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Analysis capability of alkylphosphonic acids and inorganic anions in aqueous solutions by ion exchange chromatography

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Abstract

This work describes an analytical approach to achieve accurate simultaneous separation of alkylphosphonic acids (MPA, PPA and BPA) and inorganic anions (chloride, nitrate, sulfate and phosphate) in aqueous media by ion exchange chromatography with evaporative light scattering detector (IEC-ELSD) under isocratic elution mode using Dionex Ion Pac (250 x 4 mm ID) column. Herein, we demonstrate that couples (MPA/PPA) and (MPA/BPA) can be separated by IEC because a net difference of apparent between these two couples was noted. The developed chromatographic system offers a successful method to give a good separation of a mixture of MPA, PPA, chloride, nitrate, sulfate and phosphate in aqueous media without baseline derive and interferences, and with good resolution. It can be applied to the direct analysis of aqueous matrix containing low levels of alkylphosphonic acids and high levels of inorganic anions (chloride 1000 mg/L, phosphate 1000 mg/L).

1) Introduction

Linear alkylphosphonic acids are consisting of both non-polar organic hydrophobic groups and anionic inorganic hydrophilic groups. Like the related alkylsulfonates, they are used as detergents, dispersants, emulsifiers, and chelating agents. Alkylphosphonic acids are typically sparingly soluble in both organic solvents and water, but become more soluble in water when neutralized to phosphonates at neutral to high pH.

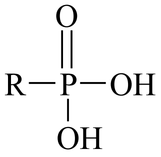
Ion exchange chromatography is the obvious method of choice for the analysis of hydrophilic organic and inorganic ions in aqueous media [1-5]. Recent methods based upon liquid chromatography [6-10] have shown that the separation of alkylphosphonic acids which have identical ionic moieties, discrete structural differences in the alkyl side chain, and consequently quite similar pKa's, [11] is difficult to obtain by a pure ion exchange mechanism.

Evaporative light scattering detector (ELSD) is generally 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. Furthermore, this detection mode has been proved to be useful for different chemical species [12-16] determination. ELSD needs a volatile mobile phase when LC-ELSD coupling is investigated,

The aim of this work is to evaluate a direct, isocratic and simultaneous analysis of alkylphosphonic acids and inorganic anions in aqueous solutions by ion exchange chromatography using an evaporative light scattering detector. Ion exchange chromatography has been investigated in this work at a working pH where the difference in the apparent charge of MPA and PPA is maximal, to promote the separation between these both alkylphosphonic acids by ionic interactions. An application of the preliminary method to spiked water containing high levels of inorganic anions is also shown.

2) Experimental

Ammonium hydrogen carbonate (NH_4HCO_3) was purchased from Fluka (St. Quentin Fallavier, France). Chloride, nitrate, phosphate, and sulfate were standard sodium salts from Sigma (St. Quentin Fallavier, France) and methylphosphonic acid (MPA) and propylphosphonic acid (PPA) and butylphosphonic acid (BPA) were purchased from Aldrich (St. Quentin Fallavier, France). All solutions were prepared from analytical reagent grade chemicals in 18 MΩ water obtained from an ELGA purification system (Antony, France). General chemical structure of alkylphosphonic acids is given in Figure 1 and Table 1 depicts some data of alkylphosphonic acids studied in this work.



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH$$

Figure 1: Chemical structure of alkylphosphonic acid

Table 1: General chemical structure of alkylphosphonic acids

Symbol	Systematic name	R-Group	pK_{a1}	pK_{a2}
MPA	Methylphosphonic acid	$-CH_3$	2.35	7.10
PPA	Propylphosphonic acid	$-(CH_2)_2-CH_3$	2.49	8.18
BPA	Butylphosphonic acid	$-(CH_2)_3-CH_3$	2.59	8.19

In a typical procedure, the necessary amount of ammonium hydrogen carbonate to produce the desired salt concentration in the mobile phase was weighed and dissolved in distilled water. The pH of each mobile phase was checked on a Beckman pH meter, model φ 10 (Gagny, France) and a value of pH equal to 7.8 was measured for the three salt concentrations studied (10 mM, 15 mM, and 20 mM). The apparent charge of the eluent anion, the ionic strength, and the buffer capacity of each eluent were calculated with the help of Phoebus software (Sedere Co., Franklin MA, USA). All concentrations of alkylphosphonic acids are of 200 mg/L.

