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Review

Separation and determination of inorganic anions by reversed-phase high-performance liquid chromatography

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Abstract

An overview and discussion is given of literature methods published after 1989 devoted to the ion-interaction chromatographic determination of inorganic anions. Seventy references are quoted. Ion-interaction chromatography makes use of commercial reversed-phase stationary phase and conventional high-performance liquid chromatography instrumentation. The basis of the technique, the modification of the stationary phase surface, the choice of the ion-interaction reagent as well as the dependence of retention on the different variables involved are discussed. Examples of application in the fields of environmental, clinical and food chemistry are presented. The experimental conditions of stationary phase, of mobile phase composition as well as detection mode, detection limit and application are also summarized in tables. © 1997 Elsevier Science B.V.

Keywords: Reviews; Ion-interaction chromatography; Inorganic anions

Contents

1. Introduction

This review is devoted to the ion-interaction chromatographic determination of inorganic anions.

Ion-interaction chromatography is a powerful technique, which permits the separation of inorganic anions on commercial reversed stationary phases and conventional high-performance liquid chromatography (HPLC) instrumentations.

The mobile phase is an aqueous or hydro–organic solution of a suitable ion-interaction reagent.

Ion-interaction methods offer, with respect to ion

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chromatography, advantages of lower cost in relation to both instrumentation and columns and can be advantageously employed in laboratories where only conventional HPLC systems are available. On the other hand, resolution and sensitivity are comparable to those obtained in ion chromatography, assuming that a suitable ion-interaction reagent is chosen.

Literature methods for the determination of inorganic anions based on both ion chromatography and ion-interaction chromatography published before 1984 have been exhaustively reviewed by Haddad and Heckenberg [1]; and a review by Marina et al. published in 1989 was devoted to HPLC applications in the analysis of inorganic species [2].

In the present review, the more recent papers concerning the ion- interaction determination of inorganic anions are considered.

For more immediate information and comparison, methods and experimental conditions are summarized in Tables 1 and 2. The packing material, the mobile phase composition, the kind of detection, the detection limit and (if given) the possible interferences and examples of application are reported [3–53].

2. Basis of ion-interaction methods

Discussion is still open about the mechanisms involved in the ion- interaction chromatographic processes and the analogies or differences compared with ion chromatography or ion-pair chromatography.

Snyder et al. [54] suggested the following definition to distinguish between ion-exchange and ion-pair chromatography: (i) ion-exchange chromatography is the technique that makes use of cationic or anionic stationary phase with an aqueous solution for the mobile phase and (ii) ion-pair reversed-phase chromatography is that technique which uses a reversed-phase column with an aqueous–organic mixture for the mobile phase, to which an ion-pairing is added.

This definition does not consider the mechanisms involved and does not take anyway into consideration the technique which uses a reversed-phase packing material and an aqueous solution of the ion-interaction reagent as the mobile phase.

The ion-interaction (or ion-pairing) reagent is essentially a salt formed by a lipophilic cationic species (alkylammonium, tetraalkylammonium, cetyltrimethylammonium, etc.) and an anion which can be both organic and inorganic.

According to many authors, the ion-pairing is added to the mobile phase to form, with the ionic analyte, an ion-pair which due to its increased lipophilicity can be retained on the reversed-phase stationary phase surface.

According to other hypotheses [55–57] the ion-pairing (or the ion-interaction reagent) added to mobile phase, when flowing in isocratic conditions, induces a dynamic modification of the surface of the reversed-phase packing material. The modification of the original packing material might proceed through a first step in which the lipophilic cation is retained onto the surface of the stationary phase through adsorption forces. Through electrostatic forces the anion is bound as well with the formation of an electrical double layer. A new moiety is adsorbed onto the surface (or on part of it), which modifies the original properties of the stationary phase and makes it able to retain both cationic (as, for examples, amines, triazines . . .) and anionic (both organic and inorganic) species. Retention can occur by three possible routes: (i) ion pairs are formed between the anions (or the cations) of the analyte and the cations (or anions) of the ion-interaction reagent and these ion-pairs are adsorbed onto the stationary phase [58,59], (ii) the analyte is retained through an ion-pair complex formed with an amphiphilic ion previously adsorbed onto the surface of the hydrophobic material [60] and (iii) the analyte is retained through ion-exchange reactions with the already adsorbed ion-pair reagent [61–65].

A general trend, even if not universally used, is to report as ion-pair chromatography the methods in which ion-pairs are formed before retention and are retained onto the unmodified reversed-phase surface, while those reported as ion-interaction chromatographic methods are the methods where the surface modification is assumed to take place.

Very likely, ion-exchange and adsorption mechanisms coexist in determining retention. This possibility is also supported by the elution sequences observed for the anionic analytes. The sequence generally does not follow the elution sequence found

Table 1
Experimental conditions of ion-interaction methods based on modified C_{18} and C_8 RP stationary phases

