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Analysis of Inorganic Anions in Various Drinking Waters by Capillary Electrophoresis

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Abstract :The quantitation of inorganic anions in various drinking waters were investigated using capillary electrophoresis(CE) and the results were compared with ion chromatography(IC). With CE, in contrast to IC, was demonstrated rapid analysis, good efficiency, a low detection limit and the low comsumption of a solvent and samples. CE analysis was used 5 mM sodium chromate(pH 8.0) containing 20 mM tetraalkylammoniumbromide at -25kV applied voltage with indirect UV detection at 254 nm. This results in exceedingly short analysis time within 3 min. with efficiencies approaching 200,000 theoretical plates. The coefficients of variants of migration time are less than 0.8% and those of peak area are less than 2.3%. Detection limits for quantitative determination were 300 ppb-50 ppm level. These optimum conditions are applicable to various samples without pretreatment.

Key words : Capillary electrophoresis, Inorganic anion, Waters

1. Introduction

The significance of separation of charged species such as anions, cations and organic acid are growing in several fields. Ionic species are routinely monitored for drinking and waste water to maintain water quality in environmental laboratories and for industrial water to protect turbines from corrosions. Food and beverage manufactures analyze organic acids to maintain quality and taste of their products. The current common technique for separation of 4 to 15 ionic species in ion mixture is ion chromatography(IC) with conductivity detection which was introduced in seventies[1-3]. While IC method has been used as standard methodology in the separation of ionic species, certain limitations exist. The polymer-based ion exchange columns implied in IC often

deliver only 1000-5000 theoretical plates yielding relatively broad peaks and long run time[4]. These low-capacity ion exchange columns are also subject to poisoning from sample excipients, often necessitating time consuming sample preparation prior to analysis[5].

Capillary electrophoresis(CE) is a powerful micro-analytical separation technique that combines the advantage of high pressure liquid chromatography(HPLC) and conventional electrophoresis. Since CE was introduced in 1980, progresses in CE techniques such as the effective temperature control of the Joule heat and the micellar electrokinetic capillary chromatography for the analysis of neutral molecules have been extending the use of CE to the separation of several types of organic molecules and enable CE to be an attractive alternative for HPLC in separation science[6-9]. Almost any mode of detection for HPLC can be modified for use in CE. The detection methods include ultraviolet(UV) absorbance[10], fluorescence[11], Laser induced fluorescence[12], RI.[13],conductivity[14, 15],amperometric[16.17],and CE-Mass[18]. In addition to the conventional detection methods, and indirect method was also developed for the analysis of UV-transparent compounds[19-21]. In an indirect detection method, UV-transparent compounds are analyzed with the mobile containing a visualization agent which has either fluorescence of UV absorption property to create an high background signal. UV-transparent analytes with the same sign of charge as the visualization agents are observed by the reduction of the background signal.

In the present study, we describe optimization of CE method to analyze bromide, chloride, sulfate and nitrate a composition with IC method in various drinking waters.

2. Experimental

2.1. Chemicals and reagents

Chromate, glyconate and boric acid were obtained from Sigma chemical Co.(St.Louis,MO,U.S.A.).100 mM NaOH as well as tetradecyltrimethyl ammoniumbromide (TTAB) were obtained from Beckman (Fullerton, CA,U.S.A). Sodium chloride, nitrate,sulfate and bromide were purchased from Fisher Scientific(Fiar,Lawn,NJ, U.S.A.).

2.2.Apparatus and method

CE system equipped a P/ACE diode array detector, and automatic injector, a fluid cooled column cartridge and a system Gold data station (Beckman Instruments, Inc.,Fullerton,CA,U.S.A.)was used in this study. All runs were carried out at 20 °C. The electrolyte was passed through 0.2μm nylon filters and degassed prior to use. The capillary inlet and outlet vials were replenished after every run. Injections were made using the pressure mode for 5 sec at 0.5 psi. Detection was performed at a wavelength of indirect UV 254 nm. A 57μm length of a 75μm I.D. fused silica capillary was rinsed with water a filled with electrolyte for 2 min. prior to sample injection. Power supply was performed reverse.

