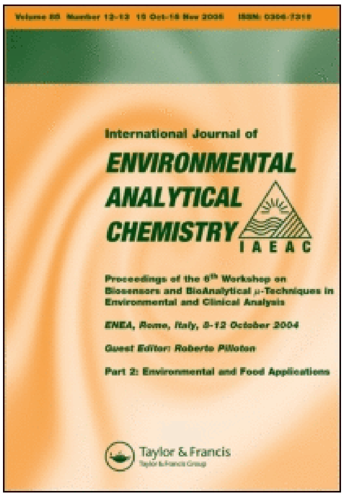

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Simultaneous and Fast Detection of Anions in Snow Using Short Tube by Capillary Zone Electrophoresis

Weiping Yang[a]; Zhujun Zhang[a]
[a] Institute of Analytical Science, College of Chemistry and Materials Science, Shaanxi Normal University, Xi'an, China

To cite this Article Yang, Weiping and Zhang, Zhujun(2002) 'Simultaneous and Fast Detection of Anions in Snow Using Short Tube by Capillary Zone Electrophoresis', International Journal of Environmental Analytical Chemistry, 82: 6, 353 — 360

To link to this Article: DOI: 10.1080/030673121000008568

URL: http://dx.doi.org/10.1080/030673121000008568

Intern. J. Environ. Anal. Chem., Vol. 82, No. 6, pp. 353–360

Taylor & Francis
Taylor & Francis Group

SIMULTANEOUS AND FAST DETECTION OF ANIONS IN SNOW USING SHORT TUBE BY CAPILLARY ZONE ELECTROPHORESIS

WEIPING YANG and ZHUJUN ZHANG*

Institute of Analytical Science, College of Chemistry and Materials Science,
Shaanxi Normal University, Xi'an, 710062, China

(Received 7 March 2002; In final form 5 June 2002)

A capillary zone electrophoresis (CZE) method applied short-effective length of capillary (11 cm) and low separation voltage (5 kV) was developed for the fast and quantitative determination of Cl^-, NO_2^-, SO_4^{2-}, NO_3^-, HCO_3^- in snow sample. Baseline separation of inorganic anions and organic anions was achieved within 55 s. Indirect absorbance detection of anions was accomplished with a chromate – based background electrolyte modified with cetyltrimethylammonium bromide (CTAB) and acetonitrile at pH 9.5. The effect of the pH, the concentration of electrolyte and modifiers on the resolution was investigated. The application of electrokinetic injection using butyric acid as internal standard created the described method fast, sensitive, and quantitative, with good relative standard deviation (RSD), for migration times from 0.1 to 0.3% and for peak areas from 1.8 to 4.0%. The limits of detection (LOD) were $0.03\,mg\,L^{-1}$ Cl^-, $0.1\,mg\,L^{-1}$ NO_2^-, $0.07\,mg\,L^{-1}$ SO_4^{2-}, $0.08\,mg\,L^{-1}$ NO_3^-, $0.05\,mg\,L^{-1}$ F^-, and $0.2\,mg\,L^{-1}$ HCO_3^-, respectively. Standard addition recoveries of Cl^-, NO_2^-, SO_4^{2-}, NO_3^-, F^-, and HCO_3^- in snow sample were between 91 and 104%. This method has been shown promising results for the determination of small anions in snow sample.

Keywords: Snow; Anions; Capillary zone electrophoresis; Short capillary

INTRODUCTION

In glaciology and environmental chemistry, the determination of various ions in snow sample is very important. The concentration of these ions in snow sample is useful for deducing the change in climate and pollution in the environment [1,2]. Their measurement in snow can also provide useful information on the atmospheric composition having prevailed at the time of the deposition of snow. Be different from the water sample analysis, the determination of contaminants collected in various depth of snow, in chilly winter, can indirectly reflect the changing situations of air pollution at different times in a specific region.

