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Application of Ion Pairing Chromatography to the Analysis of Inorganic Analytes: Review

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Abstract: The separation challenges that keep arising from the constantly evolving practical applications encountered in ion-pair chromatography (IPC) of inorganic analytes and inorganic elements containing compounds are reviewed. Emphasis is placed on species that are most important in the biochemical, biomedical areas or that are of concern in the environmental field. Examples will be given of the analysis and speciation of a wide variety of compounds in different matrixes. They assess the practical potential of this mature technique whose results are usually in agreement with those obtained via different analytical strategies. Eclectic hyphenations to achieve specific goals are also described.

Keywords: Experimental factors, Metals, Inorganic anions, Complexes, Speciation, Hyphenation

INTRODUCTION

The original and earliest aim of IPC was to obtain sufficient retention for organic ionized compounds on reversed phase stationary phase. This goal was usually achieved via the incorporation of a lipophilic counterion, usually termed Ion Pairing Reagent (IPR), in the mobile phase and optimizing the separation controlling the IPR and organic modifier concentrations in the mobile phase and the analyte charge status, via the eluent pH. It is however instructive to observe the breadth of new applications, put forth during the last decade, concerning the IPC of inorganic analytes and inorganic

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elements containing compounds: they actually witness how wide in scope is this established separation strategy that represents a valid alternative to ion chromatography for inorganic ions. Even if the expression “ion-interaction chromatography” should be preferred to “ion-pair chromatography” because the simple formation of ion pairs in the eluent does not increase but decreases analyte retention,^[1] the classical term received a greater share of credit and will be used in the following. The mechanism of IPC has been a matter of considerable debate during the last three decades. Insights into the fundamentals of the mechanism that governs the retention behaviour of charged but also neutral and zwitterionic analytes in IPC can be found elsewhere^[2] and will be taken for granted.

SPECIATION

Determination of various forms of the same element (speciation) is a challenging task for analytical chemists due to their differences in the environmental and biochemical fate and toxicity. For this purpose, among separation strategies, IPC plays an important role.

For metal ions, one of the most important procedure is complexation, because the use of ligands improves the separation resolution, prevents from metal ions hydrolysis, and high sensitivity can be obtained with conventional UV-VIS detection if absorbing ligands are selected. Typically, complexation of metal ions is performed before injection. Speciation may be problematic because of possible interference during the sample preparation or the instrumental analysis. For example, during the complexation stage, the oxidative status of the metal is usually not preserved if the stability constant of formed chelates are very different; besides, during the chromatographic run the stationary phase contamination by transition metal ions can be the source of interference and the replacement of metallic parts of the instrument into polymeric ones is usually recommended.

In order to successfully separate metal chelates via IPC, they have to be stable and kinetically inert.^[3] The retention behaviour of chelates in IPC depends strongly on complex stoichiometry, which is governed by the nature of the central metal ion and by the metal:ligand ratio. The principal parameters of interest in the mobile phase are pH, buffer (type and concentration), organic modifier and ion pairing agent nature and concentration.

As examples of metal speciation we will focus on same important elements.

Iron is the most abundant transition metal present in higher mammals. In order to determine the Fe(III)/Fe(II) ions, the formation of their chelates with pyridylazo and thiazolylazo reagents was exploited. The simultaneous separation of Fe(III) and Fe(II) chelates was obtained with a C18 stationary phase and acetonitrile/water (90:10,v/v) eluent containing sodium dodecanesulfonate as IPR. The method was used to investigate the distribution of Fe(III)/

Fe(II) ions in aqueous and micellar solutions after action of external, ultra-sonic field and has a strong practical meaning because the Fe(III)/Fe(II) couple is the object of many biochemical investigations.^[4]

The simultaneous determination of Cr(III) and Cr(VI) by IPC with 5 mM octylammonium orthophosphate (as IPR) at pH 4.0 with 35% (v/v) MeOH was performed on a C18 separating column. Since the Cr(III) did not exist as an anionic form like the Cr(VI) ($\text{Cr}_2\text{O}_7^{2-}$), Cr(III) was firstly reacted with EDTA (1:40 mole ratio) to form the anionic complex prior to injecting into the chromatographic system. A wide linear range, good repeatabilities, low detection limit (DL) and satisfactory average of percent recoveries enabled the method to be applied for the simultaneous determination of Cr(III) and Cr(VI) in water sample collected from the developed treatment of chromium removal system using algae.^[5]

Dithizone derivatives were used as chromogenic ligands for the quantitative determination of inorganic and organo-mercury compounds in aqueous matrices at ppb range in under 12 minutes with an eluent consisting of 10 mM tetrabutylammonium (TBA) bromide and 60:40 methanol water.^[6]

However speciation may also be performed without complexation for those elements that are less prone to bind by coordination than by covalent bonds.