IC analysis were performed using a Model 590 solvent delivery system, a IC PAC A anion column and a Model 430 conductivity detector(Waters,Milford, MA,U.S.A.).Chromatograms were recorded and integrated by a Model 3390A integrator(Hewlett-Parkard,Basel,Swizerland). The integrator sampling rate was set to five data point per min.(Peak width 0.2 min.).The mobile phase consisted of a mixture of an 50 mM glyconate and boric acid .The injection volume was 20 mL, the flow-rate was 1 mL/min. and the temperature was ambient. The total analysis time was 15 min.,after each sample series the column was first rinsed with mobile phase(30 min).

3. Results and Discussion

3.1. Optimization of CE conditions

CE conditions including migration time and peak shape can be optimized by the change of certain factors. The factors include electromobility, electroosmotic flow and the use of micelle forming surfactant solution to induce the interaction of solutes with micelles. Electroosmobility is dependent on the buffer type and pH and electoosmosis is a consequence of the surface charge on the buffer type and pH on the wall of capillary. Hence, electrosmobility is controlled by the change of buffer type and pH. Since electroosmotic flow is rely on the interation of the surface charge on the wall and charges in buffer solution, the buffer concentration should be the lowest possible to prevent the interruption for generating an excess Joule heat. With respect to an indirect detection method careful selection a visualization agent is very important since the sensitivity of detection directly depend on stability of base line and absorptively of a visualization agent. The use of electroosmosis flow modifier is required for the analysis of an ion. The effect of modifiers on the analysis of anions were also investigated. In order to optimize the separation of anions on CE,all of the factors mentioned above were taken into account.

3.1.1.Influence of concentration of elecoosmotic modifier

TTAB reverses the natural direction of flow observed in fused-silica capillary. TTAB effectively shields these negative charges from the bulk of the electrolytes an decreases a net positive wall charge. The magnitude of the naturally occurring EOF is greater than the mobility of the majority of inorganic anion. *Fig.1* shows the separations of with various concentrations of TTAB as a EOF modifier. Without the addition of this modifier it is not possible to analyze highly mobile inorganic anions with just broad one peak in a single run. As the concentration of TTAB increases, the shielding effect increases, and consequently the migration speeds of the solutes would be increases. Our results are in agreement with theoretical expectations and the findings of Zare et al[22]. As the concentration of TTAB in the electrolyte was higher than 20mM, the separation efficiency of analytes appeared to be slightly impaired.

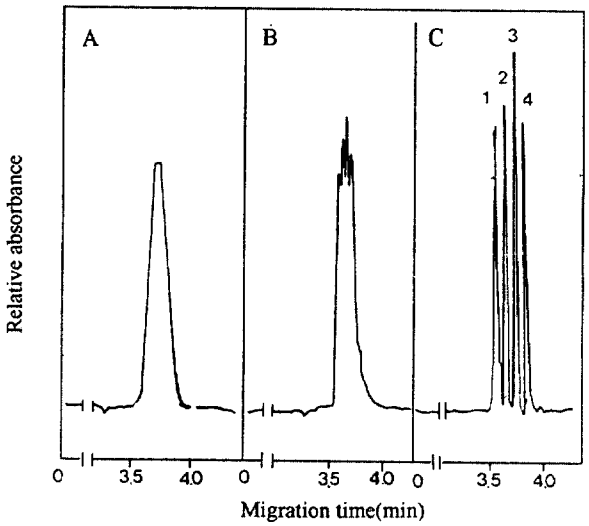

Fig.1. Effect of the concentration of TTAB as electroosmotic modifier. Concentration conditions A)no addition B)10 mM TTAB C)20 mM TTAB, Other conditions:5 mM chromate ,20KV.,Peaks identification:1-bromide,2-chloride,3-sulfate,4-nitrate.