For the determination of inorganic ions and organic acids, ion chromatography (IC) has become the technique of choice [3]. However, this method may take several minutes to hours to complete one test. Capillary electrophoresis (CE) is one of the

---

*Corresponding author. Fax: +86-29-5308748. E-mail: zzj18@hotmail.com

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/030673121000008568

best highly efficient separation techniques due to many attractive features such as high peak efficiencies, great resolution, low sample volume, and reduced analysis times in the last few years. CE has been extensively applied to the determination of inorganic and organic ions [4–8]. Several indirect UV detection methods have been developed using various background electrolytes (BGE), such as chromate, pyromellitate, benzoate, and other aromatic carboxylic acid [9–17]. Chromate has been the most commonly used carrier electrolyte for the analysis of inorganic anions since they have a similar high mobility [17]. It has been applied to the analysis of inorganic anions in water [4,24], wine and juice [18], toothpaste [19], sugar and wine [23] etc. High voltage in CE method, typically, applied from 20 to 30 kV. The capillary length usually used from 50 to 80 cm, so the analysis time was relatively long (more than 3–10 min). Recently, the short-end injection procedure in CE, which introduced short-effective length of capillary reduced analysis times, was reported [25,26].

The aim of our research work is focused on the development of a feasible CE method for rapid anions determination in snow. In this article, we successfully separated several inorganic species within 55 s in chromate–cetyltrimethylammonium bromide (CTAB)–acetonitrile (ACN) system applied short-effective length capillary (11 cm) and low-high voltage (5 kV) in our home-made CE device. Separation was performed with an electric field of 455 $\mathrm{Vcm^{-1}}$. Butyric acid (BA) was used as an internal standard to overcome the problems of quantitation and sensitivity using electrokinetic injection method during this study. Using BA as an internal standard, the peak areas of anions relative to BA as response factor, quantitative determination of chloride, sulfate, nitrite, nitrate, and bicarbonate in snow sample was carried out with standard addition method.

EXPERIMENTAL SECTION

Instrumentation

All the data were collected using a home-built capillary electrophoresis system equipped with a high voltage power supply (Tianhui Institute of Separation Science, Baoding, China), indirect UV detection scheme consisting of a UV source and detector (Tianhui Institute of Separation Science, Baoding, China) with band pass filter operating at $\lambda = 254$ nm. The data acquisition and collection were processed using commercially available software (IFFM – A data analysis system, Xi'an, China). A negative power supply was used for all separation, and the separation voltage applied was 5.0 kV. A 15 cm × 50 μm I.D fused-silica capillary tubing coated with polyimide (Polymicro Technologies, Phoenix, AZ, USA) was used. The total length of the capillary was 15 cm, and $Ld = 11$ cm. The polymer coating was burned off at 4 cm from one end of the capillary to form the detection window. Samples were injected by electrokinetic injection mode by applying a 0.5 kV for 8 s.

Reagents and Solutions

Butyric acid was purchased from Sigma (St. Louis, MO, USA). CTAB and sodium chromate were purchased from Xi'an Chemical Plant (Xi'an, China). Acetonitrile, sodium chloride, sodium sulfate, sodium nitrite, sodium nitrate, sodium bicarbonate, sodium phosphate, and sodium fluoride were provided by Shanghai Chemical Plant (Shanghai, China). All chemicals were of analytical grade. All solutions were prepared with double-distilled water. All solutions were filtered through a 0.45 µm membrane filter and degassed by ultrasound before use.

The stock solutions: 200 mM sodium chromate, 25 mM CTAB, 99.9% ACN. The BGE used was prepared by diluting 1.5 mL of 200 mM sodium chromate and 5 mL of 25 mM CTAB and 1.8 mL ACN to 50 mL total volume. The pH of the electrolyte was adjusted by the addition of 0.1 M NaOH. This working electrolyte solution was prepared fresh daily.

Capillary Electrophoresis Conditions

Before it was used, the capillary was rinsed with 0.2 M NaOH for half an hour, then rinsed with double-distilled water for 5 min and buffer solution for 30 min. Each step used a syringe purge to make the capillary filled with carrier solution. To maintain reproducible migration times, the capillary was flushed with the electrolyte for 2 min and a voltage of 5 kV was applied to it for 100 s before each sample was injected. The capillary was filled with 0.1 M NaOH overnight in order to keep the capillary wall in good condition.

The pH values of the electrolytes were determined by a Microprocessor pH/mV meter.

RESULTS AND DISCUSSION

Effect of Background Electrolyte pH

The pH of the electrolyte had a significant impact on the electrophoretic mobilities of anions. The influence of the electrolyte pH on the relative migration time or the 5 anions was studied in the pH range 8.0–11.0. The migration order for chloride, nitrite, sulfate, nitrate, and fluoride will not change in the pH range of 8.0–11.0. The electrolyte pH varied from 8.0 to 11.0, the observed electrophoretic mobilities of anions decreased. pH values lower than 8.0 and pH higher than 11.0 were not applicable because nitrite and sulfate could not separate completely. Figure 1. (A) and (B) demonstrated the separation of the 5 anions in the pH 8.0 and 9.0, respectively. The electrolyte system had been optimized at pH 9.0 or 9.5.