Selenium is an important essential trace element for animals and possibly for plants^[7–12] since it is a constituent of the active centres of antioxidative enzymes and Se-amino acids and methylated Se compounds may have anticancer activity. As expected its biological role and bioavailability depends on its oxidation state, chemical binding and dosage: its deficiency can cause disease, but it is toxic at levels relatively close to those required for health; it follows that selenium speciation is imperative. Se is leached from soil as selenite and selenate and is incorporated into animals organism sequentially through the soil to plant chain: plants metabolize inorganic Se anions, selenite and selenate to generate seleno-amino acids. Se-accumulating plants belong to the families *compositae*, *leguminosae*, *cruciferae* and *allium* and can also be used in phytoremediation of contaminated soils. The complexity of the matrixes (garlic,^[7,13] brazil nut,^[14] mushroom,^[11] chives,^[8] *Brassica juncea*,^[12,15] dill,^[9] yeast,^[16] human urine,^[17] rye seedling biomass^[18]) the concentration range (sub $\mu\text{g/L}$ in pristine conditions to hundreds $\mu\text{g/L}$ in contaminated samples) and the need that the preconcentration step must not change the Se chemical form make Se speciation particularly challenging. IPC, suitably coupled to elemental or molecular mass spectrometry, proved to be a sensitive and specific analytical strategy for this purpose^[7–23] and for the simultaneous speciation of Se and Hg- containing compounds.^[15] Actually, seleno-amino acids are too hydrophilic to be retained and separated with typical RP conditions, hence adequate retention is obtained by using IPRs. Common IPRs such as ammonium salts^[7,13,14,16,19] were used but perfluorinated carboxylic acids and particularly heptafluorobutanoic acid (HFBA),^[8–12,15] proved to be more effective for characterizing samples containing many different classes of organoselenium

compounds.^[20] Trifluoroacetic acid (0.1% TFA), pentafluoropropanoic acid (0.1%) or heptafluorobutanoic acid (0.1%; HFBA) were alternatively used as IPRs with methanol–water (1:99, v/v) solutions as mobile phases to study the effect of increasing the number of carbon atoms. Since the improved separation efficiency as a result of increase in TFA concentration did not give enough selectivity for the separation of the early eluting peaks, investigation of perfluorinated carboxylic acids of greater chain length seemed appropriate and actually 0.1% HFBA in the mobile phase allowed more than 20 selenium compounds (Table 1) to be separated in 70 min in an isocratic elution mode. Figure 1 clearly outlines the influence of increased IPR lipophilicity on analyte retention.^[20] Hyphenation with inductively coupled plasma mass spectrometry (ICP-MS)^[8–15,17–19,21,22] has adequate sensitivity and selectivity but provides no structural identification.

Table 1. List of selenium compounds in standard solution

1	Selenic acid — selenate — SeO_4^{-2} (Na_2SeO_4)
2	Selenous acid — selenite — SeO_3^{-2} (Na_2SeO_3)
3	Selenocyanate — SeCN^- (KSeCN)
4	Methaneseleninic acid — $\text{CH}_3\text{Se}(\text{O})\text{OH}$
5	Se-lanthionine — $\text{NH}_2\text{CH}(\text{COOH})\text{CH}_2\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
6	Trimethyl selenonium — $(\text{CH}_3)_3\text{Se}^+$ ($(\text{CH}_3)_3\text{SeI}$)
7	Selenocystine — $\text{NH}_2\text{CH}(\text{COOH})\text{CH}_2\text{SeSeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
8	Se-cystathionine — $\text{NH}_2\text{CH}(\text{COOH})\text{CH}_2\text{SeCH}_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2$
9	Se-methylselenocysteine — $\text{CH}_3\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
10	Se-2-propynylselenocysteine — $\text{HC}\equiv\text{CCH}_2\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
11	Selenomethionine — $\text{CH}_3\text{SeCH}_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2$
12	Degradation product of Se-2-methyl-2-propenylselenocysteine
13	γ -Glutamyl-Se-methylselenocysteine — $\text{CH}_3\text{SeCH}_2\text{CH}(\text{COOH})\text{NHC}(\text{O})\text{CH}_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2$
14	Se-allylselenocysteine — $\text{CH}_2=\text{CHCH}_2\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
15	Cis-Se-1-propenylselenocysteine — $\text{CH}_3\text{CH}=\text{CHSeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
16	Trans-Se-1-propenylselenocysteine — $\text{CH}_3\text{CH}=\text{CHSeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
17	Se-1-propylselenocysteine — $\text{CH}_3\text{CH}_2\text{CH}_2\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
18	Selenoethionine — $\text{CH}_3\text{CH}_2\text{SeCH}_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2$
19	Selenohomocystine — $\text{NH}_2\text{CH}(\text{COOH})\text{CH}_2\text{CH}_2\text{SeSeCH}_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2$
20	Degradation product of Se-1-methyl-2-propenylselenocysteine
21	Se-2-methyl-2-propenylselenocysteine — $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
22	Se-1-methyl-2-propenylselenocysteine — $\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{SeCH}_2\text{CH}(\text{COOH})\text{NH}_2$
23	Se-adenosyl-selenohomocysteine — $\text{NH}_2\text{CH}(\text{COOH})\text{CH}_2\text{CH}_2\text{SeCH}_2\text{C}_4\text{H}_5\text{O}_3\text{C}_5\text{N}_4\text{NH}_2$

