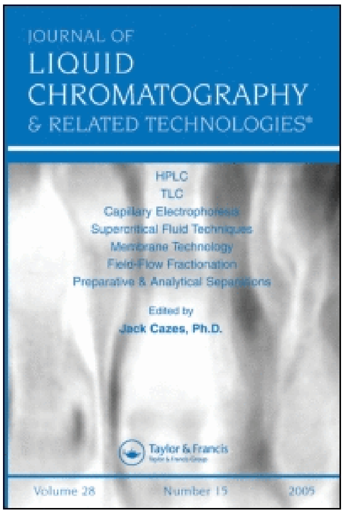

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RETENTION OF ANIONS AS A FUNCTION OF MOBILE PHASE pH IN ION-INTERACTION RP-HPLC

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ABSTRACT

Retention of typical anions as a function of pH of the mobile phase in reversed-phase ion-interaction chromatography was studied.

The different behaviours observed for anions of acids characterized by different pK_a values were discussed, in comparison with literature results obtained in reversed-phase and in reversed-phase ion-pair chromatography.

INTRODUCTION

Many separation methods in reversed-phase HPLC chromatography make use of ion-pair mechanisms, in order to improve the chromatographic response (1,2). These technique are generally reported as reversed-phase ion-pair or ion-interaction chromatography and make use of a reversed-phase stationary-phase. In most of these methods the ion-pairing agent is added to the water-organic mobile phase to form an ion-pair with the analyte, which due to its increased lipophilic properties is retained onto the reversed-phase column, without necessarily implying a modification of its surface.

Less used is the technique employed in our laboratories (3-5), in which the mobile phase is an aqueous solution of the interaction reagent. We propose that the methods which employ a mobile phase containing an organic component are called, as usually, ion-pair chromatography and the methods in which the mobile phase is an aqueous solution are refered as ion-interaction chromatography, in consideration that ionic-interaction mechanisms here predominate, with respect to adsorption mechanisms. The mechanism model in fact which characterizes ion-interaction chromatography assumes that the interaction reagent (which represents the mobile phase), when flowing under isocratic conditions, induces a dynamic modification of the surface of the reversed-phase stationary phase (6). The hydrophobic cation of the interaction reagent (for example $CH_3(CH_2)_nNH_3^+$ alkylammmonium) is adsorbed onto the $C_{18}H_{37}$-bonded apolar surface of the stationary phase, forming a primary positively-charged ion layer. In a second step, the counter-anion A^- is bound as well through electrostatic forces , to form an oppositely-charged diffuse layer. The alkylammonium ion and the counter-ion A^- give likely rise to an ion-pair which is adsorbed onto the stationary phase and at the same time participates to the equilibrium with its ions flowing in the mobile phase:

$$(CH_3(CH_2)_nNH_3^+ \, . \, A^-)_{adsorbed} ===== CH_3(CH_2)_nNH_3^+ + A^- \quad (1)$$

Due to the electrical double-layer adsorbed onto it, the surface of the original C-18 stationary phase has been modified into a new stationary phase characterized by anionic and cationic retention properties. The new column obtained, which might be called "catanionic" (in analogy with the catanodic current- potential curve) is in fact able to retain both anionic and cationic analytes, through the formation of ion-pairs respectively with the alkylammonium ion and its anion A-.

Of course, these processes can take place in pH conditions in which the species involved are present as ionized form, i.e. anions are dissociated and amines protonated. The acidic dissociation constants of the components of the interaction reagent as well as of the analytes must therefore be taken into account when planning pH working conditions.

The methods already developed in this laboratory for the separation of anions, amines, amides and imides (3-5) have been performed at pH 6.4, at which many anions are dissociated and many N-containing organic bases are protonated. Retention was shown to depend on the alkyl chain length and on the concentration of the interaction reagent and these effects have been investigated (5). In the present paper we study the effect induced on the retention of typical anions by varied pH conditions of the mobile phase.

Two effects can be expected. The first is directly connected with the molar fraction of the dissociated form of the analyte as a function of the acidic dissociation constant and the second effect could come from a pH-dependence of the composition of the moiety adsorbed onto the stationary phase surface.

Literature reports investigations concerning the effect induced on retention of anions by pH variations of the mobile phase (1,2,7-17). Generally, the capacity factor depends on the acidic dissociation constant of the acid, but different behaviours are observed in reversed-phase chromatography and in reversed-phase ion-pair chromatography (1,2,8,14-17). In this paper the dependence of retention on pH is investigated in reversed-phase ion-interaction chromatography, in which, as mentioned, the mobile phase is an aqueous solution, in the total absence of organic modifier .