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interferences	LD	Applications
[3]	NO_2^-, NO_3^-, Br^-, I^-, VO_3^-, SO_4^{2-}, CrO_4^{2-}, WO_4^{2-}, MoO_4^{2-}	Silasorb 300 ODS (100×4.0 mm I.D.), irregular particles, 10 μm (Lachema, Brno, Czechoslovakia).	1–2 m*M* TBA hydroxide aqueous solution adjusted to pH 3–7 with phosphate (50 m*M*) or Tris buffer.	Dynamic modification, (study about the influence of organic counter ion, mobile phase pH and ionic strength).	UV at 210 nm.	–	–
[4]	IO_3^-, NO_2^-, Br^-, NO_3^-, I^-	Spherisorb ODS, (250×5.0 mm I.D.), 5 μm (HPLC Technology).	0.018 *M* Phosphate buffered ACN–water (35:65 v/v) micellar mobile-phase containing $1\cdot10^{-2}$ *M* (>CMC $=9.9\cdot10^{-4}$ *M*), HDTMA chloride.	Dynamic modification.	UV at 205 nm.	μg/l NO_2^- 200 Br^- 250 NO_3^- 150 I^- 100	Nitrite and nitrate in domestic water.
[5]	NO_3^-, ClO_3^-, Cl^-, Br^-, F^-, IO_3^-, BrO_3^-, I^-	Zorbax C_{18} (150×4.6 mm I.D.), spherical particles, 6 μm (DuPont) and PRP-1, (150×4.1 mm ID), 10 μm (Hamilton).	Several mobile phases containing 1,10-phenantroline $[Fe(phen)_3]^{2+}$ salts, with different organic modifier (ACN or MeOH) percentage, pH, buffer composition, ionic strength, type and concentration of counter-anion.	Dynamic modification	Indirect UV–Vis at 510 nm	About 1 ng	–
[6]	Cl^-, NO_3^-	SB-Octyl-50 (C_8) open tubular capillary column (10 m×50 μm I.D. and 0.5 μm thickness) (Lee Scientific), precoated with cetylpyridinium chloride 50 m*M* in 2% MeOH.	Sodium salicylate aqueous solution $2.5\cdot10^{-6}$ *M*.	Permanent coating.	Indirect fluorescence (λ_{Em}: 325 nm)	Order of 0.5 μg/l.	–
[7]	Cl^-, CNO^-, SO_4^{2-}, $S_2O_3^{2-}$, SCN^-	Supelcosil LC-18 (150×4.6 mm I.D.), 5 μm; Supelcosil LC-18DB (150×4.6 mm I.D.), 5 μm (Supelco); PLRP-S (150×4.6 mm I.D.), 5 μm (Polymer Labs.); PRP-1 (150×4.1 mm I.D.), 5 μm (Hamilton). Coating: 0.5 m*M* cetylpyridinium chloride in 18 or 23% ACN–water mixture (low and high capacity column).	Mobile phases with different solvent percentage, pH, buffer (TEA, THAM, TMA) and eluent acid (1,3,5-benzenetricarboxylic acid, 5-sulphosalicylic, phthalic acid, salicylic acid) are tested.	Permanent coating.	Indirect UV at 254 nm.	About 50 μg/l	Samples from gold process effluents
[8]	PO_4^{3-}, Cl^-, NO_3^-, NO_2^-, Br^-, SO_4^{2-}, I^-, $S_2O_3^{2-}$	Resolve C_{18} Radial-Pak cartridge (10 cm×8 mm), 5 μm.	0.4 m*M* TBA, 0.4 m*M* salicylic acid water solution at pH 4.62.	Comparison between precoating and dynamic modification.	Direct and indirect UV at 288 nm and conductometric. Interference between NO_3^- and Br^- is studied.	μg/l Cl^- 120 NO_3^- 740 NO_2^- 280 Br^- 1240	–
[9]	NO_3^-, BrO_3^-, IO_3^-, F^-, Cl^-, PO_4^{3-}, SO_4^{2-}, ClO_3^-, CN^-, S^{2-}, I^-, Br^-, $S_2O_3^{2-}$, NO_2^-, SCN^-	PLRP-S (150×4.8 mm I.D.), 5 μm (Polymer Labs.); ODS Hypersil (150×4.8 mm I.D.), 5 μm (Shandon).	3.3 m*M* Citric acid, (a) 0.16 m*M* HDTMA hydroxide in ACN–water 3:7, pH 11 or (b) 4.1 m*M*, pH 5.5.	Dynamic modification	Direct and indirect UV at 220 nm and electrochemical (glassy carbon working electrode applied *V*=0.85).	(a) 50–500 μg/l: IO_3^-, NO_3^-; (b) 0.5–5 mg/l: F^-, Cl^-, PO_4^{3-} SO_4^{2-}, ClO_3^-; (c) <50 μg/l: NO_2^-, $S_2O_3^{2-}$, S^{2-}, I^-, SCN^-	–

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Table 1. Continued

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interferences	LD		Applications
[10]	Cl^-, Br^-, NO_3^-, SO_4^{2-}, ClO_3^-	Develosil ODS-3K (100×0.32 mm I.D.), 3 μm (Nomura Chemical, Seto, Japan). Coating: 3 m*M* CTA bromide in MeOH–water (50: 50, v/v).	1 m*M* Salicylate (sodium salicylate–salicylic acid, 90:10) water solution–ACN (95:5, v/v).	Permanent coating.	Indirect UV at 230 nm.	0.7–1.9 mg/l.		Cl^-, NO_3^-, SO_4^{2-} in tap water.
[11]	IO_3^-, PO_4^{3-}, $P_2O_6^{4-}$, Cl^-, CN^-, BrO_3^-, SO_3^{2-}, SO_4^{2-}, HCO_3^-, NO_2^- PO_3^{3-}, NO_3^-, PO_2^-, ClO_3^-, S^{2-}, I^-, $S_2O_3^{2-}$, SCN^-	Separon SIC 18 (150×1.0 mm I.D.), 5 μm.	0.4 mm CTA bromide, 4 m*M* citric acid water solution–MeOH (70:30, v/v) at pH 7.1.	Dynamic modification	UV at 210 nm, direct and indirect conductometric and amperometric (carbon fibre array working, stainless-steel counter and Ag/AgCl reference electrode for NO_3^-, $S_2O_3^{2-}$, SO_3^{2-}, CN^-, SCN^-, IO_3^-, PO_2^{3-}, PO_3^{3-}, $P_2O_6^{4-}$, 2–1.5 V)	IO_3^- PO_4^{3-} $P_2O_6^{4-}$ Cl^- BrO_3^- SO_3^{2-} SO_4^{2-} NO_2^- PO_3^{3-} NO_3^- PO_2^- ClO_3^- S^{2-} I^- $S_2O_3^{2-}$ SCN^- CN^-	mg/l 11.6 6.7 1.8 2.8 17.9 4.0 17.4 3.7 6.7 7.6 53.0 17.6 2.2 7.0 5.3 3.9 5.3	–
[12]	S^{2-}	μBondapak C_{18} (150×3.9 mm I.D.), 10 μm (Waters).	ACN–water (40:60, v/v) with 0.5% glacial acetic acid and 5 m*M* low UV PIC B5 (pentanesulfonic acid).	Pre-column derivatization with N,N-dimethyl-*p*-phenylendiamine of S^{2-}; RP-ion pair.	Vis at 664 nm. Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, CN^- do not interfere at 10 000 fold excess.	S^{2-}	μg/l 0.8	–
[13]	NO_2^-, Br^-, Cl^-, NO_3^-, SO_4^{2-}	Partisil 10 ODS-3 (250×4.6 mm I.D.) (Whatman).	0.5–16 m*M* TBA iodide and potassium hydrogenphthalate (0.5–2.0 m*M*), 4<pH<6.5.	Dynamic modification. (method optimization through a three factor composite experimental design).	Conductivity.	–		–
[14]	Br^-, $H_2PO_4^-$, NO_2^-, NO_3^-, Cl^-, I^-, SO_4^{2-}	μBondapak C_{18} (250×4.6 mm I.D.) 10 μm (Waters).	50 mg Papaveraldine perchlorate added to 850 ml of 7 m*M* sodium citrate buffer, 1.75 g TBA hydroxide and ACN 150 ml (pH 3.5).	Dynamic modification.	Indirect UV detection at 325 nm.	Br^- $H_2PO_4^-$ NO_2^- NO_3^- Cl^- I^- SO_4^{2-}	mg/l 3.2 9.5 2.7 2.5 1.4 4.8 3.8	Water analysis; assay of blood bromide.
[15]	NO_2^-, SO_4^{2-}, Br^-, NO_3^-	TSK gel ODS-80T_M (50×4.6 mm I.D.), 5 μm (Tosoh), coated with 0.01 *M* cetylpyridinium chloride in 10% MeOH.	1 m*M* Citrate–2.5% methanol adjusted to pH 6.5 with diluted NaOH solution.	Permanent modification.	UV at 210 nm	–		Human serum, saliva and urine.
[16]	IO_3^-, BrO_3^-, Br^-, NO_2^-, NO_3^-, I^-, SCN^-	Zorbax ODS (250×4.6 mm I.D.), 5 μm (DuPont).	ACN–water (35:65, v/v), 2 m*M* cetylpyridinium bromide (>CMC $1{\cdot}10^{-3}$) and 10 m*M* phosphate buffer.	Dynamic modification.	UV at 222 nm.	IO_3^- BrO_3^- Br^- NO_2^- NO_3^-	ng 25 30 35 8 19	NO_2^-/NO_3^- in human saliva, iodide in commercial salt.

