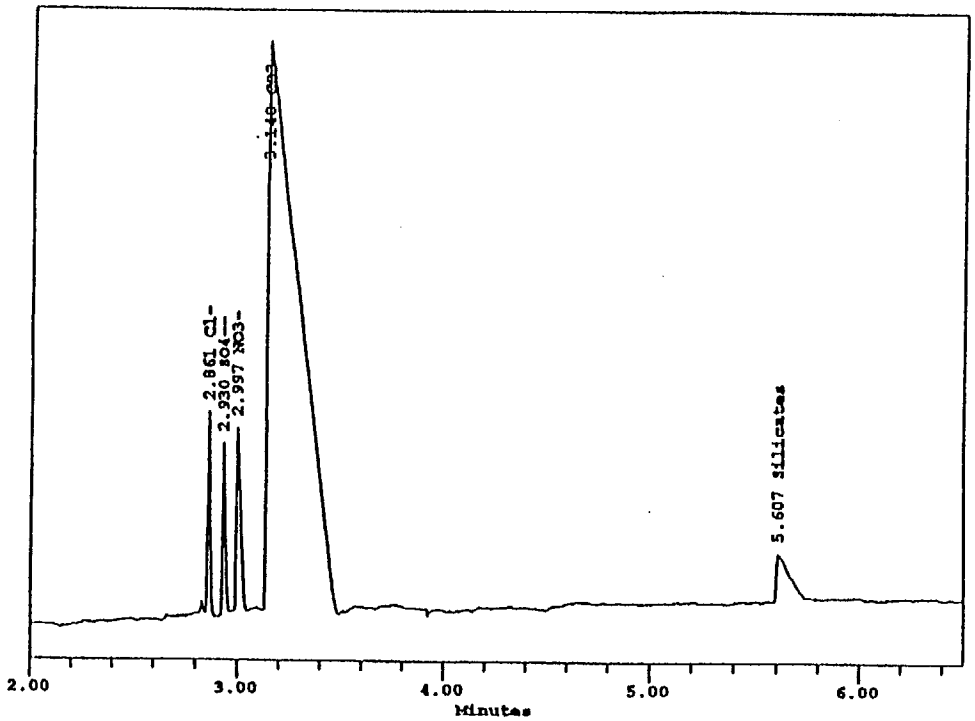
Sample treatment is most of the time limited to a dilution.

The separations are frequently more convenient than what is obtained with ion chromatography (higher efficiency, different selectivity).

The simple instrumental approach (bare silica capillaries, UV detection) reduces the cost of use and maintenance

Results obtained on the Capillary Ion Analyzer are equivalents to those of other techniques