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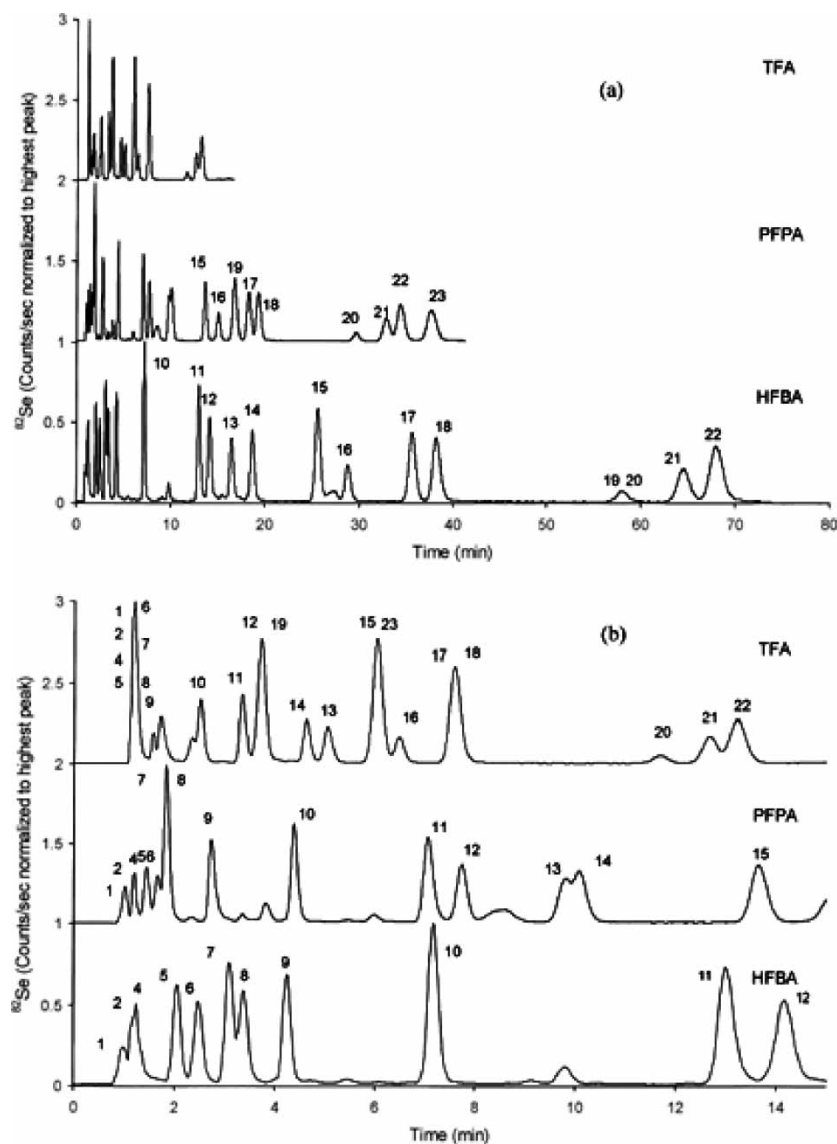


Figure 1. (a) HPLC–ICP-MS chromatograms of selenium standards using 0.1% TFA, PFPA or HFBA as ion-pairing agents (full time scale). (b) HPLC–ICP-MS chromatograms of selenium standards using 0.1% TFA, PFPA or HFBA as ion-pairing agents (extended time scale, 15 min). Reprinted from ref. [20] with permission from Elsevier.

Authentic standards of selenium uncommon compounds are seldom available for retention-based identification hence synthetic standards are required; hence hyphenation with electrospray ionization mass spectrometry (ESI-MS-MS)^[16] or with both ICP-MS and ESI-MS-MS^[14,20,21] were investigated

to gain structural information. Higher resolution ESI-QTOF-MS^[12] provided high precision and exact mass determination.