3.1.2. Influence of ionic strength in chromate electrolyte.

Ionic strength of the background electrolyte plays three different roles in the CE separations[21,23]. Firstly, increasing concentration of background electrolyte decreases the EOF, secondly it increases efficiency due to higher field strength an thirdly it is yields subtle. Separation buffers can also lead to significantly increase Joule heating, which results in low of resolution and may

lead to analyte inability. By the chromate concentration from 3 mM to 12 mM is varied while keeping 20mM TTAB and pH at 8.0., migration time are show *Fig.2*. It is seen that the sulfate anion begins to comigrate with anion at lower 5mM chromate and 4 anions separate to at higher 5mM chromate concentration.

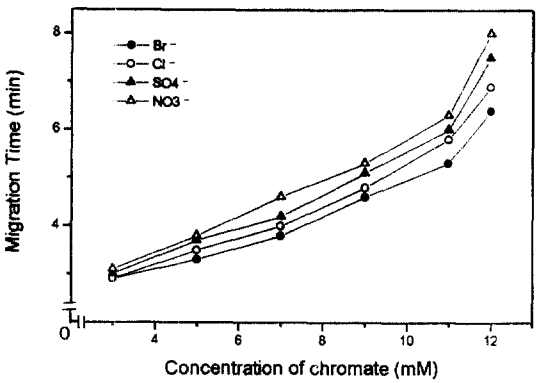

Fig.2. Effect of the concentration of electrolyte containing 20 mM TTAB. Conditions are same as *Fig.1*.

3.1.3.pH of chromate electrolytes and selectivity

The pH effect on migration time was examined with 5 mM chromate in 20 mM TTAB over the effect of electrolyte. The effect of electrolyte mobility is predictable and most pronounced for weakly acidic anions. 4 anions were evaluated a pH starting at 7.0 and increasing increments of 0.5 pH units to 9.0. The migration time values of the more strongly acidic anions with pKa below 9 are unaffected by electrolyte pH changes between pH 8 and 9.0(*Fig.3*). 4 anions are best resolved at pH 8.0 with a total comigration occurring from 8.5 to 9.0.

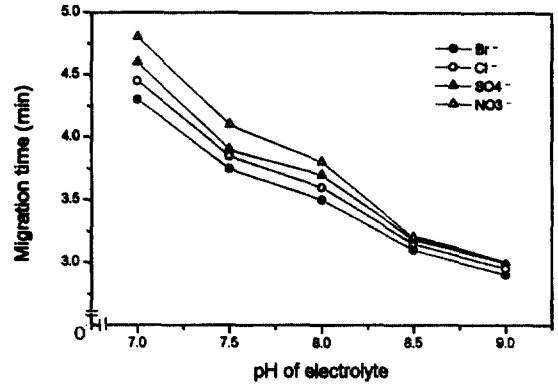

Fig.3. Effect of the pH of electrolyte .Conditions are same as *Fig.2*.

3.1.4. Applied voltage effect on selectivity

The dependence of the velocity on the applied voltage was investigated and a linear increase with increasing voltage was found (*Fig.4*). However, a positive deviation from the linearity was observed above 25-30 kV which was magnified by raising. Therefore optimum voltage is described 25 kV.

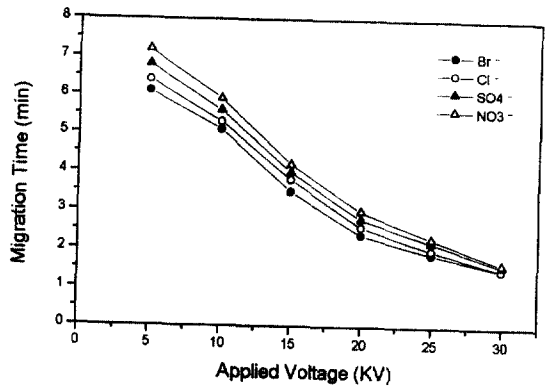

Fig.4. Effect of the applied voltage . Conditions are same as *Fig.3*.

3.1.5. Reproducibility and accuracy

The precision of the peak are is affected by variation in the migration time, stable and reproducible separation conditions must be established prior to the quantitative analysis. We carried out precision tests of migration time and peak area under the optimum conditions based on the above investigations. The coefficients of variation(CV) of the migration time were less than 0.8% and those of the peak area for bromide chloride, sulfate and nitrate 0.973%,0.650,1.005% and 2.227 respectively (*Table 1*).