The liquid chromatographic apparatus consisted of a Gilson (Villiers-le-Bel, France) Model 302 isocratic pump, a Rheodyne (Berkeley, CA, USA) Model 7125 injector with a 20 µL sample loop and an ELSD (Sedere, Alfortville, France) Model Sedex 45. The usual settings were as follows: photomultiplier, 9; evaporative temperature, 40°C; air pressure, 2.2 bar. A (150 x 3 mm I.D.) anion exchange column (Anion Dual 1, Metrohm) equipped with a guard column. Data were processed using a Shimadzu (Kyoto, Japan) Model CR 5A integrator.

3) Results and discussion

3.1) Study of apparent charge distribution of alkylphosphonic acid

In aqueous media, alkylphosphonic acid can be dissociated as described by the following chemicals equilibriums (1) and (2) given below:

$$APH_2 + H_2O \rightleftharpoons APH^- + H_3O^+ \quad \textbf{(1)}$$

$$APH^- + H_2O \rightleftharpoons AP^{2-} + H_3O^+ \quad \textbf{(2)}$$

Where:

APH_2 represent non dissociated form of alkylphosphonic acid. APH^- and AP^{2-} are mono- and di-anionic forms of acid alkylphosphonic.

Constants acidity of chemicals equilibriums are expressed by the equations (3) and (4):

$$K_{a1} = \frac{[APH^-][H_3O^+]}{[APH_2]} \quad \textbf{(3)}$$

$$K_{a2} = \frac{[AP^{2-}][H_3O^+]}{[APH^-]} \quad \textbf{(4)}$$

Equation (5) depicts the conservation of the matter in function with total concentration of alkylphosphonic acid $[AP]_0$, neutral form APH_2 and mono and di anionic forms (APH^- and AP^{2-}) as follows:

$$[AP]_0 = [APH_2] + [APH^-] + [AP^{2-}] \quad \textbf{(5)}$$

The concentrations of all chemical species can be expressed by the following expressions:

$$[APH_2] = \frac{[H_3O^+]^2}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}[AP]_0 \quad \textbf{(6)}$$

$$[APH^-] = \frac{K_{a1}[H_3O^+]}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}[AP]_0 \quad \textbf{(7)}$$

$$[AP^{2-}] = \frac{K_{a1}K_{a2}}{[H_3O^+]^2 + K_{a1}[H_3O^+] + K_{a1}K_{a2}}[AP]_0 \quad \textbf{(8)}$$

Apparent charge Z_i of each alkylphosphonic acid can be expressed by the following equation:

$$Z_i = \frac{\sum n[AP^n]}{[AP]_0} \quad \textbf{(9)}$$

$[AP^n]$ is the concentration of the corresponding from of alkylphosphonic acid with n charge. The difference between apparent charges ΔZ_i of two different alkylphosphonic acids can be expressed as follows:

$$\Delta Z_i = \left|Z_i(AP_1) - Z_i(AP_2)\right| \quad \textbf{(10)}$$

Figures 2, 3 and 4 depict the distribution of apparent charges versus pH of two couples of alkylphosphonic acids (MPA/PPA), (MPA/BPA) and (PPA/BPA) respectively. From these Figures, apparent charge of MPA, PPA and BPA decreases with increasing pH (0-14). As can be seen in Figure 2, MPA and PPA present a similarity of apparent charge under pH 6. Starting from this pH and up to pH 10, it appears a different distribution of apparent charge. This result allows us to realize a separation of both MPA and PPA by ion exchange chromatography. Furthermore, this behavior can be explained by the different inductive donor effect. In the range of pH (6-10), apparent charge of PPA is higher than of MPA. From Figure 3, similar results were obtained with the couple (MPA/BPA).