Hydride generation was used as an interface between IPC and atomic fluorescence spectrometry.^[7,23] This way, selenocystine, selenomethionine, selenite and selenate were quantitated simultaneously with DLs of 0.06, 0.08, 0.05 and 0.04 ng/mL, respectively, and relative standard deviations of 9 duplicate runs for all the 4 species less than 5%. The method was successfully applied to Se speciation analysis of cultured garlic samples, and validated by determination of total selenium and selenium species in certified reference material NIST 1946.^[7]

A chemometrical approach for speciation of As and Se compounds in tap water was pursued. A central composite design took into account the influence of the ionic strength, IPR concentration and pH; response surfaces and isore-sponses curves allowed the determination of the optimum chromatographic conditions and of the robustness of the method, coupled with plasma MS detection.^[19]

The speciation of As,^[19,24–27] known as a poison for centuries, was actually another important field of research because the total arsenic concentration is not an appropriate measure for assessing its toxicity that varies dramatically with different chemical forms. At neutral pH the main arsenic compounds are present as uncharged species (arsenic acid), zwitterions (arsenobetaine), cations (arsenocholine and tetramethylarsonium ion) and anions (arsenate and arsenosugars); it follows that IPC is a strong candidate for identification and quantitation of individual chemical forms of arsenic. It was used to speciate seven important arsenicals in human urine samples.^[26] Among hyphenation possibilities the best choice was ICP-MS^[19,24–26] even if hydride generation coupled with atomic absorption and atomic fluorescence detection provided an inexpensive alternative to ICP-MS.^[26] A step gradient operation involving heptanesulfonic acid as an initial IPR followed by methanesulfonic acid as IPR allowed the complete separation of the arsenic compounds on a single column.^[26]

The dual gradient strategy (gradient of both the organic modifier and the IPR concentrations) and ICP-MS were also exploited in the analysis of cadmium-bound phytochelators. Because of the large amount of methanol (up to 60%), post-column dilution with a solution containing 0.3% (w/w) HNO₃ was necessary.^[28]

COMPLEXATION TO STUDY DIFFERENT METAL CATIONS

The complexation of trace metals was used extensively with many coordinating and chelating agents not only for speciation purposes but also to analyze different metal cations in the same sample or to obtain the stability constants of the complexes.^[29] Commonly complexation is performed before injection

but the ligand can also be incorporated in the eluent or used as a post-column reagent.

The IPC of heavy-metal (Pb, Cd, Cu, Hg, and Ni) complexes of unithiol with phosphonium bromides as IPRs was optimized taking into account that the retention of complexes increases upon increasing the hydrophobicity and concentration of the IPR and upon decreasing the organic modifier concentration in the eluent. The method allowed the analysis of those metals in process water.^[30] An azosulfonated ligand, generally used as a metallochromic indicator for metal ion titrations, was selected as a ligand to pre-complex metal ions that are successively separated via IPC with TBA as IPR. A pH gradient allowed the separation of the anionic complexes of Ni^{2+} – Cu^{2+} and Fe^{3+} – Al^{3+} that were spectrophotometrically monitored. The method was applied to tap water analysis.^[31]

Among a range of other complexing reagents such as for example azo dyes, chelating ligands, diphenylcarbazone,^[32–36] cyanide is probably the most important. The widespread use of cyanide compounds in many industrial processes has led to its presence in the environment. Metallo cyanide complexes in aqueous solution can show varying environmental fate. Readily dissociable metallo cyanide complexes, such as Zn(II), Cu(I) and Cd(II), are regarded as toxic species. Other metallo cyanides, such as those of such as Co(III), Fe(II) and Fe(III), are more stable and are therefore less poisonous because they cannot easily release cyanide. IPC separations of metallo cyanides complexes in aqueous solution is now a well established technique.^[37–40] The determination of the metallo cyanide complexes of Cu(I), Fe(III) and Fe(II) has proven more difficult than that of Au(I), Ag(I), Ni(II), Co(II), Cr(III) owing to decomposition of Cu(I)-cyanide complex and reduction of Fe(III)-cyanide complex to Fe(II)-cyanide species during the separation process. In order to prevent these processes, strongly alkaline solutions in the presence^[37,38] of cyanide have been used as media to make up standard solutions. Mobile phases containing cyanide, that prevent the dissociation of metallo cyanide complexes, were found to give better results.^[37,39,40] A tentative retention mechanism for IPC of metallo cyanides was proposed but the estimates of the model parameters are at variance with the theoretical ones and the Authors realize that the proposed model is not able to predict the experimental behaviour.^[41] An IPC separation of cyanometallic complexes was applied to the analysis of petroleum refinery streams (sour water) without any pre-treatment. It was monitored with a suppressed conductivity detection. The mobile phase was composed of 2 mM TBA hydroxyde as IPR, 1 mM Na_2CO_3 , 0.1 M NaCN and acetonitrile (77:23, v/v). At the optimized conditions, DLs estimated by the calibration curve parameters were in the ppb range and relative standard deviation ranged from 2.5% to 3.1%.^[37]

