

**ISOCRATIC AND GRADIENT CONDITIONS FOR  
INORGANIC CATIONS ANALYSIS BY REALIZATION  
ON-LINE COUPLING OF ION EXCHANGE  
CHROMATOGRAPHY WITH EVAPORATIVE LIGHT  
SCATTERING DETECTOR**

**M. El Haddad<sup>1,2</sup>, R. Boulahjar<sup>2,3</sup>, R. Mamouni<sup>2</sup>,  
S. El Antri<sup>3</sup>, M. Akssira<sup>2</sup>, M. Dreux<sup>4</sup>, S. Lazar<sup>3\*</sup>**

<sup>1</sup>*Faculté Poly disciplinaire, Département Sciences de la Matière,  
Université Cadi Ayyad, BP 4162, 46000 Safi, Morocco*

<sup>2</sup>*Laboratoire de Chimie Bioorganique & Analytique, Université  
Hassan II-Mohammédia, BP 146, 20800 Mohammédia, Morocco*

<sup>3</sup>*Laboratoire de Biochimie, Université Hassan II-Mohammédia,  
BP 146, 20800 Mohammédia, Morocco*

<sup>4</sup>*Institut de Chimie Organique & Analytique, Université d'Orléans,  
UMR 6005, BP 6759, 45067 Orléans Cedex 2, France*

\*Corresponding author: Fax: +212 23 31 53 53; E-mail: lazar\_said@yahoo.fr

**Abstract:** Performances of three available commercial cationic exchangers: Lichrosil IC CA2 Merck, Metrosep cation 1-2 Metrohm and PRP-X200 Hamilton for ion exchange chromatography were compared. Isocratic conditions were developed for inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) separation on Metrosep cation 1-2 and Lichrosil IC CA2 columns in about 6 min and 3 min, respectively using proton as ion developer. While, ammonium was used as ion developer for inorganic cations separation with step gradient on PRP-X200 Hamilton column in about 10 min. Retentions of inorganic cations on these chromatographic supports were discussed. Evaporative light scattering detector was used as detection system. The developed method provides good linearity for the calibration curves, and

enables a 10 ng absolute detection limit for  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and a 25 ng absolute detection limit for  $\text{K}^+$ , at a signal-to-noise ratio of 3.

**Keywords:** *comparison performances, cationic exchangers, ion exchange chromatography, evaporative light scattering detection.*

## INTRODUCTION

Ion exchange chromatography (IEC) is powerful analytical method for the analysis of ionic species. It is a tool that can separate and detect a wide variety of species using essentially the same technique. IEC as developed by Small et al. [1] has allowed the rapid separation and determination of anions; their methods have also been applied successfully for alkali and alkaline earth cations. On account of the great differences in their affinity towards ion-exchangers, it has traditionally been difficult to separate both alkali and alkaline-earth cations in a single run analysis. Especially IEC instrumentation and cation-exchange resins are needed for the simultaneous determination of the alkali and alkaline earth cations. Inorganic cations have been separated on silica-based [2] and polymer-based columns [3]. Monovalent cations such as alkali cations are easily eluted with dilute nitric or hydrochloric acid [4, 5]. The separation of alkaline earth cations requires the use of strong driving ions such as ethylene diamine [6] and are further facilitated by addition of complexing agents to the mobile phase like DL-2,3-diamino propionic acid [7], histidine [8] and EDTA [9]. IEC with indirect conductimetric detection for the simultaneous determination of both alkali and alkaline earth cations is investigated using anion-exclusion chromatographic column packed with polymethacrylate-based weakly acidic cation exchange resin in the  $\text{H}^+$  form an eluent constituted by sulfuric acid, tartaric acid and methanol in water. The separation was occurred by cation-exchange mechanism in about 25 min [10]. Simultaneous determination of alkali and alkaline earth cations by gradient elution technique was carried out in a Dionex CG 12A/CS12A with  $\text{H}_2\text{SO}_4$  11 mM and  $\text{H}_2\text{O}$  in about 20 min [11]. Separation of alkali and alkaline earth cations was carried out on aluminium-silica column and using protonated tyramine (4-amino ethylphenol) as eluent. Simultaneous separation were achieved in 21 min by using 1.2 mM tyramine; 0.2 mM oxalic acid at pH 4.5 containing 0.5 mM 15-Crown-5 or 0.5 18-Crown-6 as eluent and UV-indirect detection [12]. Separation of calcium and magnesium by high performance liquid chromatography on a graphitic stationary phase with a mobile phase containing *o*-cresolphtalein complexone was realized by dynamic chelating ion exchange mechanism that allows separation of these cations, which were detected using spectrophotometric detector [13]. Determination of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in a well water sample were also obtained using a IC Pack CM/D (Waters) column with an eluent containing citric acid and pyridine-2,6-dicarboxylic acid [14]. Tartaric and dipicolinic acids have also been used for mono- and divalent cations separation [15]. Simultaneous separation and determination  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in environmental samples were obtained by Ohta et al. [16] by coupling nitric acid and pyridine-2,6-dicarboxylic acid with a selective complexation of divalent cations. The major interest of IEC for inorganic cations separation let us to contribute for the development of new