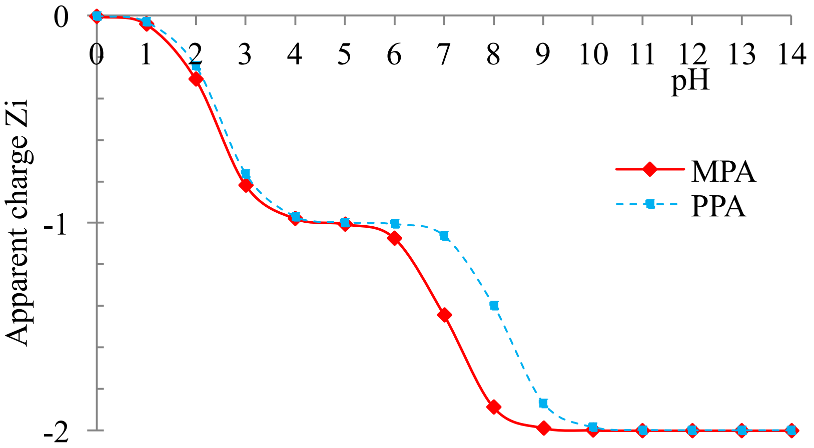


Figure 2: Apparent charge distribution versus pH of (MPA/PPA)

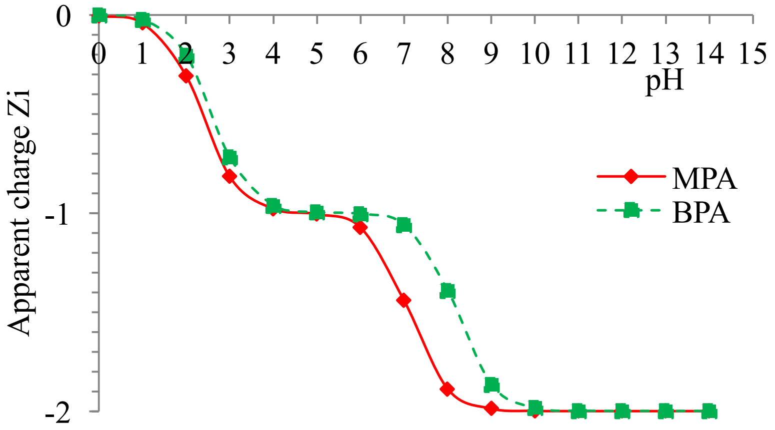


Figure 3: Apparent charge distribution versus pH of (MPA/BPA)

The most interesting result is to see the difference of apparent charges of MPA and BPA with a pH comprised between 6 and 10. Also, in the range of pH (6 – 10), apparent charge of BPA is higher than of MPA. Such result can be explained by the higher inductive donor effect of butyl group than methyl group. So, the separation between MPA and BPA can be achieved by ion exchange chromatography. Unfortunately as can be seen in Figure 4, the distribution of apparent charge of PPA and BPA present the same profile without any variation. This behavior can be explained perhaps by the fact that butyl and propyl groups have the approach inductive donor effect. Thus, the separation of PPA and BPA by ion exchange chromatography will be impossible.

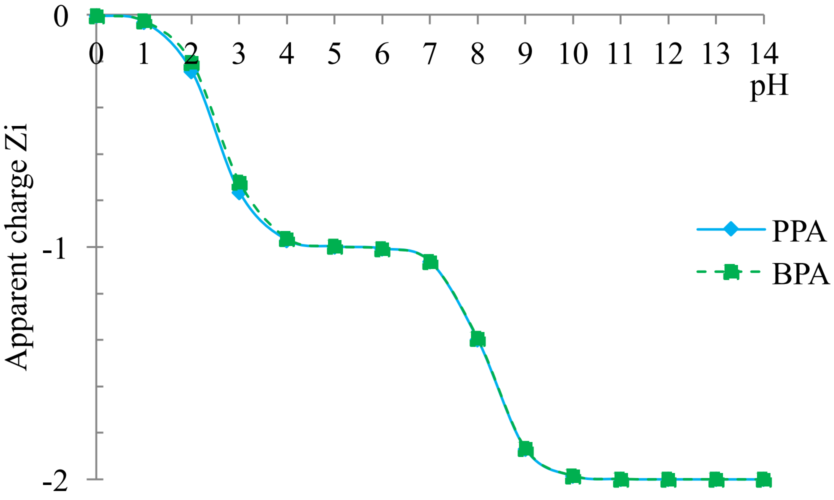


Figure 4: Apparent charge distribution versus pH of (PPA/BPA)

Figures 5, 6 and 7 depict the difference between apparent charges of two couples of alkylphosphonic acids (MPA/PPA), (MPA/BPA) and (PPA/BPA) versus pH respectively.