An alternative to precomplexation is the inclusion of the ligand in the eluent. This strategy was used in the separation of lanthanides that is of great interest in the burn-up measurement of nuclear fuels and in their

characterisation with respect to trace constituents. The lanthanides separation poses a real challenge because of the similarity in their chemical behaviour. IPC has shortened the analysis time from days to minutes thanks to a sensitive multi-elemental analysis capability using single injection. The rapid IPC of entire lanthanide series in a fission product mixture relied on the use of a reverse phase column coated with one of the best extractants available for lanthanides, that is of Di-(2-ethylhexyl) phosphoric acid and a complexing reagent, α -hydroxy isobutyric acid (α -HIBA), in the mobile phase for gradient elution. Visible detection was accomplished with Arsenazo (III), a metallochromic reagent, used as a post-column reagent.^[42]

By using dual (concentration and pH) gradient conditions, Th and U could be separated sequentially after the elution of the lanthanides with sharp, symmetric peaks and with base-line resolution using an eluent comprising octanesulfonate as IPR and α -HIBA. The recently developed procedure using two chromatographic runs, one for separation and quantification of lanthanides and the other for U and Th, offers an easy, cost effective method for the determination of burn-up of irradiated thorium samples without any pre-separation step for the matrix elements from sample, hence it permits lesser exposure to radioactivity and less chances for sample loss during transfers. The method can be used as a quick substitute for mass spectrometric analysis of the burn-up determination.^[43,44] Lactic acid, α -HIBA and α -hydroxy- α -methylbutyric acid (α -H- α -MBA) were compared as elution additives for the individual separation of 14 lanthanide elements under IPC with octanesulfonate as IPR. All the 14 lanthanides were separated in 11 minutes using a gradient of α -HIBA and α -H- α -MBA as detailed in Figure 2.^[45] These rewarding results indicate IPC as a strong candidate for routine analysis of lanthanides and actinides at trace levels.

As a second alternative to metal precomplexation that is time consuming, expensive, and prone to contamination, flow injection (FI), that is known with features of a simple, versatile, and convenient operation, was coupled to IPC for in-line batch complexation of metals with 4-(2-pyridylazo) resorcinol (PAR), as illustrated in Figure 3. A PAR reagent solution is injected into a metal ion solution flowing stream. A portion of the PAR-metal mixture zone is then sampled with the HPLC injection valve for subsequent IPC on a C18 column with the mobile phase containing 37% acetonitrile, 3.0 mM acetate buffer pH 6.0 and 6.2 mM TBA bromide and visible detection at 530 and 440 nm. The analysis cycle including in-line complexation and separation by IPC was 16 min, and allowed the separation of separate Cr(VI) and the PAR chelates of Co(II), Ni(II) and Cu(II). The method was used to analyze Cr(VI), Co(II), Ni(II), Cu(II) in chrome plating waste water and results were found in good agreement with that of AAS.^[46] A similar hyphenated FI-IPC system was optimised to obtain the on-line metal preconcentration on micro-column loaded with functionalised cellulose sorbent Cellex-P, that exhibited fast kinetics of sorption processes. Co(II), Ni(II), Cd(II) and Mn(II) were eluted with sodiumdodecylsulfate as IPR and tartaric acid as a

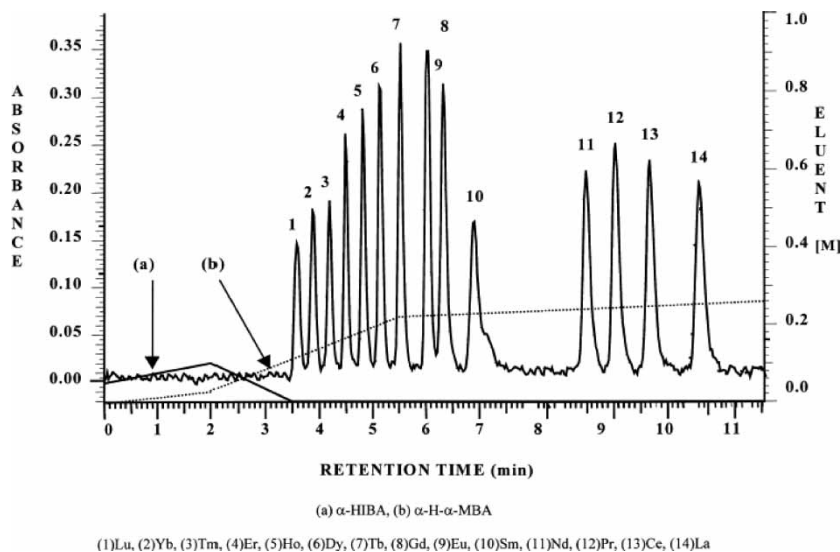


Figure 2. Separation of lanthanides using a gradient of two eluents. Mobile phase: α -HIBA: 0.05 to 0.10 M in 2 min, 0.10 to 0.0 M in 2.0 to 3.5 min; α -H- α -MBA: 0.0 to 0.03 M in 2 min, 0.03 to 0.22 M in 2.0 to 5.5 min, 0.22 to 0.28 M in 5.5 to 15 min; 0.003 M sodium n-octane sulphonate; pH 4.0; flow-rate: 1 mL/min; temperature 25°C; stationary phase: 4.6×150 mm, $5 \mu\text{m}$ C18 RP column; post-column reagent: 1.5×10^{-4} M Arsenazo (III) in 0.01 M urea and 0.1 M HNO₃; flow-rate: 0.3 mL/min; monitoring wavelength: 645 nm. Reprinted from ref. [45] with permission from Elsevier.