chromatographic conditions for separation of alkali and alkaline earth cations in single run elution. Evaporative light scattering detector (ELSD) is considered to be a very convenient and universal liquid chromatography (LC) detector for analytes without chromophore groups and which are less volatile than the chromatographic eluent. We have already used ELSD for inorganic anions separation [17, 18].

The aim of this work is to evaluate potentialities of three different cationic exchangers Lichrosil IC CA2, PRP-X200 Hamilton and Metrosep cation 1-2 for separation of usual inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) by IEC using ELSD. Isocratic and step gradient conditions were performed.

## EXPERIMENTAL

The pump of the chromatographic system used was a P200 from ThermoQuest (Les Ulis, France). It was connected to the A 100 autosampler from TSQ. An ELSD Sedex 75 from Sedere (Alfortville, France) was used for detection. The usual settings were as follows: photomultiplier 9; drift tube temperature  $60^\circ\text{C}$ ; nebulizer gas pressure 3.5 bar. Data were performed with EZChromElite software from scientific software Inc. (Pleasanton, USA) running under Windows NT 4.0. The columns were Lichrosil IC CA2 Merck (125 x 4.6 mm I. D.), Metrosep cation 1-2 Metrohm (125 x 4.0 mm I. D.) and PRP-X200 Hamilton (150 x 4.1 mm I. D.). All measurements were carried out at room temperature.

All solutions were prepared from analytical reagent grade chemicals in ultra pure water  $18\text{ M}\Omega$  obtained from an Elgast UHQII system from ELGA (Antony, France). Potassium chloride, sodium chloride, magnesium chloride and calcium chloride were purchased from Sigma (St. Louis, MO, USA), ammonium hydroxide and ethylene diamine from Fluka (St. Quentin Fallavier, France). Trifluoroacetic acid (TFA) was purchased from Interchim (Montluçon, France). PhoEBus, an application program guide for buffer studies (Sedere, Alfortville, France), was used for the mobile phase preparation. The theoretical values of pH and ionic strength of each eluent mobile phase were calculated from PhoEBus and then for each mobile phase, the pH values were checked with a Beckman pH meter (Model  $\Phi 10$ , Gagny, France). The concentration of each standard in the different injected samples was about 100 to 300 mg/L in aqueous solutions.

## RESULTS AND DISCUSSION

In order to achieve the retention of inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) by IEC and ELSD, we have used three different stationary phases. First one is Lichrosil IC CA2 packed with a polymeric coated on a spherical silica gel, bonded by carboxylate as functional group. Second one is PRP-X200 Hamilton packed with a sulphonated functional group fixed on polystyrene-divinyl benzene copolymer resin. The latest is Metrosep cation 1-2 based on a spherical silica gel coated with poly(butadiene)-maleic acid as functional group. These columns were selected for our study on the basis of the diversity of their functional groups.