Table 1. Continued

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interferences	LD		Applications
						I^-	16	
						SCN^-	20	
						(loop volume not given)		
[17]	F^-, Br^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}	LiChrosorb RP-18 (125×4.5 mm I.D.), 7 μm (Merck), coated by crystal violet or methyl green or methylene blue basic (pH 9) 1 m*M* aqueous solution.	3 m*M* *p*-Hydroxybenzoic acid aqueous solution, pH 6.0 (methylene blue) or pH 8.0 (methyl green and crystal violet).	Permanent coating	Conductivity.		μg/l	–
						F^-, Br^-	100	
						Cl^-	50	
						NO_2^-	100	
						NO_3^-	200	
						PO_4^{3-}	500	
						SO_4^{2-}	300	
[18]	CrO_4^{2-}, $Cr_2O_7^{2-}$, SCN^-, ClO_4^-	LiChrospher C_{18}, 10 μm (Merck).	MeOH–phosphate buffer (7.0 m*M* Na_2HPO_4–7.2 m*M* NaH_2PO_4), (30:70, v/v), pH 6.8 with TBA hydrogensulfide 3.0 m*M*.	Dynamic modification. Interferences: $S_2O_3^{2-}$ at 1 fold excess level; $Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$ at 100 fold excess level	Photolytic-electrochemical detection, glassy carbon working electrode at +1.15 V (vs. Ag/AgCl) and +1.00 V for CrO_4^{2-}.		μg/l	–
						CrO_4^{2-}	500	
						$Cr_2O_7^{2-}$	300	
						SCN^-	70	
						ClO_4^-	300	
[19]	Cl^-, Br^-, NO_2^-, NO_3^-, SO_4^{2-}	RP-Partisil 10 ODS-3 (250×4.6 mm I.D.) (Whatman)	8 m*M* TBA iodide, 1 m*M* potassium hydrogenphthalate water solution at pH 6.	Dynamic modification	UV at 222 nm.	0.1–0.2 mg/l.		Analysis of atmospheric precipitation and aerosols.
[20]	NO_2^-, NO_3^-	Spherisorb ODS-2 (250×4.6 mm I.D.) 5 μm (Phase Separations).	Aqueous solution of 5.0 m*M* octylamine at pH 6.40 for *ortho*phosphoric acid or for salicylic acid.	Dynamic modification	NO_2^- 5 μg/l, in the presence of chloride 0.60 *M*. Interference by high (0.60 *M*) chloride concentration is studied.	UV at 230 nm		Lagoon water.
[21]	Cl^-, Br^-, NO_3^-, SO_4^{2-}, BF_4^-, NO_2^-, ClO_3^-, I^-, K^+, Na^+	TSK gel ODS-80T$_M$ CTR (100×4.6 mm I.D.), 5 μm (Tosoh) column and SIL-C_{18}/5B (150×4.6 mm I.D.), 5 μm (Yokogawa)	Properties of different alkyl-ammonium ions as IIR are tested. Phthalate, naphthalene-1,5-disulphonic acid and naphthalene-2,6-dicarboxylic acid as absorbing eluent ions are examined. Eluents are prepared by mixing the eluent ion, the hydroxide of the IIR, CH_3OH and water.	Dynamic modification	Indirect photometric detection at 300 nm.	Several ppbs		River, tap, rain and sea waters
[22]	NO_2^-, NO_3^-, IO_3^-, Br^-, $S_2O_3^{2-}$, I^-, SCN^-	Capcellpak C_{18} (150×4.6 mm I.D.), 5 μm (Shisheido). TSK gel ODS-80T$_M$, (150×4.6 mm), 5 μm (Tosoh). Coating with CTA 1 m*M* in water–MeOH (80:20, v/v).	0.1 *M* NaCl aqueous solution, 5 m*M* sodium phosphate buffer (pH 5.8).	Permanent precoating	UV at 225 nm and amperometric (AMP) (glassy carbon working electrode (+1.0 V) vs. Ag/AgCl). Interference free from Cl^-, SO_4^{2-}, Br^-.		μg/l	Artificial sea water.
						UV		
						NO_2^-	4	
						NO_3^-	8	
						amperometric		
						NO_2^-	2	

(Continued on p. 186)