MATERIALS AND METHODS

Apparatus

Analyses were carried out with a Merck-Hitachi Lichrograph chromatograph Model L-6200, equipped with a two-channel Merck-Hitachi model D-2500 Chromato-integrator, interfaced with a UV-vis detector model L-4200 and a L-3720 conductivity detector with temperature control, of the same firm.

A Metrohom 654 pH-meter equipped with a combined glass-calomel electrode was employed for pH measurements and a Hitachi mod.150-20 spectrophotometer for absorbance measurements.

Chemicals and Reagents

Ultrapure water from Millipore Milli-Q was used for the preparation of all solutions. Sodium nitrite, sodium nitrate, sodium bromide, sodium iodide, ascorbic acid and methanol were Merck analytical grade reagents. Octylamine, sodium azide and sodium bromate were Fluka analytical grade chemicals. Potassium thiocyanate was C.Erba analytical grade chemical.

Chromatographic conditions

A 5 µm ODS-2 Spherisorb Phase Separation column fully end-capped 250.0 x 4.6 mm with a carbon load of 12% (0.5 mM/g) and a 5 µm Merck Polyspher RP-18 250.0 x 4.0 mm were used , together with a 150.0 x 4.6 mm Lichrospher RP-18 , 5 µm guard pre-column.

The solutions to be used as mobile phase were prepared by adding to the amount of octylamine weighed to prepare a 5.0 mM solution the required amount of ortho-phosphoric acid up to get the desired pH value. The solutions prepared at the different pH values contained therefore the same analytical concentration of octylamine (5.0 mM) and different analytical concentrations of the acid. With this procedure the presence in the mobile phase of any other component different from octylamine and o-phosphoric acid is avoided.

The chromatographic system was conditioned by passing the eluent through the column until a stable baseline signal was obtained; a minimum of 1 hour was necessary. This procedure was always followed when a new mobile phase was used. After use, the column was washed and regenerated by flowing a 50/50 v/v water/methanol mixture (0.5 ml/min for 1 hour). No particular degradation of the column was observed with pH variations.

RESULTS AND DISCUSSION

Experiments with polymer-based reversed-phase C-18 stationary phase.

In order to explore the widest pH range , a C-18 reversed-phase polymeric (styrene-divinylbenzene)-based stationary phase (Merck

Polyspher) whose working conditions range between pH 0 and 14 was firstly employed. The same procedures of dynamic functionalization as described for the silica-based reversed-phase columns have been employed. Several experiments under different conditions have been performed. The use of interaction reagents formed by amines characterized by different structure and chain length (such as tetrabutylammonium, aethylammonium,aethanolammonium,octylammonium,dodecylammonium) was experimented as well as of different anions, namely o-phosphate, salicylate and tartrate, in concentrations ranging between 0.5 mM and 5.0 mM. In order to allow column wettability, mobile phases containing methanol or acetonitrile in concentrations ranging between 5 and 50 % were also used. Unfortunately, in no way it was possible to obtain an appreciable and reproducible dynamic coating of this column. We cannot explain the negative result. The most relevant difference between the two stationary phases can be individuated in the lack of sylanolic residua groups in the polymer-based column. But a series of experiments previously performed for different silica-based reversed-phase stationary phases (18,19) had shown that the best results in dynamic coating were obtained with fully-endcapped stationary phases. The unsuccess in obtaining a stable dynamic functionalization of the polymeric stationary phase surface might likely be correlated to the per cent carbon load which is generally lower in polymer-based stationary-phase with respect to the silica-based ones.

Study of anions pH-dependence with a silica-based reversed--phase C-18 stationary phase.

The pH-dependence of anions retention was therefore investigated in the range imposed by a prudent use of a silica-based -C18 column and experiments in the pH range between pH 2.5 and 8.0 were performed for some typical anions. Octylamine o-phosphate was the interaction reagent and conductometric and spectrophotometric detections were comparatively employed. The dead time, evaluated through the injection of $NaNO_3$ solutions and conductometric detection of the unretained Na^+, resulted to be practically pH-independent, so that the obtained retention times at different pH values could be directly compared.