ligand. Spectrophotometric detection at 510 nm was possible thanks to a post-column derivatisation with PAR and the method was used for the determination of these metals in river water. The agreement with results obtained with electrothermal AAS determination were reasonable.^[47] Metal preconcentration was also obtained via enrichment using supported liquid membranes: the sample solution is pumped through the donor size of the membrane and the enriched sample is then analyzed via IPC with octane sulfonate as IPR and tartaric acid as a ligand on a C 18 column. Again, spectrophotometric detection of Zn(II), Co(II), Ni(II), Cd(II) and Mn(II) in river water at 510 nm was possible thanks to a post-column derivatisation with PAR.^[48] Analytical strategies described above lowered the DLs for trace metal ions at and at sub $\mu\text{g/L}$.^[46–48]

OTHER APPLICATIONS CONCERNING METALS

Free metals were also amenable of IPC. For heavy metals a novel amperometric detector based on the electrochemical transfer of the metal ions

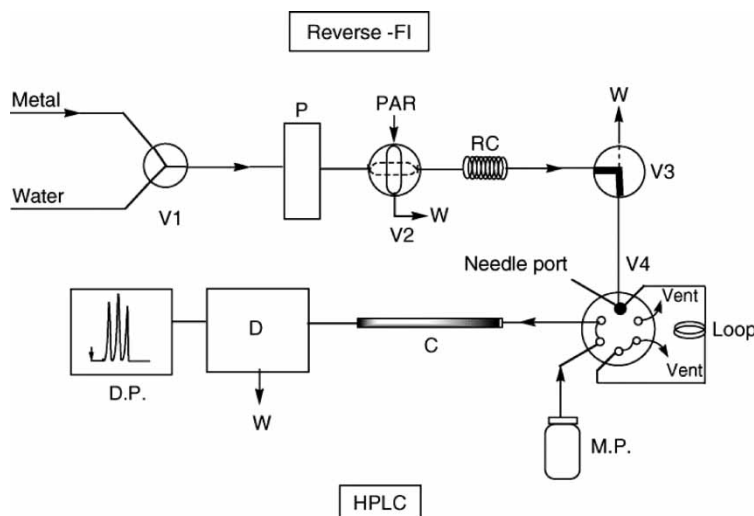


Figure 3. Diagram of FI-HPLC in-line derivatization system: P, peristaltic pump; RC, reaction coil; V1, three way valve; V2, low pressure injection valve; V3, switching valve; V4, high pressure injection valve; C, analytical column; M.P., mobile phase; D, UV-vis detector/photodiode array detector; D.P., data processor; W, waste. Reprinted from ref. [46] with permission from Elsevier.

across an array of water/nitrobenzene micro interfaces was advantageously used: the linearity was quite satisfactory, whereas the limit of decision was in the ppb range. More than 8 metals are separated in less than 15 minutes on a C18 column using octyl sulfonate as IPR.^[49]

Ion pairing was demonstrated to dominate the retention mechanism of separation of charged, polydisperse, water-soluble gold nanoparticles, protected by monolayers of N-acetyl-L-cysteine and of tiopronin ligands, whose size range encompasses the transition from bulk metal to molecular properties.^[50]

ANALYSIS OF INORGANIC ANIONS AND INORGANIC COMPOUNDS CONTAINING ANIONS

IC is the dominant analytical method for determining ions. Nevertheless the IC efficiencies continues to be lower than that of HPLC used to separate organic ions. It followed that the modification of a RP column to obtain efficient ion chromatographic separations was the focus of interest of many investigations. This may be obtained via a permanent coating during a strongly hydrophobic surfactant loading step or via a dynamic coating by

the IPR incorporated in the eluent. A permanent coating allow for eliminating IPR from the eluent. This way analytical costs are significantly reduced, even if permanent coating has to be repeated if the column performance is impaired and involve column regeneration. However, usually, RP materials under IPC conditions, that involves dynamic coating, give good results in the analyses of inorganic ions.