Effect of Chromate Concentration

The composition and concentration of the BGE plays a central role in CE methods as it determines the fundamental migration behvaior of the analytes. A good BGE must guarantee suitable electrophoretic behavior of all individual analytes. In this work, the influence of chromate concentration over the range 2 to 10 mM on separation was studied. Sulfate and nitrate were separated poorly when the chromate concentration was 2 mM, and nitrite and sulfate could not separated completely when the chromate concentration was more than 10 mM. With the chromate concentration increasing, high electrophoretic current generated. In this investigation, 6 mM chromate

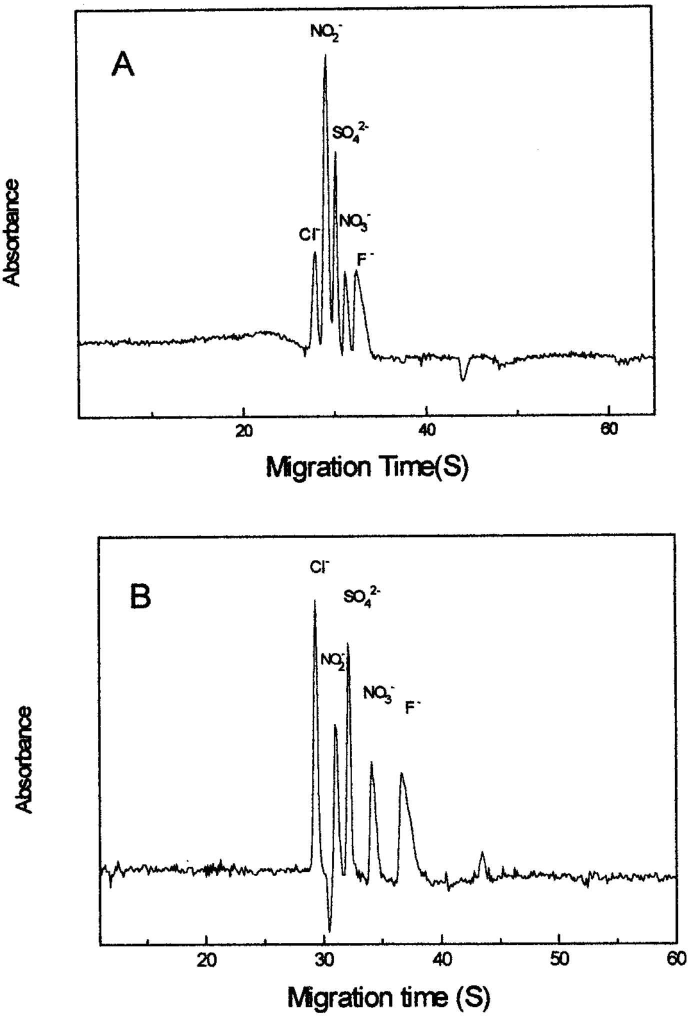

FIGURE 1 Effect of BGE pH on separation. (A): pH 8.0, anions, Cl^- 0.5 mg L^{-1}, NO_2^- 2 mg L^{-1}, SO_4^{2-}, NO_3^-, F^- 1 mg L^{-1}; (B): pH 9.0, anions, each 1 mg L^{-1}; $Ld = 11$ cm; $HV = 5$ kV; 6.0 mM chromate; 2.5 mM CTAB; 3.6% ACN.

was found to be optimal, and selected to perform the determination of anions in following study.

Effect of Electroosmotic Flow Modifiers

Alkyltrimethylammonium bromide compounds (Cationic surfactants) such as CTAB [27] and tetradecyltrimethylammonium bromide (TTAB) [28] being commonly used for suppressing or reversing the electroosmotic flow (EOF) [22]. To investigate the effect of EOF modifier (CTAB) on the separations of analytes, six solutions with different concentrations (1.0–3.5 mM) of CTAB were used as electrolytes. Similar to pH value, CTAB was found to be the main parameter influencing the resolution of NO_2^-