Table 1. Continued

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interferences	LD		Applications
[23]	I^-, SCN^-, NO_2^-, $S_2O_3^{2-}$	Capcellpack C_{18} (AG 120) (150×4.6 mm I.D.), 5 μm (Shiseido), precoated with silicone polymer, equilibrated with 1 m*M* CTA chloride in water–MeOH (80:20, v/v).	0.1 *M* NaCl, 5 m*M* sodium phosphate buffer (pH 5.8).	Permanent precoating	UV at 225 nm and amperometric (AMP) (glassy carbon working electrode (+1.0 V) vs. Ag/AgCl)	UV NO_2^- $S_2O_3^{2-}$ amperometric NO_2^- $S_2O_3^{2-}$	μg/l 4 60 20 100	Determination of anionic-impurities in inorganic analytical-reagent grade chemicals.
[24]	NO_2^-, NO_3^-	Spherisorb ODS-2 (250×4.6 mm I.D.), 5 μm (Phase Separations).	Several aqueous mobile phases at pH 6.40 for *ortho*phosphoric acid with different ion-interaction reagents (IIR) (alkylamines), and IIR concentration were studied.	Dynamic modification	UV at 230 nm.	–		–
[25]	N_3^-	ODS-2 column 250×4.6 mm I.D., 5 μm Spherisorb (Phase Separations).	Aqueous solution of 5.0 m*M* octylamine at pH 6.40 for *ortho*phosphoric acid.	Dynamic modification.	UV at 230 nm. Interference free from Cl^-, CO_3^{2-}, $S2^-$, NO_3^-, I^-, SCN^-, Br^-, F^-.	30 μg/l		Azide in tap water.
[26]	NO_2^-, S^{2-}, I^-, $S_2O_3^{2-}$, SCN^- oxidizable anions	Shim-Pack CLC-C_8 (150×6 mm I.D.), 5 μm.	MeOH–phosphate buffer (15:85, v/v), (pH 5), 3.0 m*M* TBAOH and 0.1 m*M* EDTA.	Dynamic modification.	Amperometric, glassy carbon electrode *V*=+1.0 V (vs. Ag/AgCl). For 0.4 mg/l NO_2^-, S^{2-}, I^- and 40 mg/l $S_2O_3^{2-}$ no interference by 1000 fold excess of SO_4^{2-}, SiO_4^{4-}, CO_3^{2-}, PO_4^{3-}, BrO_3^-, NO_3^-, MoO_4^{2-}, Cl^-; 500 fold excess of oxalate, Br^- and 100 fold of SO_3^{2-}.	NO_2^- S^{2-} I^- $S_2O_3^{2-}$ SCN^-	μg/l 0.8 1.1 3.6 99 104	Lake water.
[27]	NO_2^-, NO_3^-, I^-, Cl^-, SO_4^{2-}	Spherisorb ODS-2 (250×4.6 mm I.D.), 5 μm (Phase Separations).	Aqueous solution of 5.0 m*M* octylamine at pH 6.4 for *ortho*phosphoric acid or for salicylic acid.	Dynamic modification	UV at 230 nm (direct) and at 254 nm (indirect); Conductivity (Cl^-, SO_4^{2-}). Interference free from sea water.	NO_2^- NO_3^- I^- Cl^- SO_4^{2-}	μg/l. 20 47 6 8 25	Lagoon water
[28]	NO_2^-, NO_3^-	PR-18 (250×4.0 mm I.D.), 5 μm (ZOCh, Poland).	2.0 m*M* Nonylammonium phosphate, pH 6.5.	Dynamic modification.	UV at 205 nm and 190 nm in presence of Cl^-.	NO_2^- NO_3^-	μg/l 2.0 1.5	–
[29]	I^-, SCN^-	Develosil ODS-5 (150×0.35 mm I.D.), 5 μm (Nomura Chemical, Seto, Japan) microcolumn and L-Column ODS (250×4.6 mm I.D.). Columns are coated with zwitterionic surfatants (CHAPS, CHAPSO, Zwittergent 3–14).	Pure water	Electrostatic ion chromatography (EIC)	Spectrophotometric at 220 nm.	I^- SCN^-	μ*M* 0.3 1.2	I^- and SCN^- in human saliva.

Table 1. Continued

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interferences	LD	Applications
[30]	SO_4^{2-}	Spherisorb ODS-2 column (250×4.6 mm I.D.), 5 μm (Phase Separations)	Aqueous solution of 5.0 m*M* octylamine salicylate at pH 6.40.	Dynamic modification. Method validation. Proficiency tests.	Conductivity	–	Lagoon water
[31]	Br^-, SCN^-	ODS-L column (250×4.6 mm I.D.) (Chemical Inspection and Testing Institute Tokyo, Japan), coated with strong/strong positive/negative charged zwitterionic surfactant reagents (CHAPS) micelles.	Pure water.	Electrostatic ion chromatography (EIC).	ICP-AES (230 nm) conductivity.	–	–
[32]	N_3^-	Spherisorb ODS-2 column (250×4.6 mm I.D.), 5 μm (Phase Separations)	Different aqueous solutions of alkylamines at different concentration and pH are tested. Chemometric optimisation.	Dynamic modification.	UV at 230 nm	–	–
[33]	NO_2^-, SCN^-, N_3^-, BrO_3^-	Spherisorb ODS-2, (250×4.6 mm I.D.), 5 μm (Phase Separations).	Aqueous solution of 5.0 m*M* octylamine at different pH (*ortho*phosphoric acid) ranging between 3.0 and 8.0	Dynamic modification.	UV at 230 nm.	–	–
[34]	$S_2O_3^{2-}$, I^-, SCN^-, NO_3^-	Microcolumn (150×0.35 mm I.D.) packed with Develosil ODS-5, 5 μm (Nomura Chemical) micelle-coated by taurine-conjugated bile salts (sodium taurodeoxicholate and sodium taurocholate).	5 m*M* Cu(II) sulfate aqueous solution (pH=4.5).	Micellar coating.	Indirect photometric detection at 210 nm.	–	–
[35]	NO_3^-, NO_2^-	ODS-2 (25×4.5 mm I.D.), 10 μm (Spherisorb).	Water–MeOH (80:20) containing 1 m*M* TBA.	Dynamic modification.	Spectrophotometric at 214 nm. Interference free from SO_4^{2-} and PO_4^{3-}.	ng NO_3^- 0.32 NO_2^- 0.26	Natural waters
[36]	Cl^-, Br^-, I^-, SCN^-, SO_4^{2-}, NO_3^-, NO_2^-	ODS-L column (250×4.6 mm I.D.) (Chemical Inspection and Testing Institute) coated with zwitterionic surfactants (CHAPS, CHAPSO, Zwittergent 3–14) (see Refs. [30,37,39]).	Pure water	Electrostatic ion chromatography (EIC)	Conductimetric and photodiode array UV–Vis	–	–
[37]	Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, CrO_4^{2-}, MoO_4^{2-}	Nucleosil 5 C_{18} (250×4.0 mm I.D.) (Macherey–Nagel).	1 m*M* TBA +0.5 m*M* DCTA in ACN–water (10:90, v/v) pH 6.2.	Ion-pair of inorganic anions and cations by on-column derivatization with chelating agents.	UV at 210 nm	mg/l Cl^- 200 NO_2^- 200 NO_3^- 7.6 SO_4^{2-} 8.5 CrO_4^{2-} 850 MoO_4^{2-} 35	–
[38]	SeO_3^{2-}, SeO_4^{2-}	Teknokroma ODS-1 (250×4.6 mm I.D.), 5 μm.	5.0 m*M* TBA phosphate in MeOH–water (5:95, v/v).	Dynamic modification. Comparison with ion-exchange.	ICP-MS	μg/l SeO_3^{2-} as Se 50 SeO_4^{2-} as Se 80	River, tap, well waters
[39]	F^-, Cl^-, NO_2^-, Br^-, NO_3^-	Spherisorb ODS (50×4.6 mm I.D.), 3 μm, coated with 0.1 m*M* CTA bromide.	0.5 m*M* Potassium chromate water solution at pH 7.0	Permanent coating.	Indirect UV–Vis at 328 nm.	mg/l F^- 0.24 Cl^- 0.55 NO_2^- 0.72 Br^- 0.83 NO_3^- 0.97	NO_3^- In tap-water. Separation together of organic acids.