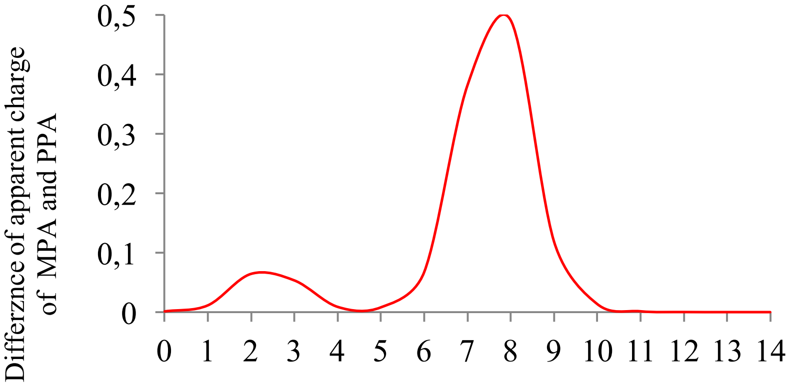


Figure 5: Difference of apparent charge between MPA and PPA versus pH

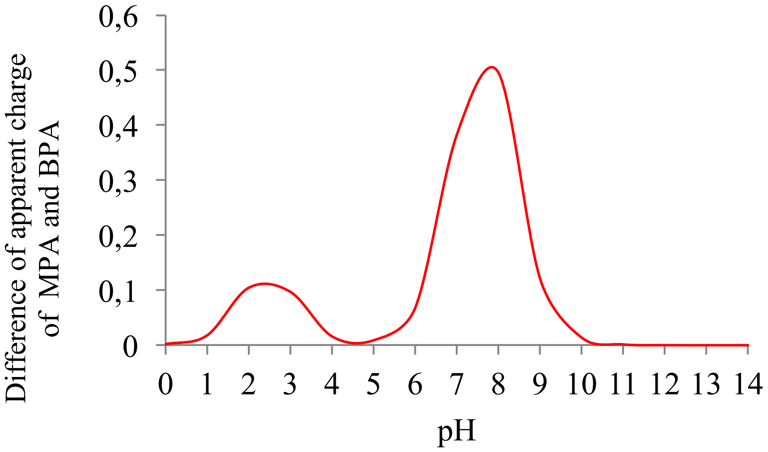


Figure 6: Difference of apparent charge between MPA and BPA versus pH

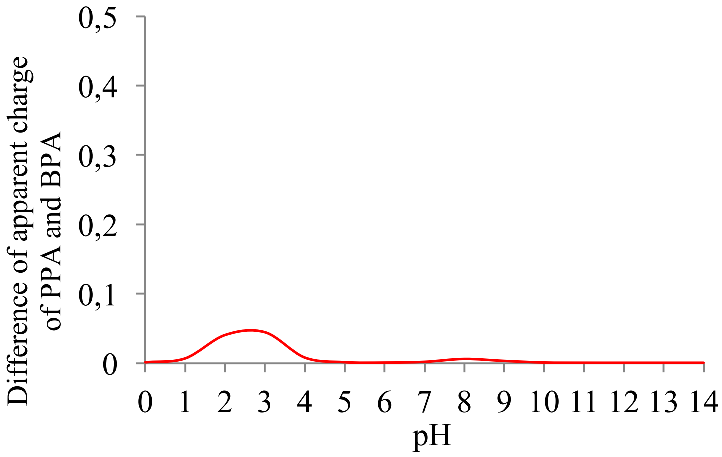


Figure 7: Difference of apparent charge between PPA and BPA versus pH

Net maximum of the difference between apparent charges was observed for the two couples (MPA/PPA) and (MPA/BPA) as can be seen from the Figures 5 and 6. In the light of these Figures, it appears that the maximum reached a value of 0.5 under pH condition close to 7.8. The resulting curve depicted in Figure 7 shows no significant maximum of the difference of apparent charge between PPA and BPA versus pH.