As expected, the retention of some analytes could be obtained only at pH values at which ionized forms are present. So for example at pH

8.0, the retention of phenol (pKa=10.0) (20) was obtained , which is instead precluded at lower pH values.

The following anions were studied, which all can be separated at different pH values, are characterized by different chemical properties and non null molar absorptivity at 230 nm: nitrate, bromide, bromate, iodide, tiocyanate, nitrite, hydrazoate and ascorbate.

As mentioned, two effects can be played on the retention of anions by pH variations of the mobile-phase.One arises from the acidic dissociation equilibria of the analytes and a second effect could be originated by the pH-dependence of the moiety adsorbed onto the surface of the stationary phase.

Figure 1 shows the behaviour, as a function of pH, of the capacity factors K' for anions of weak acids as nitrite (pK_a = 3.14) , hydrazoate (pK_a = 4.74) and ascorbate (pK_{1a}= 4.14, pK_{2a}= 11.57). All the plots show a maximum for intermediate pH values and could be fitted (r^2 always > 0.84) by a polynomial function of the type : $y=ax^3+bx^2+cx+d$ (y are the capacity factor, x the pH values and the coefficients a ,b,c and d for each regression are reported in the caption of figure 1). The shapes obtained are very similar to the theoretical plots predicted by Snyder in reversed-phase ion-pair chromatography (21), even if the maximum of the function corresponds to different α (fraction of the dissociated species) values.

The increase in retention observed for lower pH values is explained through the increasing concentration of the dissociated species when pH increases. For pH values > about 4, even if the molar fraction of the dissociated species is still increasing, retention decreases. This result could be ascribed to modifications induced at these pH values on the moiety adsorbed onto the surface of the stationary phase, which prevail on the effect due to the dissociation equilibria of the analytes. Other effects can furthermore intervene at higher pH values in decreasing retention, such as : a) a possible lower functionalization extent of the stationary phase , b) a lower attraction electrostatic effect exerted towards the anions by the positevely-charged first electrical layer adsorbed onto the surface (as pH increases, the molar fraction of protonated octylamine decreases) and c) a competition effect of OH^- anions for higher pH values (21).

The hypothesis that at higher pH values, retention of anions depends on the effects that pH plays on the modified stationary phase more than on

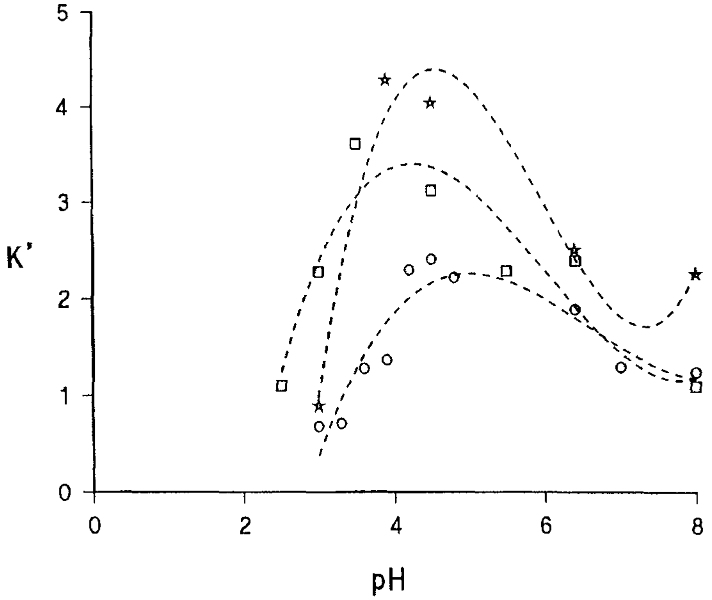

Figure 1.
Capacity factor K' (Y) as a function of pH (X).

✫ ascorbate	$Y = 0.25\,X^3 - 4.45\,X^2 + 24.97\,X - 40.62$	$r^2 = 0.9625$
□ nitrite	$Y = 0.10\,X^3 - 1.80\,X^2 + 9.94\,X - 13.88$	$r^2 = 0.8403$
○ hydrazoate	$Y = 0.07\,X^3 - 1.36\,X^2 + 8.47\,X - 14.63$	$r^2 = 0.8535$

the analyte dissociation, can find a confirm in the retention behaviour shown by anions of strong acids (figure 2), for which the unexpected retention decrease observed with pH increase is ascribable only to a pH-dependence of the moiety adsorbed onto the stationary phase.