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Table 1. Continued

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interferences	LD		Applications
[40]	SO_4^{2-}	Waters NovaPak C_{18} (150×3.9 mm I.D.), 4 μm, precoated with 1,12-diaminododecane 5 m*M* in water–MeOH (90:10, v/v), at pH 4.20 (H_2SO_4).	30 μ*M* Potassium hexacyanoferrate water solution.	Permanent coating.	Indirect UV at 205 nm. Alogenides, NO_3^-, NO_2^-, PO_4^{3-}, HCO_3^- do not interfere at concentrations up to 64:1. Interference by some organic acids was studied.	SO_4^{2-}	mg/l. 0.1	Water analysis (tap, well, surface, mineral, waste).
[41]	Cl^-, NO_3^-, Br^-	ODS-L column (250×4.6 mm I.D.) (Chemical Inspection and Testing Institute), coated with CHAPS or Zwittergent 3–14 micelles.	Pure water	Electrostatic ion chromatography (EIC).	Conductivity	–		–
[42]	NO_2^-, NO_3^-, I^-, Br^-, Cl^-, SO_4^{2-}	Spherisorb ODS-2 column (250×4.6 mm I.D.), 5 μm (Phase Separations).	Aqueous solution of 5.0 m*M* octylamine at pH 6.40 for orthophosphoric acid or for salicylic acid.	Dynamic modification	UV at 230 nm	–		Lagoon water.
[43]	Cl^-, NO_3^-, Br^-	ODS-L column (250×4.6 mm I.D.) (Chemical Inspection and Testing Institute), coated with CHAPS or Zwittergent 3–14 micelles.	Pure water (WMP-IC:water mobile phase ion chromatography).	Electrostatic ion chromatography (EIC).	Conductivity	–		–
[44]	AsO_3^{3-} and AsO_4^{3-} with organo-As species	C_{18} LiChrospher (250 mm), 5 μm (Hewlett–Packard).	6 m*M* TBA hydroxide at pH 7.3.	Dynamic modification.	Simultaneous UV at 200 nm and amperometric (vitreous carbon working electrode, voltage range: *V*=−1.5–+2.5 (Ag/AgCl ref. electrode).	AsO_4^{3-}	μg/l. 56.2	Arsenic species in urine.
[45]	Br^-, NO_2^-, NO_3^-, Cl^-, SO_4^{2-}	Nova-Pak C_{18} (150×3.9 mm I.D.), 4 μm, coated with 0.01 *M* *n*-cetylpyridinium chloride in water–MeOH (90:10, v/v).	Aqueous solution of potassium hydrogenphthalate 0.4 m*M*, pH 4.9.	Potassium coating.	UV at 254 nm.	Br^- NO_2^- NO_3^- Cl^- SO_4^{2-}	mg/l 0.10 0.09 0.29 0.05 0.10	Determination of inorganic anions in wines together with carboxylic acids.
[46]	SO_4^{2-}, Cl^-, Br^-	ODS-L column (250×4.6 mm I.D.) (Chemical Inspection and Testing Institute) coated with zwittergent 3–14 surfactant micelles.	Pure water.	Electrostatic ion chromatography (EIC).	UV–Vis and conductivity.			Br^- in sea water.

Table 2
Experimental conditions of ion-interaction methods based on modified stationary phases other than C_{18} and C_8

Ref.	Anions	Stationary phase	Mobile phase	Method	Detection and interference	LD	Application
[47]	F^-,	Bischoff Hyperchrome SC	$6.0 \cdot 10^{-3}$ *M* 4-hydroxybenzoic acid	Permanent coating.	Indirect UV detection at	Ranging between 20 and	Tap water.
	HCO_3^-,	column (125×4.6 mm I.D.)	(eluent A) or 2,4-dihydroxybenzoic		311 nm.	1500 μg/l with eluent B	
	Cl^-,	packed with Hamilton PRP-1,	acid (eluent B).			and between 100 and	
	NO_3^-,	5 μm, coated with 0.5 g/l				1000 μg/l with eluent A.	
	Br^-, SO_4^{2-}	methyl green (pH=9.0).					
[48]	F^-, Cl^-, NO_2^-, HPO_4^{2-}, $H_2AsO_4^-$, NO_3^-, ClO_3^-, SO_4^{2-}, CrO_4^{2-}, BF_4^-	Hamilton PRP-1 (150×4.1 mm I.D.), spherical particles, 10 μm.	0.1 m*M* Ru(II) complex with 1,10-phenanthroline or 2,2′-bipyridine ($Ru(phen)_3^{2+}$, $Ru(bpy)_3^{2+}$)+0.1 m*M* succinate buffer at pH 6.1.	Dynamic modification.	Direct and indirect Vis at 445 nm and fluorescence detection (phen: λ_{Ex} 465 nm, λ_{Em} 600; bpy: λ_{Ex} 460 nm, λ_{Em} 580).	–	–
[49]	F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, $H_2AsO_4^-$, $HAsO_4^{2-}$, $H_2BO_3^-$, HS^-, HCO_3^-, CO_3^{2-},	Hamilton PRP-1 (150×4.1 mm I.D.), 5 μm column coated with 0.2 m*M* CTA bromide.	1 m*M* Potassium phthalate+Tris 1 m*M* in 24% methanol at different pH values.	Permanent coating.	Indirect UV at different wavelengths, ranging between 282 nm and 254 nm.	–	–
[50]	$S_2O_3^{2-}$,	PRP-1 Hamilton (150×4.1 mm I.D.),	0.001 *M* Na_2CO_3+0.002 *M* of TBA	Dynamic modification.	UV at 231 nm and	0.2 mg/l of $S_2O_3^{2-}$ and	Commercial products of sodium sulphide.
	SO_3^{2-}	5 μm and PLPR-S (120×4 mm I.D.), 8 μm (Polymer Labs.).	hydroxide in water–ACN (85:15, v/v), pH=11.		UV diode-array detection.	0.4 μg/l of SO_3^{2-}.	
[51]	F^-, Cl^-, Br^-, NO_3^-	Macroporous polystyrene–divinyl-benzene RP-1 (Hamilton) column, (150×4.6 mm), 10 μm.	Different amounts of $Ru(phen)_3(ClO_4)_2$ (0.1–0.01 m*M*) and of sodium tartrate (0.02–0.1 m*M*) in water are tested.	Dynamic functionalization.	Indirect fluorimetric detection; λ_{Ex}=447, λ_{Em}=261 nm.	μg/l F^- 5 Cl^- 5 Br^- 10 NO_3^- 10	–
[52]	Selenite, seleniate	Hamilton PRP-1 (150×4.6 mm I.D.), 5 μm.	3% methanol+5 m*M* tetrabutylammonium phosphate pH=7.6	Dynamic functionalization.	ICP-MS	22–74 pg (as Se)	Selenium species in urine.
[53]	F^-, Cl^-, Br^-, NO_3^-	Macroporous polystyrene–divinyl-benzene RP-1 (Hamilton) column, (150×4.6 mm I.D.), 10 μm.	0.01 m*M* $Ru(phen)_3(ClO_4)_2$+0.02 sodium tartrate (0.01–0.1 m*M*) water solution.	Dynamic functionalization.	Indirect fluorimetric detection; λ_{Ex}=447, λ_{Em}=261 nm.	μg/l F^- 3 Cl^- 2 Br^- 5 NO_3^- 5	

in ion chromatography, is different for the different ion-interaction reagents and, in addition, can also vary for the same ion-interaction reagent, as a function of different experimental conditions, as, for example, the mobile phase pH [6] or the ionic strength [3].