**Comparison of Lichrosil IC CA2 and Metrosep cation 1-2**

A preliminary comparison was made between Lichrosil IC CA2 and Metrosep cation 1-2 cation exchange columns in order to establish optimum selectivity. Proton provided by TFA was used as ion developer for inorganic cations separation. TFA was chosen for his volatility requirements exigencies of ELSD. It was already demonstrated that TFA is evaporable when analyzing anions inorganic that given  $\text{CF}_3\text{COO}^-$  as ion developer [18] and gives a background noise equal to 1 mV. For evaluating the effect of TFA concentration in the mobile phase on inorganic cations retention, we have used the potentially of PhoeBus software to give the values concentrations of ionic strength, ion developer ( $\text{H}^+$ ), co-ion ( $\text{CF}_3\text{COO}^-$ ) and pH of each eluent. Three different eluent concentrations TFA have been studied: 2, 3 and 4 mM to manage the retention of inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) on Lichrosil IC CA2 and Metrosep cation 1-2 columns. Table 1 reports the different values cited below.

**Table 1.** Values of ionic strength (mM), concentrations of ion developer ( $\text{H}^+$ ), co-ion ( $\text{CF}_3\text{COO}^-$ ) and pH of different concentrations of TFA in aqueous mobile phase

Eluent	TFA 2 mM	TFA 3 mM	TFA 4 mM
Ionic strength (mM)	1.99	2.98	3.96
$\text{H}^+$	1.99	2.98	3.96
$\text{CF}_3\text{COO}^-$	0.01	0.02	0.04
pH	2.72	2.55	2.43

The ionic strength of mobile phase increases when the TFA concentration is increasing. The  $\text{H}^+$  concentration is comparable to the ionic strength of each mobile phase and their pH are very close to the range of use of Lichrosil IC CA2 and Metrosep cation 1-2 columns. Table 2 reports the retention factors, k, of inorganic cations with different concentrations of TFA on Lichrosil IC CA2 and Metrosep cation 1-2 columns under isocratic conditions elution.

**Table 2.** Retentions factors, k, of inorganic cations with different concentrations of TFA on Lichrosil IC CA2 and Metrosep cation 1-2 columns

Column	Eluent	$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
Lichrosil IC CA2	TFA 2 mM	1.92	2.63	6.58	8.28
	TFA 3 mM	1.35	1.86	3.47	4.21
	TFA 4 mM	1.09	1.50	2.35	2.75
Metrosep cation 1-2	TFA 2 mM	1.81	2.48	5.90	7.44
	TFA 3 mM	1.16	1.60	2.73	3.40
	TFA 4 mM	0.90	1.25	1.77	2.13

As usually observed in IEC an increase in the ion developer concentration or in the ionic strength of the mobile phase results a decrease in the cation retention factor. Whatever, the concentration of the ion developer, the increasing elution order is:  $\text{Na}^+ < \text{K}^+ < \text{Mg}^{2+} < \text{Ca}^{2+}$ . These results are concerning both Lichrosil IC CA2 and Metrosep cation 1-2 columns. After comparison of retention factors, k, of all inorganic cations studied, it appears that Metrosep cation 1-2 column is more retentive than Lichrosil IC

CA2 column. It is recognized that silica-based polymer coated stationary phase containing carboxylate cation exchange functional groups was already developed for non-suppressed ion chromatography utilizing an isocratic eluent consisting of mildly acidic complexing agents to elute mono- and divalent cations and the retention mechanism was occurred by IEC and a mild chelating agent mechanism for divalent cations [19]. Polymer-based cation exchange column (Ion Pac CS12) with carboxylate functional groups was introduced [20]. So, this column has a high selectivity for hydronium ion. A simple acidic isocratic eluent was used for the separation of both alkali and alkaline earth cations. The retention mechanism of inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) was occurred by a pure IEC on Lichrosil IC CA2 and Metrosep cation 1-2 columns. In this fact, the theoretical slope of linear curve representing  $\log k$  versus of  $\log$  of the eluent cation ( $\text{H}^+$ ) concentration should be (+1) for  $\text{Na}^+$  and  $\text{K}^+$ , and (+2) for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  [21]. The results are very close to (+1) for monovalent cations and (+2) for divalent cations.