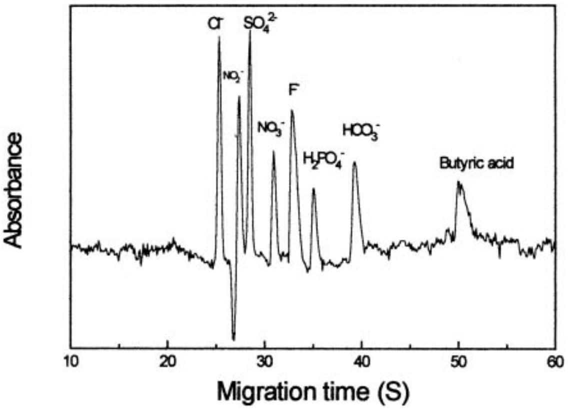

FIGURE 2 Typical electropherogram of standard anions using indirect UV detection. *Ld* = 11 cm; pH 9.5; *HV* = 5 kV; 6.0 mM chromate; 2.5 mM CTAB; 3.6% ACN; Anion, each 1 mg L^{-1}.

and SO_4^{2-} peaks. Low concentration of CTAB (< 1.5 mmM) resulted the resolution of NO_2^- and SO_4^{2-} peaks was poorly separated. On the other hand, the resolution of SO_4^{2-} and NO_3^- peaks was low when using high concentration of CTAB (> 3.5 mM). In this article, 2.5 mM CTAB was selected.

Organic solvents, such as methanol, ethanol, and ACN were not only used for improving resolution of metal ions, but also employed for improving the selectivity of inorganic anions [6]. Buchberger [20] added 30% methanol to alter the migration order of anions in chromate–CTAB system, but nitrite and nitrate could not be baseline separated. In this experiment, ACN as added to chromate–CTAB system. The concentration of ACN varied from 1.0 to 6.0%. The migration times of anions decreased with increasing concentration of ACN in the carrier electrolyte. In this article, 3.6% ACN was chosen.

Background electrolyte consisted of 6.0 mM sodium chromate, 2.5 mM CTAB and 3.6% ACN at pH 9.5 was chosen as the final separation electrolyte. This gave excellent resolution of the anions, as shown in Fig. 2. Baseline separation of nine species of inorganic anions and organic anions was achieved within 55 s.

Linearity

In CE, the injection methods are very important. The two most widely used methods for sample introduction are the hydrodynamic (gravity) and electrokinetic injection methods. Both methods have their advantages and disadvantages. The hydrodynamic methods has wide linear range, but insufficient sensitivity. On the other hand, electrokinetic injection provides high sensitivity, but a narrow range of linearity. In our work, good linearities using hydrodynamic injection were found in the range 1–100 mg L^{-1} for Cl^-, SO_4^{2-}, NO_3^-, and F^-; 3–100 mg L^{-1} for NO_2^-. However, the low sensitivity could not be sufficient for determining the level (about sub-mg L^{-1}) of anions in snow sample. In order to overcome the problems of quantitation and sensitivity, the internal standard was added for evaluation of the anion concentrations in real sample and electrokinetic injection was used [19]. In this article, BA was chosen as an internal standard for linearization because of its stability and migration time far away from inorganic anions (Fig. 2) to eliminate any possibility of accidental overlap with an analyte peak. Its occurrence in snow samples is not likely. The regression equations, correlation coefficients (R) and linear ranges presented in Table I. The data shown in Table I suggests that the correlations are > 0.999 and the limits of detection (LOD) are in the sub-ppm to ppb range.

Precision and Limit of Detection (LOD)

Reproducibilities of migration times and peak areas were tested with electrokinetic injection. The relative standard deviations (R.S.D.s) of migration times and peak areas of anions ($n = 6$) were no more than 0.8 and 8.3%, respectively. Using BA as an internal standard, the R.S.D.s. of migration times and peak areas of inorganic anions to BA ($n = 6$) were no more than 0.3 and 4.0%, respectively. The results were shown in Table II. The LOD for all analytes were determined (Table I) using the following equation: [21]

$$\mathrm{LOD} = 3NC/h$$

where N is the noise defined as peak area, C is the sample concentration and h is the peak height.