3. Modification of the reversed-phase stationary phase; choice of the ion-interaction reagent; detection

The modification process can be essentially performed through two different ways:

1. a dynamic process in which the mobile phase contains (or sometimes only consists of) the ion-interaction reagent. When eluting in isocratic conditions, the mobile phase itself modifies the surface, or
2. through a process, referred to as permanent coating, in which the modifier agent is firstly adsorbed onto the stationary phase (often dynamically, by passing it through the column for a certain time); then the column is rinsed and used with a different mobile phase.

Once modified, no great difference can be found in the behaviour of permanently- and dynamically-modified columns, apart from the composition of the mobile phase which, as said, is generally different from the modifier agent when using the permanently-coated stationary phases and in contrast contains (and often consists of) the ion-interaction reagent itself for the dynamically-coated.

The modifications essentially concern C_{18} and C_8 packing material, sometimes in capillary microcolumns [9,13]. Examples are also reported of modifications induced on other packing materials, such as cyano-, diol- or polymeric support. The experimental conditions of these methods are reported in Table 2 [47–53].

Comparisons between the performances obtained in ion-interaction chromatography by the use of different original packings and their possible modifications have been studied [8,10,12]. So, for example, in the modification with iron(II)-1,10-phenanthroline as the ion-interaction reagent, a polymeric base gave results more advantageous with respect to a C_{18} base regarding: (i) retention reversibility of the modifier on the surface, (ii) stability in relation to pH variation, (iii) greater efficiency, (iv) longer column life, (v) higher modifier load [8]. In contrast, when using ion-interaction reagents formed by salicylic, 1,2,4-benzenetricarboxylic, 1,3,5-benzenetricarboxylic or 5-sulphosalicylic acid with tris(hydroxymethyl)aminomethane and tetramethylammonium hydroxide and tetraethyammonium hydroxide as counter ions, the bonded C_{18} silica columns were more efficient than the polystyrene–divinylbenzene (PS–DVB) ones. Furthermore the PS–DVB phases were slower to equilibrate when elution conditions were changed [10]. With a methanol–water mixture of hexadecyltrimethylammonium hydroxide and citric acid [12] as the ion-interaction reagent, comparable retentions were obtained for inorganic anions with polymeric and octadecylsilica stationary phases, while organic anions displayed significant differences in the two systems.

So, no general rule showing advantages for a stationary phase composition can be drawn out, because retention, resolution and sensitivity depend on a number of factors, whose effect is difficult to predict.

According to Haddad and Heckenberg [1] the ''ability'' in developing a new ion-interaction method is ''to tailor the mobile phase composition to suit the particular solute ion being studied'' or to separate the particular mixture.

In principle each salt consisting of a lipophilic cation can be used as the ion-interaction reagent.

Generally, in dynamic coating the ion-interaction reagent is usually characterized by relatively low hydrophobicity, as, for example, are salts of alkylammonium (with alkyl chain length generally ranging between 4 and 10) and tetraalkylammonium (with alkyl chain lengths generally ranging between 1 and 4).

In permanent coating, for the surface modification process, more lipophilic ion-interaction reagents are used, as, for example, salts of cetyltrimethylammonium. For the mobile phase, less hydrophobic reagents (as, for example, tetraalkylammonium salts) are then employed.

Concerning the anion of the salt, both inorganic (*ortho*phosphate, chloride, hydroxide . . .) and organic (salicylate, tartrate . . .) anions are used. Re-

garding their choice, the compatibility with the kind of detection used must be considered.

When conductivity is employed and the background conductivity of the eluent must be minimized, methods which make use of pure water or of very diluted solutions as the mobile phase are highly appreciable.

For UV detection, on the other hand, the eluent must be characterized by the lowest absorptivity at the detection wavelength for direct detection or by the highest for the indirect one. Eluents like phosphate or hydroxide should be avoided when conductometric detection is used but are very suitable for UV detection [13]. Salicylate ions are suitable for conductometric detection and for indirect UV detection. For indirect UV detection papaveraldine perchlorate [17] has also been used. Since some anions (nitrate, nitrite, bromide, bromate, iodide, iodate, periodate, thiocyanate and thiosulfate) absorb between 195 and 220 nm, detection selectivity with respect, for example, to chloride even if present at very higher concentration can be advantageously used, as, for example, in the determination of bromide in common salt [18] and sea-water [42], and of nitrite and nitrate in sea-water [21]. Amperometric detection has been selectively used for oxidable anions [14,19,22,26,44].

4. Dependence of retention on different variables

There are many variables which must be considered in planning the mobile phase composition and which must be optimized to control retention. They include the organic modifier content, the concentration and type of the ion-interaction reagent (regarding both the lipophilic cation and the counter anion), the pH value and the ionic strength. The effect of the variables on retention is often non-linear and interdependent and therefore it is difficult to predict, taking also into account that the mechanisms which govern retention are still not completely understood.

A good optimization of the variables could be obtained through chemometric treatment of experimental design [16,24,32] which optimizes sensitivity and resolution of analytes in a mixture in the lowest total analysis time.

The dependence of retention on the different variables involved has been studied by different authors [3,5,6,8,10,14,16,39–41]: besides the packing material of the stationary phase, retention is greatly affected by the chemical properties of the ion-interaction reagent, the presence and the concentration of the organic modifier in the mobile phase, the concentration of the ion-interaction reagent, the ionic strength of the mobile phase, and the temperature.

Concerning the effect of the organic modifier contained in the mobile phase, it was shown that, as expected, retention decreases when the concentration of the organic modifier increases. This effect is due to (besides the increased eluotropic strength of the solvent) desorption effects exerted by the organic solvent towards the moiety adsorbed onto the surface and to competition equilibria taking place between the solvent and the modifier. The adjustment of organic modifier concentration in the mobile phase can therefore regulate the amount of the ion-interaction reagent adsorbed and by consequence the retention [11,66,67].

Many examples of methods which make use of aqueous solutions of the ion-interaction reagent can be found (Table 1), that offer advantages of low cost and environment protection.