3.2) Chromatographic study of alkylphosphonic acids and inorganic anions

Figure 8 depicts the retention factors (k) of MPA, PPA and BPA versus NH_4HCO_3 concentration (10-20 mM). The choice of hydrogen carbonate as ion developer is in the basis of requirements of ELSD use. Herein we choose ammonium hydrogen carbonate as salt of the composition of mobile phase for the following chromatographic studies. Hence, the addition in the aqueous mobile phase of a common competing agent for ion exchange chromatography should be compatible with ELSD volatility requirements. Ammonium hydrogen carbonate (NH_4HCO_3) was selected to compose the volatile mobile phase for several reasons. Dissolution of ammonium hydrogen carbonate in water, give a value of pH of 7.8 respectively for 10 mM, 15 mM, and 20 mM as concentration of the salt in aqueous solution. Thus, we don't need any adjustment of the eluent pH. Furthermore, the buffer capacity of the eluent varied from 1.2 mM/pH unity to 3.8 mM/pH unity, was sufficient to avoid any variation of pH buffer into the chromatographic system. Consequently, this allowed us to obtain reproducible capacity factors even with different preparations of mobile phase.

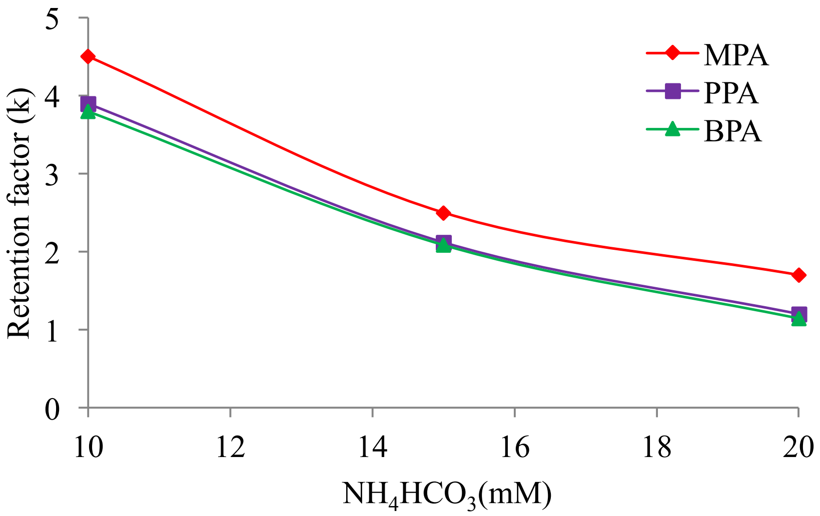


Figure 8: Retention factors (k) of alkylphosphonic acids versus NH_4HCO_3 concentration

Whatever the alkylphosphonic, the retention factor (k) decreases when increasing the concentration of developer ion in mobile phase. MPA was the more retained solute and was well separated between PPA and BPA. While, PPA and BPA offer the same behavior overlooked stationary phase because these two solutes don't present a significant difference of apparent charges as can be seen in Figure 4. Table 2 shows the selectivity between all studied alkylphosphonic acids (MPA, PPA and BPA) versus NH_4HCO_3 concentration. An obvious result was found such constant selectivity between PPA and BPA.

Table 2: Selectivity between all studied alkylphosphonic acids versus NH_4HCO_3 concentration

NH_4HCO_3 concentration	(BPA/PPA)	(MPA/PPA)	(MPA/BPA)
10 mM	1.02	1.15	1.18
15 mM	1.04	1.18	1.19
20 mM	1.04	1.42	1.48

The selectivities for the couples (MPA/PPA) and (MPA/BPA) are superior to unity suggesting the separation possibility. In addition to this for the two couples the selectivity can be improved by increasing NH_4HCO_3 concentration. Furthermore, the selectivity of the two couples (MPA/PPA) and (MPA/BPA) were comparable. Figure 9 describes the profile separation of the three couples (MPA/PPA), (MPA/BPA) and (PPA/BPA).

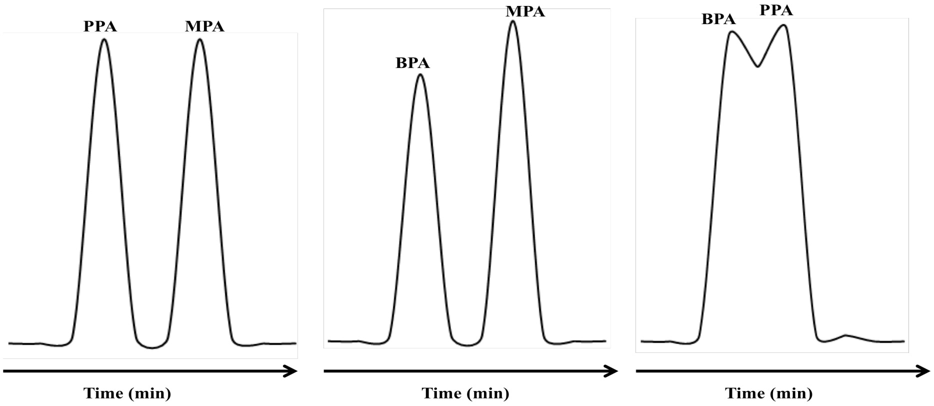


Figure 9: Separation profiles of the different alkylphosphonic acids couples (MPA/PPA), (MPA/BPA) and (PPA/BPA)