Recovery

The recovery of the method was studied using snow water spiked with 2 mg/l of chloride, nitrite, sulfate, nitrate, fluoride, bicarbonate. The results of the analysis by capillary electrophoresis are in good agreement with the concentration effectively introduced

TABLE I The linear range, regression equation, correlation coefficient (R) and limits of detection (LOD) of anions

Anions	*Linear range* ($\mathrm{mg\,L^{-1}}$)	*Regression equation* ($Y = AX + B$)	*R*	*LOD* ($\mathrm{mg\,L^{-1}}$)
Cl^-	0.08–100	$Y = 0.3860X + 0.1268$	0.9992	0.03
NO_2^-	0.3–100	$Y = 0.5148X + 0.0128$	0.9990	0.1
SO_4^{2-}	0.1–100	$Y = 0.3526X + 0.0932$	0.9993	0.07
NO_3^-	0.1–100	$Y = 0.2159X + 0.0074$	0.9992	0.08
F^-	0.1–100	$Y = 0.6920X + 0.0437$	0.9994	0.05
HCO_3^-	0.4–100	$Y = 0.1985X + 0.2143$	0.9991	0.2

TABLE II Reproducibilities of migration times and peak areas of anions

	R.S.D. ($n = 6$) (%)					
	Cl^-	NO_2^-	SO_4^{2-}	NO_3^-	F^-	HCO_3^-
Migration time	0.7	0.7	0.6	0.6	0.6	0.8
Migration time/BA*	0.2	0.3	0.1	0.2	0.2	0.3
Peak area	5.4	6.4	3.6	8.3	3.5	4.8
Pear area/BA**	2.0	2.3	1.8	4.0	2.6	2.5

*Relative migration time to BA, **Relative peak area to BA, BA: butyric acid (internal standard).

in the sample, since the recoveries are 96 ± 5% for chloride, 99 ± 3% for nitrite, 99 ± 5% for sulfate, 97 ± 4% for nitrate, 99 ± 3% for fluoride, and 99 ± 5% for bicarbonate.

Application

Snow samples were collected from Xi'an suburb (snow Sample 1#) and Taibei Mountains (elevation 3100 m a.s.l.) (snow Sample 2#) in December 2000. Each sample was stored in two new polyethylene bottles. In order to add the internal standard (BA) in real samples for quantification, the snow water samples were diluted (1 : 1 v/v). All samples solutions were filtered through a 0.45 μm membrane filter. The concentration of BA was 10 mg L^{-1} in the samples. Figure 3 shows the electropherogram of a snow sample. The results of snow sample are shown in Table III. The results obtained by this method were consistent with those of IC.

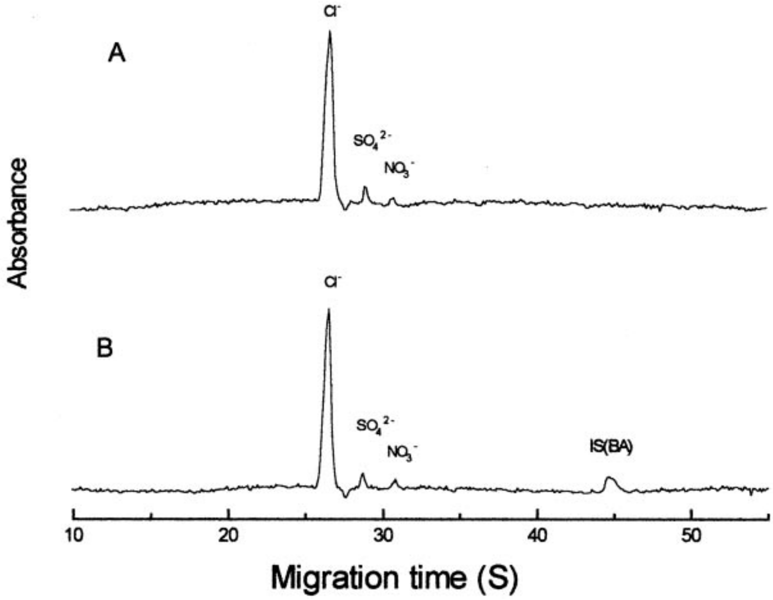

FIGURE 3 The electropherogram for the separation of anions in a snow sample. (A): Electropherogram of snow. (B): Electropherogram of snow spiked with internal standard (Butyric acid (BA)).

TABLE III Results for determination of anions in snow samples

		Determination (mg L^{-1})				
Method	*Sample*	*Cl^-*	*NO_2^-*	*SO_4^{2-}*	*NO_3^-*	*HCO_3^-*
CE	Snow 1#	21.7	ND	1.1	1.5	ND
	2#	29.6	ND	0.90	0.57	ND
IC	Snow 1#	21.0	ND	1.3	1.4	ND
	2#	30.1	ND	0.87	0.59	ND

ND: Not Determined.