Table 1. Reproducibility of the migration time and relative peak area of inorganic anions.

	Migration time(min)			Area		
	Mean	S.D.[1)]	C.V.[2)]	Mean	S.D.	C.V.
Bromide	3.713	0.010	0.269	2310	24.74	0.973
Chloride	3.767	0.010	0.265	1171	18.02	0.650
Sulfate	3.845	0.030	0.780	1378	13.71	1.005
Nitrate	3.954	0.020	0.505	1336	6.00	2.227

[1)] **S.D.;Standard deviation**

[2)] **C.V.(%);Coefficient of variations(n=15)**

3.2. Comparison with CE and IC

All the experiments were performed unparalleled to compare CE to IC (*Fig.5*). Sample concentrations in CE and IC are bromide ; 2 ppm and 30 ppm, chloride ; 4 ppm and 30 ppm, sulfate ; 4 ppm and 70 ppm and nitrate ; 4 ppm and 60 ppm respectively. Analysis time of all 4 anions is about 4 times faster CE(ca 3 min.) than in IC(ca 13 min.).Plate count numbers which show separation efficiencies were found to be 3784, for chloride, 1388 for nitrate and 1050 for sulfate on IC, while it was about 200,000 in CE. The higher separation efficiency in CE compared to IC is mainly due to the small inner diameter of capillary CE. An injection volume in CE(15 nL) was 1000 times less than in IC(20 uL).In continue 10 times analysis case, IC required total 1600 mL including a 50 mL for pre-washing and 1500 mL(15 mL per 1 run) for 10 times-analysis and 50 mL for post-washing while CE consumed only within

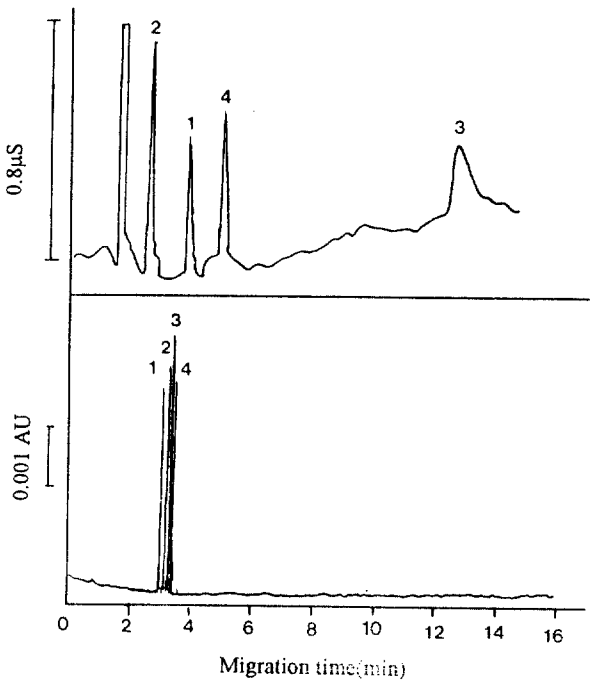

Fig.5. Comparison with CE-electropherogram (top) and IC-chromatogram(bottom). Peaks identification:1-bromide,2-chloride,3-sulfate,4-nitrate

10uL of solvent including pre-rinse run and post-rinse. Detection limit was increased by 3 detection in CE with an indirect UV detection method, compared to IC with a conductivity detection. Detection limits were in a ppm range in IC and about 300 ppb - 500 ppb in CE at 1:3 of a signal-to-noise ratio. Detection limits were previously reported to be in the order of ppb in IC and ppt in CE[24]. With respect of reproducibility of retention times In IC

and migration times in CE, the coefficients of variants(CV) was 1.0% in IC and 0.8% in CE. In the analysis of tab water an drinking water, the results of CE is quantitatively 98-102% identical to the results of IC.

In summary, CE exhibited advantages over IC in several aspects such as high reproducibility, less consumption of analytes and a solvent, shorter analysis time and higher separation efficiency. In addition, analytes of low concentration can be analyzed on CE without a pre-concentration due to the low detection limit of CE.