Determination of silicate in tap water

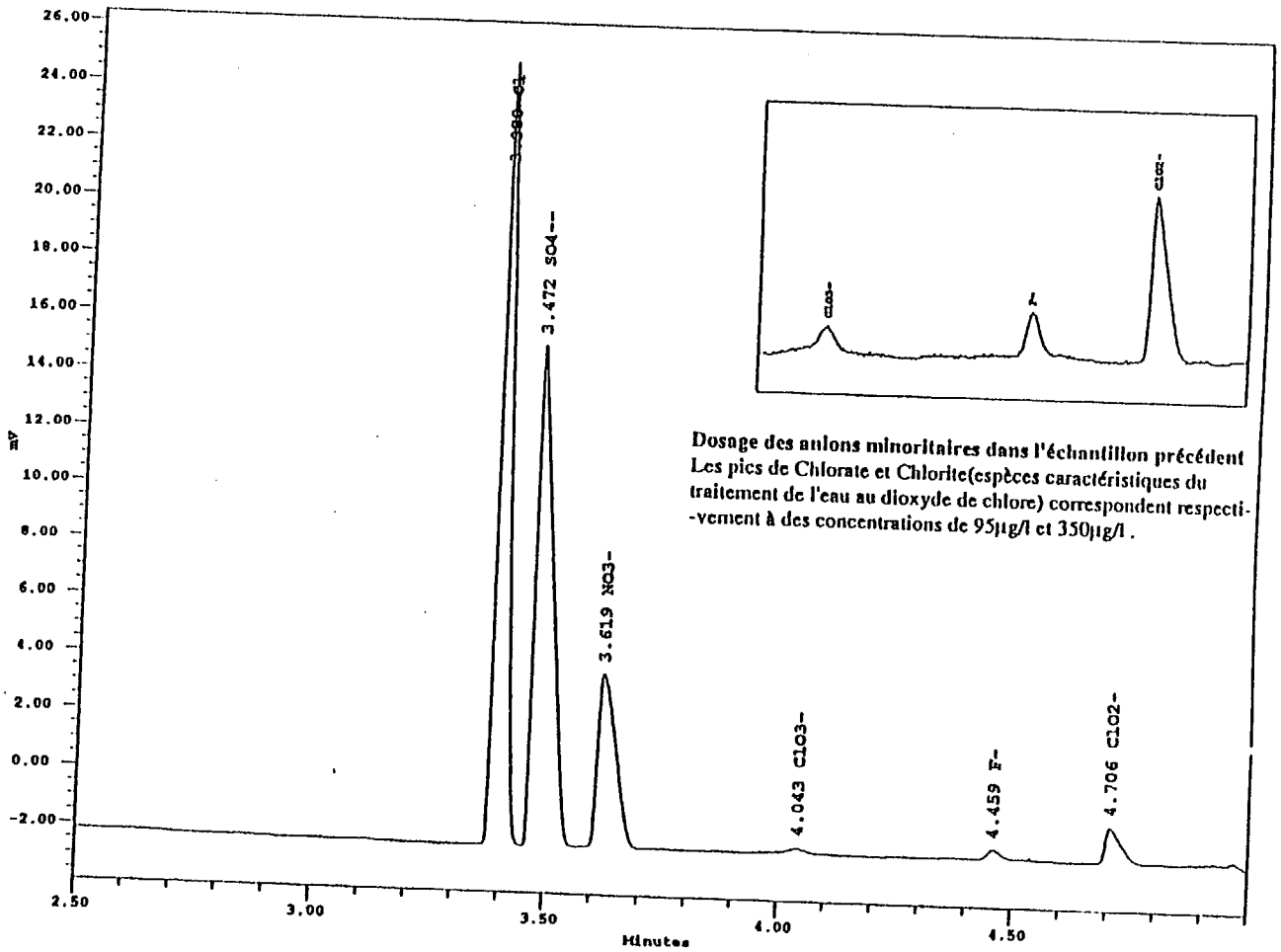


Electrolyte: Sodium chromate + flow modifier: pH = 10.5

Carbonate is detected as CO3=, which migrate earlier than HCO3-

Detection: indirect UV, 254 nm

Determination of Chlorite and chlorate in tap water



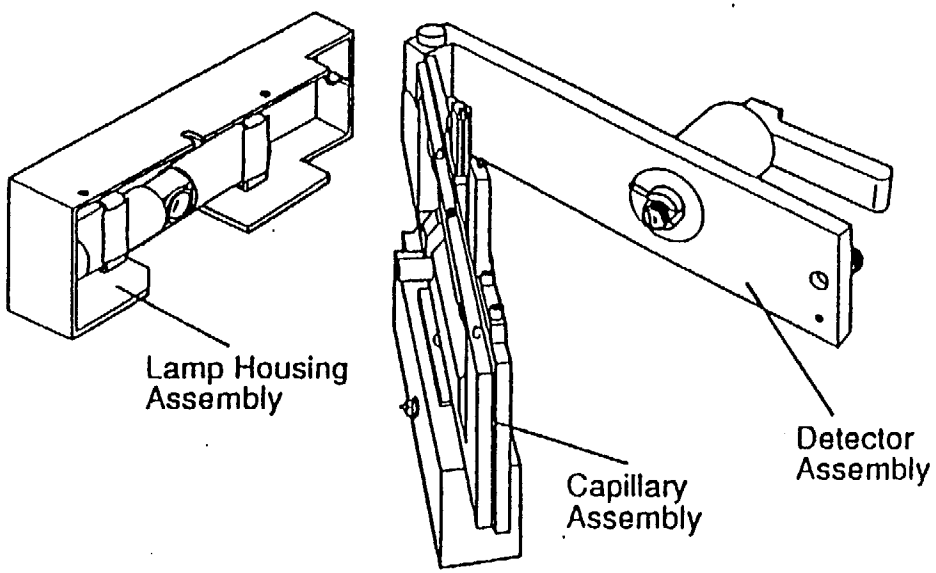
ClO2: 350 ppb, ClO3: 95ppb

Electrolyte: Sodium chromate + flow modifier