The retention factors of four common inorganic anions (chloride, nitrate, sulfate and phosphate) and of alkylphosphonic acids (MPA, PPA and BPA) have been achieved at different ammonium hydrogen carbonate concentrations in the aqueous mobile phase (25 mM, 15 mM, and 10 mM) and are reported in Figure 10. As usually observed in ion chromatography, a decrease in the competing ion concentration in the eluent (20 mM to 10 mM) involves an increase in the anion retention factor. The elution order of inorganic anions depends on their apparent charge. For inorganic anions, di-anion species (phosphate and sulfate) were eluted after mono-anions, such as chloride and nitrate. For alkylphosphonic anions, MPA is more retained than PPA and BPA at pH 7.8.

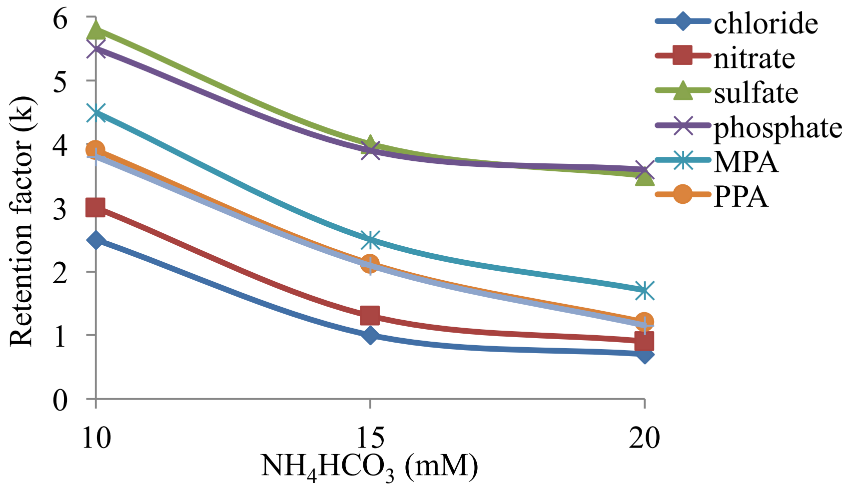


Figure 10: Retention factors of chemical species versus NH_4HCO_3 concentration

Apparent charges of MPA, PPA and BPA are comprised between – 1 and – 2. The elution order of the mixture organic and inorganic anions with an eluent constituted by NH_4HCO_3 10 mM is as follows:

Chloride < nitrate < PPA = BPA < MPA < phosphate < sulfate

A co-elution has been noted in this order because BPA and PPA have a similarity distribution of apparent charge. Figure 11 depicts the selectivity of adjacent species studied in this mixture. Thus, several behaviors can be seen. The bad results are shown for couple (PPA/BPA) whatever the concentration of ion developer. An any way PPA and BPA can be well separated.

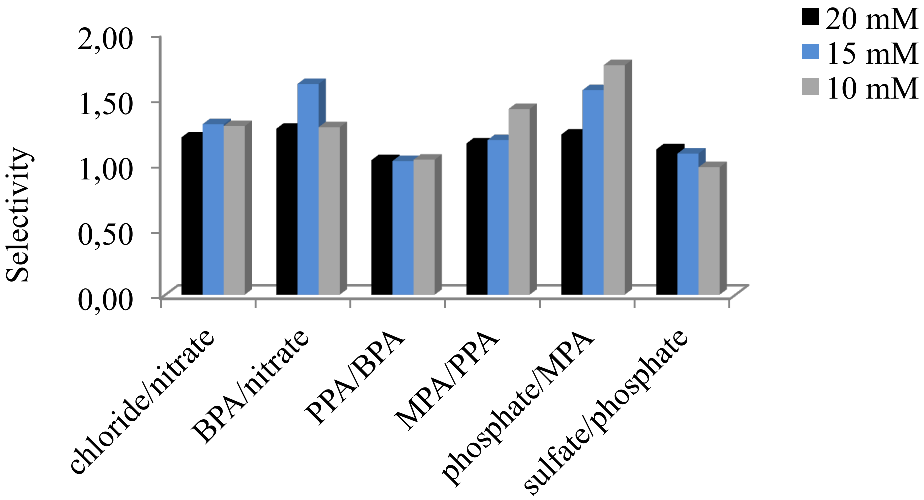


Figure 11: Selectivity study of chemical adjacent species versus NH_4HCO_3 concentration