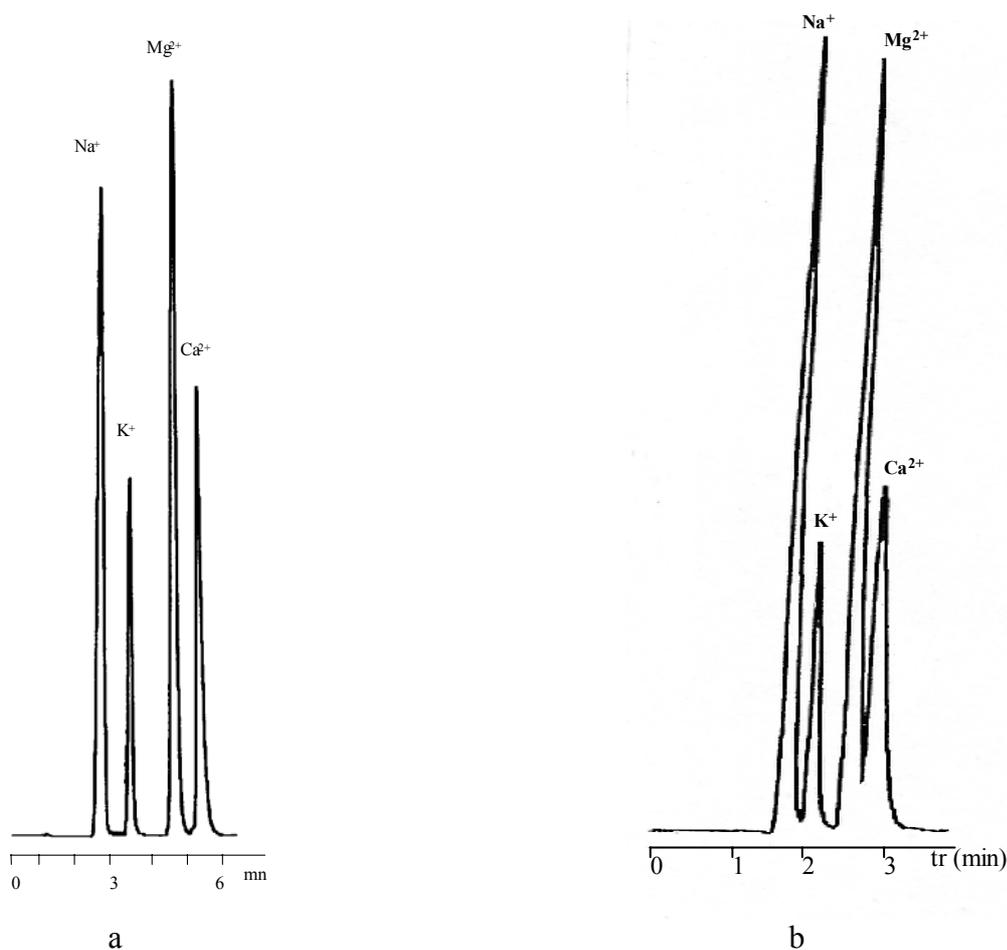
The proposed methodology has been successfully applied to the direct separation of inorganic cations with out use of complexing agents with a reasonable time. The difference of retention factors,  $k$ , of inorganic cations can be explained by the different functional groups of the two chromatographic supports. So, the ionic equilibrium of inorganic cation and functional group of Metrosep cation 1-2 is very rapid than with Lichrosil IC CA2 and also because it has two carboxylate functions provided by maleic acid.

Figure 1a,b depict, respectively, an example of a separation obtained with TFA 4 mM for a standard mixture of ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) on Lichrosil IC CA2 and Metrosep cation 1-2 columns.. After examination of two chromatograms, it appears that inorganic cations were analyzed in less than 3 min on Metrosep cation 1-2 column, but the system developed do not give a good selectivity essentially between  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The best separation was achieved by Lichrosil IC CA2 column.