Taking on the other hand into account that the adsorbed moiety depends on the mobile phase composition, a calculation was performed of the distribution, in the pH range between 2.0 and 11.0, of all the chemical species involved in the mobile phase. Acid-base equilibria of octylamine and o-phosphoric acid (20,22) were considered as well as ion-pair equilibria. Octylamine is reported (23) to form with o-phosphate five

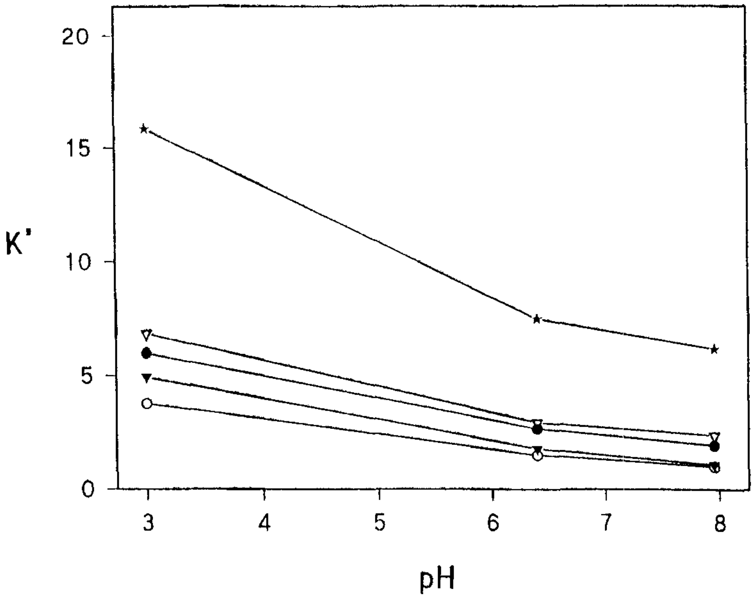

Figure 2.
Capacity factor K' as a function of pH.
★ thiocyanate, ▽ iodide, ● nitrate, ▼ bromate, ○ bromide.

differently-protonated ion-pair species (two of which present electroneutrality) containing octylamine to phosphate molar ratios equal to 1 and 2 . Table I reports the input data of: a) the analytical concentrations of octylamine and of ortho-phosphoric acid and b) the formation constants used (20,22,23) expressed according to the general equilibrium:

$$n\, OctNH_2 + p\, PO_4^{3-} + q\, H^+ ==== H_q(PO_4)_p(Oct\, NH_2)_n{}^{(3p-q)-} \quad (2)$$

and table II the results obtained. In the pH range investigated octylamine, in agreement with its dissociation constant (20), is predominantly present (>98%) under its protonated form, the remaining portion being distributed, as a function of pH, among the five ion-pair species formed with phosphate. To the two electrically-neutral ion-pairs, for their less

TABLE I

Input data for the calculation of species distribution of table II

a) analytical concentrations

pH	***Octylamine***	***o-phosphoric acid***
2.00	5.00 mM	38.0 mM
3.00	5.00 mM	5.26 mM
3.98	5.00 mM	4.58 mM
6.01	5.00 mM	4.00 mM
6.39	5.00 mM	2.94 mM
7.00	5.00 mM	2.19 mM
7.96	5.00 mM	2.00 mM
10.00	5.00 mM	1.85 mM
11.00	5.00 mM	0.24 mM

b) formation constants logarithms (logK) according to the equilibrium:

$$nOctNH_2 + p\,PO_4^{3-} + qH^+ \quad ========== \quad H_q(PO_4)_p(OctNH_2)_n^{(3p-q)-}$$

species	***logK***
H_3PO_4	22.00
$H_2PO_4^-$	19.88
HPO_4^{2-}	12.67
$OctNH_2$	10.65
$OctNH_3^+.H_2PO_4^-$	31.09
$(OctNH_3^+)_2.HPO_4^{2-}$	35.57
$OctNH_3^+.HPO_4^{2-}$	24.19
$(OctNH_3^+)_2.PO_4^{3-}$	24.28
$OctNH_3^+.PO_4^{3-}$	11.98

energetical content, the higher probability to be adsorbed onto the surface of the stationary phase must be assigned. From the data of table II, it can be observed that the sum of the concentrations of these species is decreasing as pH increases. Moreover, according to Stahlberg (24-26), Liu and Cantwell (27), different concentrations of the adsorbed moiety induce onto the stationary phase different surface potentials Ψ_0 and, as a consequence, different capacity factors (25).