Detection: indirect UV, 254 nm

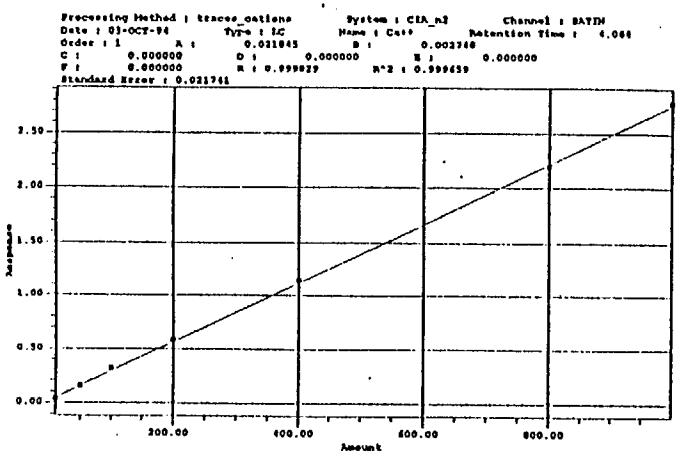
Waters European Marketing,
HPLC 95

Detector design

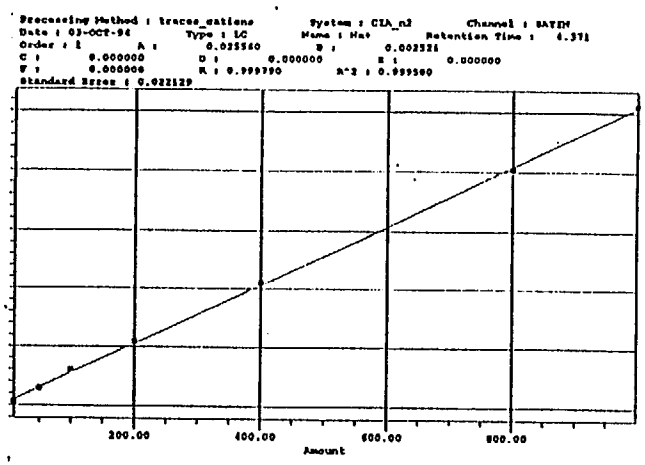


Waters European Marketing
HPCE 1995

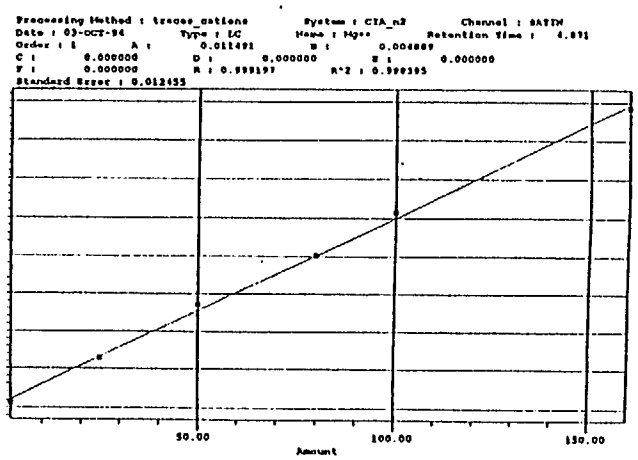
Detection linearity for cations at low concentration



Calcium



Sodium



Magnesium

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