Proton doesn't give adequate retention of inorganic cations on PRP-X200. So it is important to use another ion developer more eluent such as ammonium. The latter is evaporable and compatible with ELSD requirements. This study evaluate three ions developer for retention and separation of inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) on PRP-X200 provided by ammonium formate, triethylammonium formate and ethylene diammonium formate.

For evaluating the effect of ionic strength of mobile phase, we have used the potentially of PhoeBus software to give the values concentrations of ionic strength, ion developer (corresponding ammonium), co-ion ( $\text{HCOO}^-$ ) at pH 4 of each composition of eluent. Table 3 reports the different values cited below.

The ionic strength of each mobile phase at pH 4 constituted by ammonium formate or triethylammonium formate give the same value of formate concentration (mM) and practically the same value of corresponding ion developer (mM). Hence, for a mobile phase constituted by ethylene diammonium formate at pH 4, it gave the ( $\text{HCOO}^-$ ) concentration plus and ethylene diammonium concentration equal to ionic strength of mobile phase. These values of ion developers are very important to know for evaluation of eluent strength of each mobile phase for inorganic retention. The choice of a salt constituting mobile phase is very important because it generate a background (0.2 mV) less important that found with acidic eluent.



**Figure 1.** Isocratic separation of inorganic cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ )

Eluent: TFA 4 mM. Flow rate: 1.0 mL/mn; injected volume 100  $\mu\text{L}$ . Detection: ELSD Sedex 75, drift tube temperature 60°C, nebulizer gas pressure 3.5 bar, photomultiplier 9. Columns: (a) Lichrosil IC CA2, (b) Metrosep cation 1-2

Table 4 reports the retention factors,  $k$ , of inorganic cations with ionic strength of mobile phase constituting by (ammonium formate, triethylammonium formate and ethylene diammonium formate) at pH 4 on PRP-X200 Hamilton column. Whatever the concentration of ammonium formate at pH 4 permit to elute essentially monovalent cations but it is needed a concentration higher to 100 mM for eluting the divalent cations. Concerning ethylene diammonium formate in the range of studied concentrations, monovalent cations are eluted in void volume and permit the elution of divalent cations in a reasonable time. Triethylammonium formate gives an intermediate property of inorganic cations retention.

The order of eluent strength is: ammonium < triethylammonium < ethylene diammonium. In the light of these results, it appeared that the use of PRP-X200 Hamilton column with ammonium formate gradient elution should provide an efficient means of analyzing in a single run, monovalent and divalent cations. Unlike conductivity detection, ELSD is compatible with gradient elution mode since its detection principle is linked to mobile phase volatility. Figure 2 depicts a chromatogram

illustrating a satisfactory resolution in 11 min of a standard mixture of ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ).

**Table 3.** Values of ionic strength (mM), concentrations of ion developer (Ammonium), co-ion ( $\text{HCOO}^-$ ) of different amounts of ammonium formate, triethyl ammonium formate and ethylene diammonium formate at pH 4