Sulfur compounds were extensively analyzed by IPC.^[51–57] Sulfur (IV) and sulfur (VI) species play an important role in the atmospheric environment and received a great deal of scientific attention. The transition metal ion catalyzed autoxidation products of sulfur dioxide is involved in acid rain formation. Ion-interaction chromatography was used for the separation of sulfate and dithionate, that are oxidation products formed in the presence of Fe (III). TBA hydroxide was selected as IPR. The chromatographic method was optimized by varying the IPR and acetonitrile concentrations and the ionic strength (Na_2CO_3). As expected from the theory^[2] the retention was found to increase with increasing IPR concentration and to decrease with increasing acetonitrile concentration or with increasing ionic strength.^[51]

Sulfite, sulfate, hydroxymethanesulfonate (HMS), and other inorganic anions in atmospheric liquids were analyzed in less than 10 min via IPC with indirect photometric detection at 265 nm and with DLs in the pmol range. Separations were accomplished in a cetylpyridinium permanently coated C18 column with 0.5 mM potassium hydrogen phthalate-0.015% triethanolamine-3% methanol at pH 7.9 as mobile phase. Absorption responses were linear over a wide concentration range from several hundred μmoles to the DLs of each anion. A representative chromatogram can be observed in Figure 4.^[53]

In natural waters or industrial effluents, sulfur exists in different chemical forms such as sulfide, sulfite, sulfate and thiosulfate. Polythionates are produced by the reaction of hydrogen sulfide with sulfite in an acidic medium, and are usually present as mixtures in hot spring waters. Sulfur oxyanions were separated via IPC on an C18 column with an acetonitrile–water (20:80, v/v) mobile phase (pH 5.0) containing 3 mM tetrapropylammonium hydroxide as IPR and 6 mM acetic acid. A reaction solution containing azide and iodine was mixed with the column effluent. Since polythionates and thiosulfate catalyzed the reduction of iodine with azide, the measurement of the residual iodine can be followed photometrically and allow the indirect detection of these sulfur oxyanions that showed negative peaks as a result of the decrease in absorbance of background. The conditions for the catalytic postcolumn reaction were optimized and the DLs were 4.3 μM for trithionate, 0.10 μM for tetrathionate, 2.7 nM for pentathionate, 5.0 nM for hexathionate and 1.1 nM for thiosulfate. The proposed system gave a much higher sensitivity compared to earlier methods, and was applied successfully to the analysis of polythionates and thiosulfate added to hot-spring water samples.^[54]

Since sulfide and sulfite in an aqueous solution are very unstable, readily yielding sulfate and thiosulfate via air oxidation, a planned stoichiometric

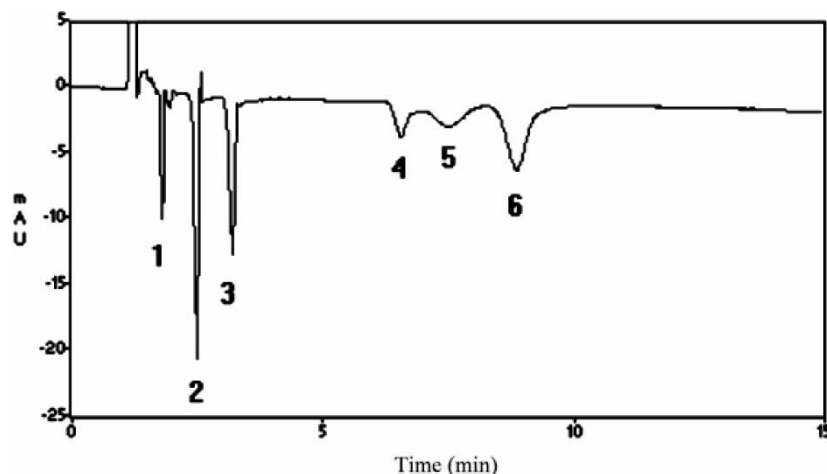


Figure 4. Chromatogram of standard anions at 265 nm. Peak 1, HMS (148 μM); peak 2, chloride (506 μM); peak 3, nitrite (414 μM); peak 4, nitrate (203 μM); peak 5, sulfite (160 μM); peak 6, sulfate (252 μM). Sample volume, 10.0 μl . Reprinted from ref. [53] with permission from Elsevier.

conversion of sulfide and sulfite into stable thiocyanate and sulfate, respectively, prior to the chromatographic run was pursued. Sulfate, thiosulfate and thiocyanate were separated within 32 min on an C18 column with an acetonitrile–water mobile phase pH 5.0 containing tetrapropylammonium salt as an ion-pairing reagent. Thiosulfate and thiocyanate in the effluent could be measured photometrically (220 nm) while sulfate with a suppressed conductivity detector. Excellent linearities of the calibration plots, low RSDs, quantitative recoveries for sulfide, sulfite plus sulfate, and thiosulfate in hot-spring water samples demonstrated the figures of merit of the proposed method that does not suffer from interference from the most common ions.^[57]