CONCLUSIONS

Using our novel CE device applied short capillary of separation and quantification of Cl^-, NO_2^-, SO_4^{2-}, NO_3^-, HCO_3^- in snow were investigated. Results of this work show that using of a short capillary and a relatively low separation voltage for analysis, is combined with an optimized background electrolyte, provides the basis for an instrument with fast operation and adequate resolution. Furthermore, electrokinetic injection using an internal standard may become much more attractive than both electrokinetic injection and gravity injection in terms of linearity, sensitivity and reproducibility. The promising aspect of this method compared to other methods is that it can detect inorganic and organic anions in a single run and total analysis in a very short time (less than 1 min).

Acknowledgments

Financial support from the National Natural Science Foundation of China, grant No. 20175039.

References

[1] Y. Yang, J. Kang, H. Lu, Q. Ou and F. Liu, *J. Chromatogr. A*, **834**, 387–391 (1999).
[2] J. Wen and R.M. Cassidy, *Anal. Chem*., **68**, 1047–1056 (1996).
[3] P.R. Haddad and P.E. Jackson, Ion chromatography: principles and applications. *Journal of Chromatography Library*, **466** (1990).
[4] J.P. Romano and J. Krol, *J. Chromatogr. A*, **640**, 403–412 (1993).
[5] T. Soga and G.A. Ross, *J. Chromatogr. A*, **767**, 223–230 (1997).
[6] Y. Yang, F. Liu, J. Kang and Q. Ou, *J. Chromatogr. A*, **834**, 393–399 (1999).
[7] P. Kubáň, P. Kubáň and V. Kubáň, *J. Chromatogr. A*, **836**, 75–80 (1999).
[8] P. Kuban, R. Pirmohammadi and B. Karlberg, *Anal. Chim. Acta*, **378**, 55–62 (1999).
[9] W.R. Jones and P. Jandik, *J. Chromatogr. A*, **546**, 431–443 (1991).
[10] B.F. Kenney, *J. Chromatogr. A*, **546**, 423–430 (1991).
[11] W.R. Jones and P. Jandik, *J. Chromatogr. A*, **546**, 445–458 (1991).
[12] K.A. Hargadom and B.R. McCord, *J. Chromatogr. A*, **602**, 241–247 (1992).
[13] J.B. Nair and C.G. Izzo, *J. Chromatogr. A*, **640**, 445–463 (1993).
[14] J.P. Romano and J. Krol, *J. Chromatogr. A*, **640**, 403–412 (1993).
[15] R. Sthal, *J. Chromatogr. A*, **688**, 143–148 (1994).
[16] E.D. Zlotorzynska and J.F. Dlouhy, *J. Chromatogr. A*, **671**, 389–395 (1994).
[17] J. Ramano, P. Jandik, W.R. Jones and P.E. Jackson, *J. Chromatogr. A*, **546**, 411–421 (1991).
[18] M. Arellano, J. Andrianary, F. Dedieu, F. Couderc and Ph. Puig, *J. Chromatogr. A*, **765**, 321–328 (1997).
[19] P. Wang, S.F.Y. Li and H.K. Lee, *J. Chromatogr. A*, **765**, 353–359 (1997).
[20] W. Buchberger and P.R. Haddad, *J. Chromatogr. A*, **608**, 59–67 (1992).
[21] Y. Mrestani, R.H.H. Neubert, A. Hartl and J. Wohlrab, *Anal. Chim. Acta*, **349**, 207–213 (1997).
[22] T. Faller and H. Engelhardt, *J. Chromatogr. A*, **853**, 83–94 (1999).
[23] B. O'Flaherty, W. Yang, S. Sengupra and A.L. Cholli, *Food Chemistry*, **74**, 111–118 (2001).
[24] M.C.B. Alonso and R. Prego, *Anal. Chim. Acta*, **416**, 21–27 (2000).
[25] M. Blanchin, B. Baalbaki, N. Bosc and H. Fabre, *Anal. Chim. Acta*, **415**, 67–73 (2000).
[26] X. Cahours, C. Viron, Ph. Morin, I. Renimel, P. André and M. Lafosse, *Anal. Chim. Acta*, **441**, 15–21 (2001).
[27] F. Han, J.L. Faschingand and R.I. Kingston, *J. Chromatogr. B*, *Biomed-Appl*., **669**, 103–112 (1995).
[28] M. Albert, L. Debusschere, D. Demesmay and J.L. Rocca, *J. Chromatogr. A*., **757**, 291–296 (1997).