TABLE II.

Calculation of species distribution (molar concentration), as a function of pH, in solutions containing octylamine and o-phosphoric acid.

Input data of analytical concentration and formation constants in table I.

pH

	2.00	3.00	3.98	6.01	6.39	7.00	7.96	10.00	11.00
$OctNH_2$	$1.1.10^{-11}$	$1.1.10^{-10}$	$1.05.10^{-9}$	$1.13.10^{-7}$	$2.71.10^{-7}$	$1.11.10^{-6}$	$1.00.10^{-5}$	$6.91.10^{-4}$	$3.34.10^{-3}$
H_3PO_4	$2.14.10^{-2}$	$6.03.10^{-4}$	$6.12.10^{-5}$	$4.76.10^{-7}$	$1.34.10^{-7}$	$1.74.10^{-8}$	$4.2.10^{-10}$	$3.2.10^{-16}$	$1.2.10^{-19}$
$OctNH_3^+.H_2PO_4^-$	$2.79.10^{-4}$	$8.17.10^{-5}$	$7.93.10^{-5}$	$6.60.10^{-5}$	$4.43.10^{-5}$	$2.37.10^{-5}$	$5.22.10^{-6}$	$2.8.10^{-10}$	$5.1.10^{-13}$
$(OctNH_3^+)_2.HPO_4^{2-}$	$<10.^{-30}$	$2.7.10^{-10}$	$6.5.10^{-30}$	$6.1.10^{-16}$	$3.67.10^{-7}$	$2.4.10^{-10}$	$1.58.10^{-6}$	$6.11.10^{-4}$	$8.11.10^{-5}$
$H_2PO_4^-$	$1.63.10^{-2}$	$4.57.10^{-3}$	$4.44.10^{-3}$	$3.69.10^{-3}$	$2.50.10^{-3}$	$1.32.10^{-3}$	$2.92.10^{-4}$	$2.47.10^{-8}$	$9.5.10^{-11}$
$OctNH_3^+.HPO_4^{2-}$	$3.51.10^{-9}$	$1.03.10^{-7}$	$9.53.10^{-8}$	$8.50.10^{-6}$	$1.39.10^{-5}$	$2.99.10^{-5}$	$6.00.10^{-5}$	$3.48.10^{-7}$	$6.47.10^{-9}$
$(OctNH_3^+)_2.PO_4^{3-}$	$<10.^{-30}$	$1.4.10^{-18}$	$6.3.10^{-27}$	$6.1.10^{-17}$	$4.6.10^{-12}$	$7.1.10^{-13}$	$7.4.10^{-10}$	$9.63.10\text{-}^{8}$	$3.32.10^{-8}$
HPO_4^-	$1.00.10^{-7}$	$2.82.10^{-6}$	$2.61.10^{-6}$	$2.33.10^{-4}$	$3.78.10^{-4}$	$8.15.10^{-4}$	$1.64.10^{-3}$	$1.52.10^{-5}$	$5.84.10^{-7}$
$OctNH_3^+. PO_4^{3-}$	$2.1.10^{-19}$	$6.3.10^{-17}$	$5.6.10^{-16}$	$5.4.10^{-11}$	$2.1.10^{-10}$	$1.8.10^{-10}$	$3.37.10^{-9}$	$2.15.10^{-9}$	$4.0.10^{-10}$
PO_4^{3-}	$2.1.10^{-18}$	$6.0.10^{-17}$	$5.3.10^{-15}$	$5.1.10^{-12}$	$2.0.10^{-10}$	$1.75.10^{-9}$	$3.20.10^{-8}$	$3.25.10^{-8}$	$1.25.10^{-8}$
$OctNH_3^+$	$4.72.10^{-3}$	$4.92.10^{-3}$	$4.92.10^{-3}$	$4.92.10^{-3}$	$4.94.10^{-3}$	$4.94.10^{-3}$	$4.92.10^{-3}$	$3.08.10^{-3}$	$1.49.10^{-3}$

On the basis of these considerations , the decrease in retention that we observe for anions of strong acids (figure 2) and of weak acids (figure 1) for the higher pH values could be ascribed to a decreasing number of active sites adsorbed onto the surface of the stationary phase as pH increases as well as to a decrease in the electrical double-layer potential.