Systematic studies performed in the pH range between 3 and 8 permitted investigation of the effect exerted on the retention by the pH value of the mobile phase. It was shown that retention of both organic and inorganic anions always decreased with pH increase. The behaviour which holds for both strong and weak anions is likely related to the effect that mobile phase pH plays on the moiety already adsorbed onto the stationary phase surface [33,66]. A pH increase induces a decrease of concentration of the cationic form adsorbed and forming the primary electrical layer. Consequently the number of the total active sites available for retention also decreases. Regarding sensitivity, this, as expected, is practically constant in the whole pH range for the anions of strong acids, while increases with pH increase for the weak ones.

The effect of the counter-anion is also very important [5]. The retention dependence on chloride

concentration of nitrate and nitrite ions, when chloride concentration is high as in sea-water can be ascribed to a substitution of the original phosphate counter-anion with chloride ions [21].

The dependence of retention on ion-interaction concentration as well as the effect of mobile phase ionic strength has been also studied [3,14,67]. The anion of the salt seems to compete for solute for the active site on the stationary phase or to exert an electrostatic shielding, that affects not only retention (which generally decreases with ionic strength increase) but also selectivity and elution order [3,67].

Examples are also reported of micellar chromatography, in which the modifier agents in the mobile phase are used at concentrations greater than their critical micellar concentration [4,18].

Also worth noting is a relatively new technique, known as electrostatic ion chromatography, based on the modification of the reversed-phase octadecylsilica and in which the modifier agent is a zwitterion surfactant immobilized on it; the mobile phase is pure water. The analytes are inorganic ions which are eluted as ion-pairs. Sometimes specific ions are added to the mobile phase in order to perform the exclusive partitioning of the analytes as specific ion-pairs [29,31,35,41,43,46]. The analytes are released from the Stern layer to the diffuse layer. Due to the zwitterion which coats the stationary phase, the analytes are forced into a state of simultaneous electrostatic attraction and repulsion in the column, under a ''ion-pairing-like'' form. Detection sensitivity is enhanced by the low background deriving from using pure water as the mobile phase.

As a general consideration, it can be said that no general rule can be given about the choice of the optimal experimental conditions for developing a new ion-interaction chromatographic method. They strictly depend on the particular application. On the other hand, the dependence of retention on so many experimental conditions makes the technique very versatile for solving many separation and resolution problems. In addition, the technique can be advantageous in overcoming matrix interference, in particular towards more lipophilic components. For the same reasons, no general comparison can be made between the performance of ion chromatography or ion-interaction methods.

5. Examples of applications

Ion-interaction methods can be also advantageously used in the determination of metals through formation of anionic complex species. Different complexones (nitrilotriacetic acid, 1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid, diethylenetriaminopentaacetic acid, ethylenedioxybis(ethylenenitrilotetraacetic acid, [N-(2-hydroxyethyl)-diaminoethylene]-N,N,N-triacetic acid, and triethylenetetraaminohexaacetic acid) and direct and indirect UV detection have been used for determination of a number of metals [37]. For the determination of selenium the formation of selenotrisulfide has been employed [68] and metal cyano complexes have been formed for the analysis of precious metals in gold processing solutions [69].

Concerning the application of ion-interaction methods in the determination of inorganic anions in real samples, a sensitive application concerns the determination of impurities in analytical grade reagents [23]. Many examples can be found in the fields of environmental, clinical and food chemistry.

Typical inorganic anions have been determined in tap [4,5,13,25,38–40] and surface waters [26,38–40], sea or lagoon waters [21,26,37,38,41,70], atmospheric precipitation as rain, snow, aerosols in correlation with temperature, urban and rural sites [7].

Examples of applications in clinical chemistry are the determination of nitrite and nitrate in human saliva [18], of bromide in blood [17] and of arseniate in urine [44].

Food chemistry applications are the determination of inorganic and organic anions in wines [45] and in fruit juices [6] and of iodide in commercial salt [18].

6. Abbreviations

ODS	octadecylsilica
TBA	tetrabutylammonium
ACN	acetonitrile
CMC	critical micellar concentration
EIC	electrostatic ion chromatography
I.D.	internal diameter
MeOH	methanol
HDTMA	hexadecyltrimethylammonium

TEA	tetraethylammonium
THAM	tris(hydroxymethyl)aminomethane
TMA	tetramethylammonium
CTA	cetyltrimethylammonium
CHAPSO	3-[(3-cholamidopropyl)dimethylammonio]-2-hydroxy-1-propanesulfonate
CHAP	3-[(3-cholamidoproyl)dimethylammonio]-1-propanesulfonate
Tris	tris-(hydroxymethyl)aminomethane