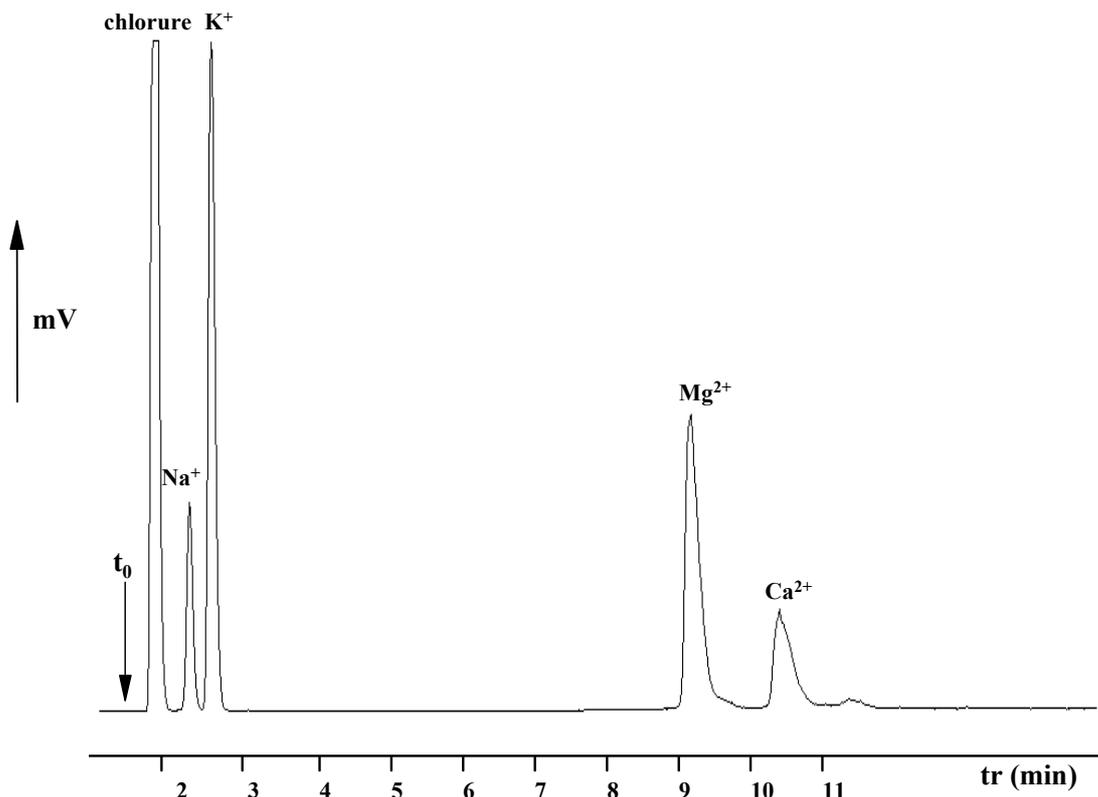
Mobile phase	Ionic strength (mM)	Ammonium concentration (mM)	Formate concentration (mM)
Ammonium formate pH 4	50	49.9	50
	20	19.9	20
	10	9.9	10
	5	4.9	5
	2	1.9	2
Triethyl ammonium formate pH 4	30	29.9	30
	20	19.9	20
	10	9.9	10
	5	4.9	5
	2	1.9	2
Ethylenediammonium formate pH 4	30	10.0	20.0
	20	6.6	13.4
	10	3.3	6.7
	5	1.6	3.4
	2	0.6	1.4

**Table 4.** Retention factors,  $k$ , of inorganic cations on a Hamilton PRP-X200 column with different mobile phases constituted of aqueous solution of formic acid, ammonia and ethylene diammonium in variable amounts

Mobile phase	Ionic strength (mM)	Retention factor (k)			
		$\text{Na}^+$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
Ammonium formate pH 4	50	0.2	0.3	5.9	10
	20	0.7	1.0	35.4	- <sup>a</sup>
	10	1.6	2.1	-	-
	5	3.1	4.2	-	-
	2	5.4	7.2	-	-
Triethyl ammonium formate pH 4	30	0.03	0.20	1.98	1.75
	20	0.16	0.22	5.41	8.22
	10	0.24	0.36	-	-
	5	0.37	0.54	-	-
	2	1.18	1.52	-	-
Ethylene diammonium formate pH 4	30	0.0	0.0	0.1	0.2
	20	0.0	0.0	0.3	0.7
	10	0.0	0.0	0.8	1.3
	5	0.1	0.0	1.8	2.7
	2	0.4	0.3	7.0	11.1

<sup>a</sup> - not eluted

These solutes are detected by ELSD, following separation on the cation-exchange with salt gradient elution which consisted of an aqueous solution of 20 mM ammonium formate for 4 min then a step gradient to aqueous solution of 100 mM ammonium formate for 10 min for a total run time of 14 min. A good selectivity between last eluted monovalent cation  $K^+$  and first eluted divalent cation  $Mg^{2+}$  is observed. So this is the first time that alkali and alkaline earth cations have been simultaneously analyzed on PRP-X200 Hamilton using gradient elution with good selectivity.