3.3 Quantitative sample analysis using CE

For the quantitative analysis, the correlation between the peak area and the sample concentrations in the range of 300 ppb-50 ppm was studied (*Fig.6*). The respective linear regression equations for bromide, chloride, sulfate

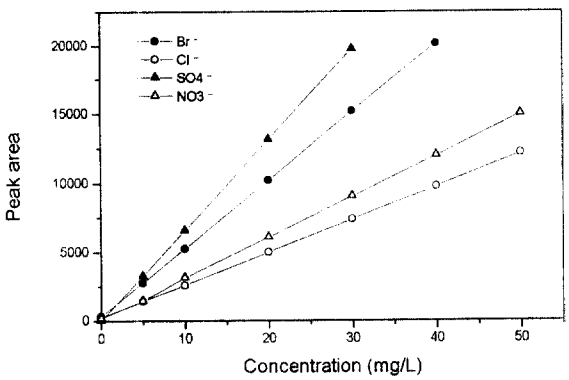

*Fig.*6. Linearity of detection

and nitrate were y = 494.96 x + 321.30 (r = 0.996), y = 239.21 x + 214.33 (r=0.998), y = 294.78 x + 198.78 (r=0.999) and y = 656.85 x + 21.89 (r=1.000) respectively. Under above optimum conditions, we separated to inorganic anions in various samples(*Fig.7*). Tap water and commercial drinking water were described chloride;20.9 ppm and 8.1 ppm, sulfate;16.6 ppm and 10.7 ppm, and nitrate;7.8 ppm and 16.8 ppm, respectively.

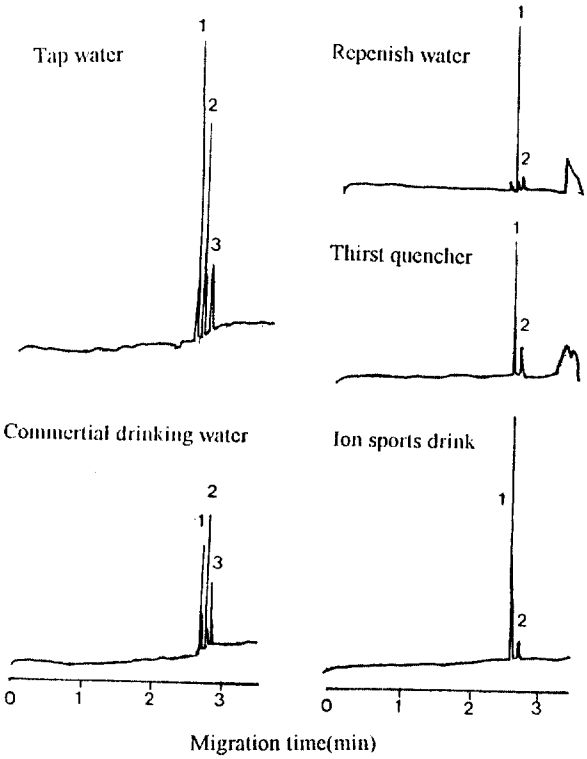

Fig. 7. Separation of inorganic anions in various drinking water. Conditions are same as *Fig.5*. Peaks identification: 1-chloride,2-sulfate,3-nitrate

Others sample as ion sports drink, thirst quencher and replenish water were injected 1:50 dilution in electrolyte and were determined 400-600 ppm range of chloride with other anions and organic acid.

Conclusion

Capillary electrophoresis with an indirect UV detection is applicable to analysis of inorganic anions. CE showed an excellent run-to-run reproducibility and a good linearity in a plot of concentration vs area under the curve. This method was also applicable to analysis of tab water, commercial drinking water and sports drinking water. Compared to IC, CE offers many benefits such as a high theoretical plate count number, 200,000 which is 100 times higher efficiency than IC, low consumption of a solvent and samples and rapid analysis time low analytical expense due to the low consumption of a solvent and samples, and a low detection limit. The results described here show that the role of CE could be extended to the quality control of food and beverage products and analysis of pollutants in environmental laboratories.

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