It can be useful comparing the results here obtained in reversed-phase ion-interaction chromatography with results reported in literature for reversed-phase chromatography (6-17). In these conditions sigmoidal shapes of *K' vs. pH* are generally obtained, the greater retention corresponding to the lower pH values (6-13). The behaviour is explained (8,9) through the additive property of retention, the experimental retention time observed at the different pH values being the sum of the contributions of the differently-protonated forms of the acid (7) :the undissociated more hydrophobic species is more retained onto a reversed-phase stationary phase than the dissociated one.

On the contrary, in ion-interaction chromatography, the dissociated species is more retained and of consequence the observed retention is increasing with pH, at least at lower pH values and until other effects, as above described, intervene.

The reversed-phase ion-interaction chromatography (an aqueous solution of the interaction reagent being the mobile-phase) and the reversed-phase chromatography (an aqueous-organic mixture as the mobile-phase) can therefore be considered as two extreme situations. Intermediate cases can be identified in ion-pair techniques in which the mobile phase contains the ion-pairing agent and organic modifier. The results obtained with this technique can be explained by mixed mechanisms in which ion interaction or adsorption mechanisms can alternatively predominate, as a function of the experimental conditions like: a) analyte chemical properties, b) organic modifier and c) ion-pairing concentration. When ionic mechanisms prevail parabolic functions of *K'* vs. *pH* with lower retention at lower pH values are observed (2,6). When on the contrary reversed-phase partition mechanisms prevail (1), a retention decrease is obtained with pH increasing. In agreement, to mixed mechanisms can be assigned the different behaviours shown, under the same chromatographic conditions (14) by anions characterized by different pK values.

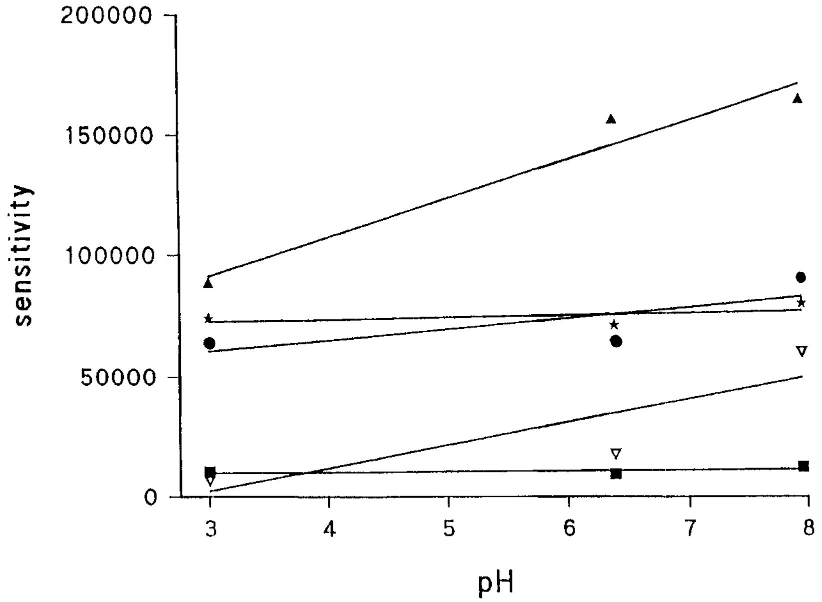

Figure 3.
Sensitivity (peak area for 1.00 ppm) as a function of pH.
▲ nitrite, ★ thiocyanate, ● nitrate, ▽ hydrazoate , ■ bromate.

Some considerations can also be made as concerns the sensitivity obtained in the anion separation. Figure 3 shows that the sensitivity (expressed as peak area for concentration of 1.00 ppm) is , as expected, independent on pH for the anions of strong acids while on the contrary increases with pH for the anions of weak acids, as increases the concentration of the dissociated species.

The results here obtained can very usefully assist in the development of separation methods. Some anions in fact show at different pH values comparable sensitivities together with remarkably different retention times. Of consequence resolution ($R_s = (t_2-t_1) /[(1/2\ (t_{w1} + t_{w2})]$) (21) can depend on pH, being for example between ascorbate and hydrazoate 0.62 at pH 3.0 , 1.80 at pH 6.39 and 3.00 at pH 8.0. A good choice of the pH value of the mobile-phase can therefore be usefully employed as a confirm criterion in the identification process, to improve resolution or to avoid matrix interference.

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