Figure 12 represents an example of simultaneous separation of MPA, PPA, chloride, nitrate, sulfate and phosphate.

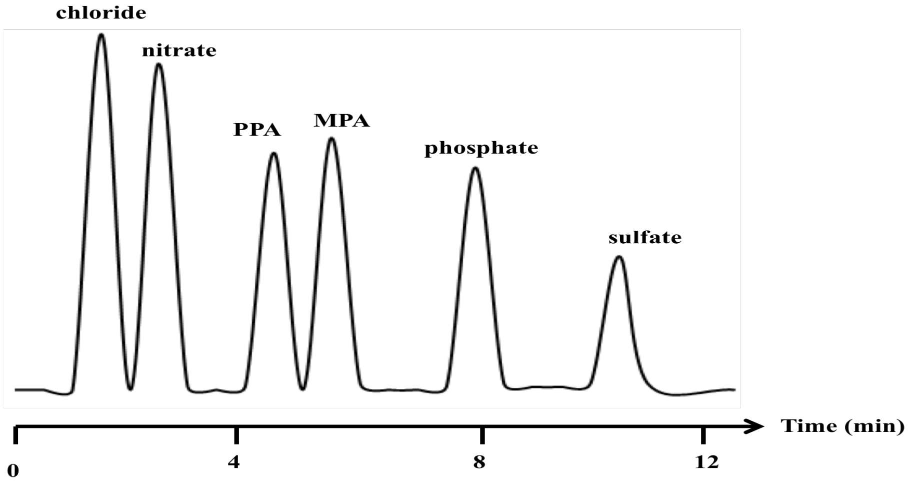
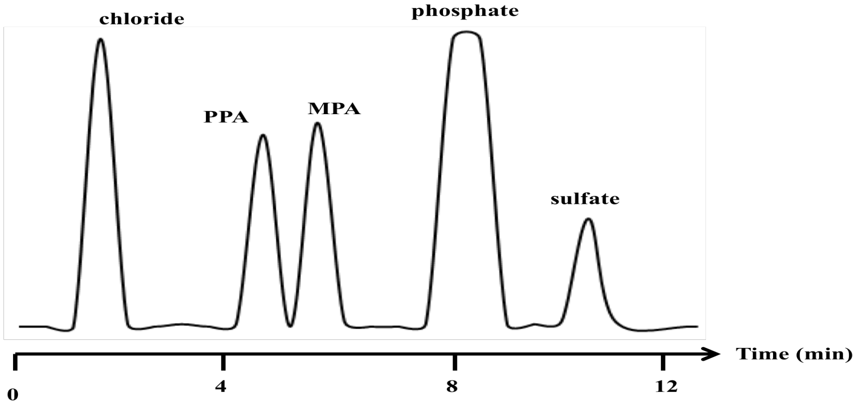


Figure 12: Profile of simultaneous separation of inorganic anions and alkylphosphonic acids (PPA and MPA)

In order to demonstrate the effect of charged matrix with inorganic anion onto the separation quality of MPA and PPA, we have achieved accurate analysis with matrix reached with chloride (1000 mg/L) and with other matrix reached with phosphate (1000 mg/L). These analysis proved that the separation quality of MPA and PPA are not affected with higher concentrations of chloride or phosphate. Figure 13 depicts the chromatograms of the separations. The two separations were achieved without perturbation of baseline and without any interference.

a) Phosphate (1000 mg/L)



b) Chloride (1000 mg/L)