**Figure 2.** Inorganic cations ( $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ) separation

Column Hamilton PRP-X200 (150 x 4.1 mm I. D.). Step gradient elution: aqueous solution of 20 mM ammonium formate during 4 min then step gradient to aqueous solution of 100 mM ammonium formate during 10 min; flow rate: 1.0 mL/min; injected volume 100  $\mu$ L. Detection: ELSD Sedex 75, drift tube temperature 60°C, nebulizer gas pressure 3.5 bar, photomultiplier 9.

### Limit of detection (LOD) and calibration curves

In order to achieve accurate quantitative analysis of inorganic cations ( $Na^+$ ,  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$ ), calibration curves have been carried out with TFA 4 mM as aqueous mobile phase in an isocratic mode. Although the variation of the ELSD response is very complex, it was assumed that in a large range of sample size the measured peak area could be related to sample size by the following relation:  $A = aC^b$ . Where  $b$  is the slope of the response line,  $C$  is the solute concentration, and  $a$  is the response factor. As a result, the linearity between peak area response,  $A$ , and concentration is obtained in double logarithmic coordinates [22, 23] according to:  $\text{Log } A = b \text{ Log } C + \text{Log } a$ . For each cation, linear logarithmic curves have been obtained in two different concentration

ranges: 1 to 100 mg/L (20 µL injected volume) and 0.2 to 10 mg/L (100 µL injected volume), using six replicate injections. Seven different concentrations of standard solutions were prepared in the range 1 to 100 mg/L (1, 2, 5, 10, 20, 50, 100 mg/L) and six different concentrations of standard solutions in the range 0.2 to 10 mg/L (0.2, 0.5, 1, 2, 5, 10 mg/L). Curves parameters are reported in Table 5. For the four cations studied, graphs were linear with acceptable correlation coefficient ( $R^2$  better than 0.9977). Slope  $b$  mentioned in the literature has generally comprised between 1 and 1.6 with 1.3 being the most representative value [22, 23]. Slopes obtained for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are contained in the expected interval.

**Table 5.** Calibration curves  $\log A = b \log C + \log a$  for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$

Solute	b	log a	Correlation coefficient ( $R^2$ )
Concentration range: 1-100 mg/L			
$\text{Na}^+$	1.45	3.77	0.9989
$\text{K}^+$	1.51	3.25	0.9993
$\text{Mg}^{2+}$	1.43	4.24	0.9977
$\text{Ca}^{2+}$	1.40	3.72	0.9997
Concentration range: 0.2-10 mg/L			
$\text{Na}^+$	1.52	5.16	0.9996
$\text{K}^+$	1.65	4.64	0.9991
$\text{Mg}^{2+}$	1.65	5.49	0.9989
$\text{Ca}^{2+}$	1.53	5.05	0.9995

Studied concentrations ranges: 1 to 100 mg/L and 0.2 to 10 mg/L.

A = measured peak-area, C = cation concentration, b = slope, log a = y-intercept

The mechanism of the light scattering by particles is complex and may result from different contributions [22, 23]. The results shown in Table 5 indicate that both the slope  $b$  and the detector response, log a, depend not only on the nature and concentration range of analyte but also on the sample volume injected. The repeatability of the analysis expressed by the relative standard deviation of the area of each inorganic cation peak has been also evaluated. The repeatability determined from six replicate injections was satisfactory for all the inorganic studied  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and the deviation varies from 1.2% to 2.6%. Using the most sensitive range of the ELSD, a 10 ng (100 µL of 100 µg/L) LOD of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and a 25 ng (100 µL of 250 µg/L) LOD of  $\text{K}^+$  are obtainable, at a signal-to-noise ratio of 3.