References

[1] P.R. Haddad, A.L. Heckenberg, J. Chromatogr. 300 (1984) 357–394.
[2] M.L. Marina, J.C. Diez-Masa, M.V. Dabrio, J. Liq. Chromatogr. 12 (1989) 1973–2030.
[3] R. Vespalec, J. Neca, M. Vrchlabský, J. Chromatogr. 286 (1984) 171–183.
[4] F.G.P. Mullins, G.F. Kirkbright, Analyst 109 (1984) 1217–1221.
[5] P.G. Rigas, D.J. Pietrzyk, Anal. Chem. 58 (1986) 2226–2233.
[6] W.D. Pfeffer, T. Takeuchi, E.S. Yeung, Chromatographia 24 (1987) 123–126.
[7] D.J. Barkley, T.E. Dahms, K.N. Villeneuve, J. Chromatogr. 395 (1987) 631–640.
[8] B.A. Bidlingmeyer, C.T. Santasania, F.V. Warren Jr., Anal. Chem. 59 (1987) 1843–1846.
[9] B.B. Wheals, J. Chromatogr. 402 (1987) 115–127.
[10] T. Takeuchi, E. Suzuki, D. Ishii, J. Chromatogr. 447 (1988) 221–224.
[11] W. Mingjia, V. Pacáková, K. štulík, G.A. Sacchetto, J. Chromatogr. 439 (1988) 363–372.
[12] P.R. Haddad, A.L. Heckenberg, J. Chromatogr. 447 (1988) 415–420.
[13] Q. Xianren, W. Baeyens, Y. Michotte, J. Chromatogr. 514 (1989) 15–30.
[14] P. Dorland, M. Tod, E. Postaire, D. Pradeau, J. Chromatogr. 478 (1989) 131–140.
[15] Y. Michigami, Y. Yamamoto, K. Ueda, Analyst 114 (1989) 1201–1205.
[16] B. Maiti, A.P. Walvekar, T.S. Krishnamoorthy, Analyst 114 (1989) 731–733.
[17] G. Müller, H.U. Meisch, J. Chromatogr. 483 (1989) 145–151.
[18] L. Dou, I.S. Krull, J. Chromatogr. 499 (1990) 685–697.
[19] Q. Xianren, W. Baeyens, J. Chromatogr. 514 (1990) 362–370.
[20] M.C. Gennaro, P.L. Bertolo, A. Cordero, Anal. Chim. Acta 239 (1990) 203–209.
[21] J. Zou, S. Motomizu, H. Fukutomi, Analyst 116 (1991) 1399–1405.
[22] K. Ito, Y. Ariyoshi, H. Sunahara, Anal. Chem. 63 (1991) 273–276.
[23] K. Ito, Y. Ariyoshi, H. Sunahara, J. Chromatogr. 598 (1992) 237–241.
[24] E. Marengo, M.C. Gennaro, C. Abrigo, Anal. Chem. 64 (1992) 1885–1893.
[25] M.C. Gennaro, C. Abrigo, E. Marengo, A. Liberatori, J. Liq. Chromatogr. 15 (1993) 2715–2730.
[26] J. Xu, M. Xin, T. Takeuchi, T. Miwa, Anal. Chim. Acta 276 (1993) 261–264.
[27] M.C. Gennaro, C. Abrigo, G. Saini, Ann. Chim. 83 (1993) 125–146.
[28] E. Pobozy, B. Sweryda-Krawiec, M. Trojanowicz, J. Chromatogr. 633 (1993) 305–310.
[29] W. Hu, T. Takeuchi, H. Haraguchi, Anal. Chem. 65 (1993) 2204–2208.
[30] M.C. Gennaro, C. Abrigo, G. Saini, H. Muntau, G. Serrini, H. Geiss, Fresenius J. Anal. Chem. 350 (1994) 702–705.
[31] W. Hu, H. Tao, H. Haraguchi, Anal. Chem. 66 (1994) 2514–2520.
[32] E. Marengo, M.C. Gennaro, C. Abrigo, A. Dinardo, Anal. Chem. 66 (1994) 4229–4235.
[33] M.C. Gennaro, C. Abrigo, E. Marengo, J. Liq. Chromatogr. 17 (1994) 1231–1244.
[34] W. Hu, H. Tao, M. Tominaga, A. Miyazaky, H. Haraguchi, Anal. Chim. Acta 299 (1994) 249–256.
[35] W. Hu, H. Haraguchi, Anal. Chem. 66 (1994) 765–767.
[36] M.J. Gonzalez, A.I. Valle, M.L. Marina, Microchem. J. 50 (1994) 1–5.
[37] A. Padarauskas, G. Schwedt, Fresenius J. Anal. Chem. 351 (1995) 708–713.
[38] Y. Cai, M. Cabañas, J.L. Fernández-Turiel, M. Abalos, J.M. Bayona, Anal. Chim. Acta 314 (1995) 183–192.
[39] S.J. Albazi, T. Gharib, J.C. Cortes, J. Liq. Chromatogr. 18 (1995) 489–503.
[40] X. Jun, J.L.F.C. Lima, M. Conceição, M.C.B.S.M. Montenegro, Analyst 120 (1995) 2469–2473.
[41] W. Hu, A. Miyazaki, H. Tao, A. Itoh, T. Umemura, H. Haraguchi, Anal. Chem. 67 (1995) 3713–3716.
[42] M.C. Gennaro, C. Abrigo, D. Giacosa, G. Saini, J. Environ. Sci. Health A30 (1995) 675–687.
[43] W. Hu, H. Haraguchi, J. Chromatogr. A, 723 (1996) 251–258.
[44] P. Boucher, M. Accominotti, J.J. Vallon, J. Chromatogr. Sci. 34 (1996) 226–229.
[45] X. Jun, J.L.F.C. Lima, M.C.B.S.M. Montenegro, Anal. Chim. Acta 321 (1996) 263–271.
[46] W. Hu, S. Cao, M. Tominaga, A. Miyazaki, Anal. Chim. Acta 322 (1996) 43–47.
[47] R. Golombek, G. Schwedt, J. Chromatogr. 452 (1988) 283–294.
[48] P.G. Rigas, D.J. Pietrzyk, Anal. Chem. 60 (1988) 1650–1654.
[49] E. Papp, A. Fehervari, J. Chromatogr. 447 (1988) 315–322.
[50] R. Steudel, G. Holdt, T. Gobel, J. Chromatogr. 475 (1989) 442–446.

[51] Y.S. Fung, W.M. Tam, J. Chromatogr. Sci. 32 (1994) 157–161.
[52] K.L. Yang, S.J. Jiang, Anal. Chim. Acta 307 (1995) 109–115.
[53] Y.S. Fung, W.M. Tam, Anal. Chim. Acta 326 (1996) 67–76.
[54] L.R. Snyder, J.L. Glajch, J.J. Kirkland, Practical HPLC Method Development, Wiley, New York, 1988.
[55] B.A. Bidlingmeyer, J. Chromatogr. Sci 18 (1980) 525–539.
[56] B.A. Bidlingmeyer, S.N. Deming, W.P. Price Jr., B. Sachoc, M. Petrusek, J. Chromatogr. 186 (1979) 419–439.
[57] M.C. Gennaro, Adv. Chromatogr., (1995) 343–381.
[58] M.C. Gennaro, J. Liq. Chromatogr. 10 (1987) 3347–3375.
[59] M.C. Gennaro, E. Marengo, Chromatographia 25 (1988) 603.
[60] R.S. Deelder, H.A.J. Linssen, A.P. Koijnendiik, J.L.M. Van de Venne, J. Chromatogr. 185 (1979) 241–257.
[61] R.A. Wall, J. Chromatogr. 175 (1980) 353–363.
[62] R.P.W. Scott, P. Kucera, J. Chromatogr. 175 (1973) 51–63.
[63] R.L. Smith, Z. Iskandarani, D.J. Pietrzyk, J. Liq. Chromatogr. 7 (1984) 1935–1959.
[64] O.A.G.J. Der Houwen, R.H.A. Sorel, A. Hulshoff, J. Teeuwesen, A.W.M. Indemans, J. Chromatogr. 209 (1981) 393–404.
[65] J.L.M. Van de Venne, J.L.H.M. Henrikx, R.S. Deelder, J. Chromatogr. 167 (1978) 1–16.
[66] M.C. Gennaro, D. Giacosa, C. Abrigo, J. Liq. Chromatogr. 17 (1995) 4365–4380.
[67] M.C. Gennaro, C. Abrigo, E. Pobozy, E. Marengo, J. Liq. Chromatogr. 18 (1995) 311–330.
[68] A. Jain, A. Chaurasia, B. Sahasrabuddhey, K.K. Verma, J. Chromatogr. A, 746 (1996) 31–41.
[69] T. Nakagawa, E. Aoyama, N. Hasegawa, N. Kobayashi, H. Tanaka, Anal. Chem. 61 (1989) 233–236.
[70] D.F. Hilton, P.R. Haddad, J. Chromatogr. 361 (1986) 141–150.