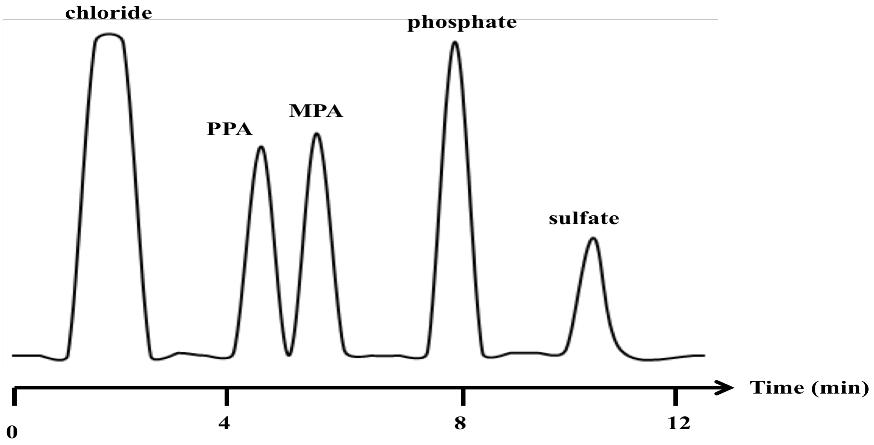


Figure 13: Profile separations of MPA and PPA in matrix rich with phosphate (1000 mg/L) (a) and with chloride (1000 mg/L) (b)

Conclusion

This work illustrates the separation of two alkylphosphonic MPA and PPA, using ion exchange chromatography at controlled pH in the presence of common inorganic anions of aqueous media. The choice of adequate pH (pH 7.8) allows an elution order according to the apparent charge of the two alkylphosphonic acids: PPA then MPA, with satisfactory baseline resolution.

Moreover, the proposed chromatographic system can be used for the direct and simultaneous determination of PPA and MPA in aqueous media, since inorganic anions such as chloride, nitrate, sulfate, and phosphate do not coelute with alkylphosphonic anions. The presence of such inorganic anions, even at high concentration, does not perturb the separation of PPA and MPA, thus, good resolution has been obtained.

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References

1. C. Foulon, P. Giulio, M. Lecoeur, *J. Chromatogr. A*, 1534 (2018) 139-149.
2. Y. Fa, Y. Yu, F. Li, F. Du, X. Liang, H. Liu, *J. Chromatogr. A*, 1554 (2018) 123-127.
3. A.S. Uzhel, A.V. Zatirakha, A.D. Smolenkov, O.A. Shpigun, *J. Chromatogr. A*, 1567 (2018) 130-135.
4. K. Zhang, C. Lou, Y. Zhu, M. Zhi, X. Zeng, *Talanta* 184 (2018) 491-498.
5. M. El Haddad, R. Mamouni, M. Ridaoui, S. Lazar, *J. Saudi Chem. Soc*., 19 (2015) 108-111.
6. T. Baygildiev, A. Zatirakha, I. Rodin, A. Braun, A. Stavriaudi, N. Koryagina, I. Rybalchenko, O. Shpigum, *J. Chromatogr. B*, 1058 (2017) 32-39.
7. T. Baygildiev, I. Rodin, A.N. Stavriauidi, A.V. Braun, A.T. Lebedev, I. Rybalchenko, *J. Chromatogr. A*, 1442 (2016) 19-25.
8. C. Liu, G. Huang, H. Xi, L. Yuan, *J. Chromatogr. B*, 1036-1037 (2016) 57-65.
9. A. Appel, B. Logue, *J. Chromatogr. B*, 1031 (2016) 116-122.
10. A. Weissberg, M. Madmon, S. Dagan, *Inter. J. Mass Spectrom*., 408 (2016) 20-27.
11. J.P. Mercier, Ph. Morin, M. Dreux, A. Tambute, *Chomatographia,* 48 (1998) 529-534.
12. C. Foulon, P. Diulio, M. Lecoeur, *J. Chromatogr. A*, 1534 (2018) 139-149.
13. R. Parmar, A. Ghanta, R. Haware, P. Johnson, W. Stagner, *J. Pharm. Sci*., 105 (2016) 3603-3610.
14. C. Annaratone, A. Roeck, M. Hertogi, B. Nicolai, *Food Chem*., 229 (2017) 296-303.
15. A. Domenech, E. Alfonso, G. Ramos, *Anal. Chim. Acta*, 932 (2016) 106-113.
16. Z. Tan, P. Ihnat, V. Nayak, R. Russel, *Pharm. Biomed. Anal*., 59 (2012) 167-172.

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