## CONCLUSION

Separation of both alkali ( $\text{Na}^+$ ,  $\text{K}^+$ ) and alkaline earth cations ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) was achieved by IEC and ELSD using isocratic elution conditions with proton as ion developer provided by TFA on Lichrosil IC CA2 in about 6 min and on Metrosep cation 1-2 in less than 3 min. The resulting selectivity is better for Lichrosil IC CA2 than for Metrosep cation 1-2 particularly to ward ( $\text{Na}^+/\text{K}^+$ ) and ( $\text{Mg}^{2+}/\text{Ca}^{2+}$ ). A step gradient was optimized for separation of ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ) on PRP-X200 with ammonium as ion developer in less than 10 min. The high resolution between the cation allows the quantization of low levels of one in the presence of high levels of the other. Such a

chromatographic system also permits quantization of low levels of non-volatile ions in the presence of high levels of volatile ion (as ammonium) without any base line perturbation.

## REFERENCES

1. Small, H., Stevens T.S., Bauman, W.C.: *Analytical Chemistry*, **1975**, **47**, 1801.
2. Ohta, K., Morikawa, H., Tanaka, K., Haddad, P.R.: *Journal of Chromatography A*, **1998**, **804**, 171.
3. Mc Aleese, D.L.: *Analytical Chemistry*, **1987**, **59**, 541.
4. Fritz, J.S., Gjerde, D.T., Becker, R.M.: *Analytical Chemistry*, **1980**, **52**, 519.
5. Singh, R.P., Abbas, N.M.: *Journal of Chromatography A*, **1996**, **733**, 93.
6. Sevenich, G.J., Fritz, J.S.: *Journal of Chromatography*, **1985**, **347**, 147.
7. Nuwenborg, J.E.V., Stockl, D., Thienpont, L.M.: *Journal of Chromatography A*, **1997**, **770**, 137.
8. Hajos, P.: *Journal of Chromatography A*, **1997**, **789**, 141.
9. Kim, J.H., Lee, J.H.: **1997**, **782**, 140.
10. Tanaka, K., Ohta, K., Haddad, P.R., Fritz, J.S.: *Journal of Chromatography A*, **1998**, **804**, 179.
11. Hodge, E.M., Martinez, P., Sweetin, D.: *Journal of Chromatography A*, **2000**, **884**, 223.
12. Ohta, K.: *Journal of Chromatography A*, **2000**, **884**, 113.
13. Paull, B., Macka, M., Haddad, P.R.: *Journal of Chromatography A*, **1997**, **789**, 329.
14. Kallio, M.P., Manninen, P.K.G.: *Analytica chimica acta*, **1995**, **314**, 67.
15. Hong, U.S., Kown, H.K., Nam, H., Cha, G.S., Kown, K.H., Paeng, K.: *Analytica chimica acta*, **1995**, **315**, 303.
16. Ohta, K., Sando, M., Tanaka, K., Haddad, P.R.: *Journal of Chromatography A*, **1996**, **752**, 167.
17. El Haddad, M., Lazar, S., Akssira, M., Dreux, M.: *Journal of separation science*, **2002**, **25**, 23.
18. El Haddad, M., Mamouni, R., El Antri, S., Khouili, M., Akssira, M., Dreux, M., Lazar, S.: *Journal of liquid chromatography & related technologies*, **2003**, **26**, 3115.
19. Kolla, P., Kohler, J., Schromburg, G.: *Chromatographia*, **1987**, **23**, 465.
20. Jensen, D., Weiss, J., Rey, M.A., Pohl, C.A.: *Journal of Chromatography*, **1993**, **640**, 65.
21. Djerde, D.T., Fritz, J.S.: *Ion chromatography*, 2<sup>nd</sup> Ed., Huthing, Heidelberg, **1987**.
22. Stolyhwo, A., Colin, H., Martin, M., Guichon, G.: *Journal of Chromatography*, **1984**, **288**, 253.
23. Oppeinheimer, L.E., Mourey, T.H.: *Journal of Chromatography*, **1985**, **323**, 297.