During the optimization of the IPC method for the determination of mixtures of thiosulfate, thiocyanate and polythionates in hot-spring water samples, the IPR chain length, its concentration, and the organic modifier percentage in the eluent were selected to give the best performance and selectivity. 19 common anions and 11 common cations were demonstrated not to interfere at concentrations as high as 0.005 M.^[56]

The selective and sensitive analysis of sulfite in wine was performed via the pre-column derivatization of sulfite with iron(III)-1,10-phenanthroline complex and IPC on a C18 column with direct photometric detection. The acetonitrile–water (60:40) mobile phase contained 50 mM NaClO_4 and 5 mM acetate buffer (pH 5.0). The DL was 5×10^{-7} M. The recoveries from wine samples were within the range 94–105%. The IPC results agreed with those obtained by the established iodometric titration technique.^[55]

Tetramethylene oxide, an unusual organic modifier, played an important role in adjusting the retention behavior of $(\text{NH}_4)_2\text{S}$ and NH_4SCN in the IPC of NH_2CSNH_2 , $(\text{NH}_4)_2\text{CS}_3$, $(\text{NH}_4)_2\text{S}$, and NH_4SCN in synthesis and isomerization samples.^[52]

Other important inorganic anions are nitrite and nitrate that interlock with each other in the nitrogen cycle. Their presence in water, food, biological and environmental matrices pose a concern due to adverse human health effects of nitrite (methaemoglobinemia, production of highly carcinogenic N-nitrosoamines from the reaction with secondary amines and amides, which are generally present in food where nitrite is used as a food preservatives). Relative to nitrites, nitrates represent a danger only if ingested in excessive doses. Degradation of the organic matter, faecal pollution and leaching of nitrate from fertilizer are some potential sources of nitrite and nitrate contamination. Nitrite and nitrate in dew water droplets may constitute an important source of atmospheric hydroxyl radicals. Accurate and precise determination of these analytes in relevant matrices is of vital importance.

Nitrite and nitrate were analyzed in spinach and lettuce by normal phase IPC with tetraethylammonium chloride as IPR: the developed IPC method showed excellent sensitivity and had the advantage of avoiding the interference of chloride ion. EDTA was also used to suppress the masking of nitrite peak by excess of iron.^[58] A fast (<50 s) determination of nitrite and nitrate at trace concentrations in water samples relied on the use of a short 3.0 cm ODS column and a mobile phase comprising 20 mM tetrabutylammonium chloride. The method was configured for the continuous monitoring of tap water samples and the fast run time allowed up to 60 analyses/h which matches FI analysis rate. Results compared well with the conventional ion chromatographic ones.^[59] A similar system was optimized to separate up to eight UV absorbing anions with excellent efficiencies (>50000 plate/m) thanks to the $3\text{ }\mu\text{m}$ ODS particles.^[60] Simple, fast, sensitive and accurate IPC for simultaneous determination of nitrite and nitrate in atmospheric liquids and lake waters was accomplished on a C18 column with a mobile phase containing 83% 3.0 mM TBA hydroxide and 2.0 mM sodium phosphate buffer at pH 3.9 and 17% acetonitrile. UV light absorption responses at 205 nm were linear over a wide concentration range from $100\text{ }\mu\text{g/mL}$ to the DLs of $10\text{ }\mu\text{g/L}$ for nitrite and $5\text{ }\mu\text{g/L}$ nitrate. The relative standard deviation was less than 3.0%.^[61] Simultaneous determination of nitrite and nitrate in culture media of *Staphylococcus* strains was optimized varying the IPR concentration.^[62]

Separations of common inorganic anions mixtures were deeply studied. A full factorial experimental design was used model their separation on a RP column dynamically coated with a dye, crystal violet, that behaved as an IPR. Analytes were monitored via indirect photometric detection at the absorption maximum of the dye. The affinity of the analytes decreased in the order $\text{S}_2\text{O}_3^- > \text{SO}_4^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^-$, which is the same as that observed with anion exchange chromatography.^[63]

A fast IC of common anions was obtained by converting a small particle reverse-phase column, stable from pH 2–11.5 because of a bidentate linkage of the bonded C18, into an ion exchanger by coating it with hydrophobic didodecyltrimethylammonium bromide (DDAB) and eliminating this IPR from the eluent. The high pH of the mobile phase dramatically reduced the retention of doubly charged analytes and allowed a fast IPC of seven common anions. Separation is achieved in just 40 s at 2 mL/min with a 2.5 mM 4-hydroxybenzoic acid eluent at pH 10 on a 1.3 cm long column, alternatively their baseline separation can be obtained in less than 2 minutes on a 2 cm long column at 1 mL/min, as demonstrated in Figure 5.^[64] Ultra-fast (15 s) separation of common anions was performed with a monolithic stationary phase using TBA phthalate as IPR. Separations were monitored using either direct conductivity (with DLs in the low ppm range) or indirect absorbance (with DLs up to an order of magnitude higher). The reproducibility was 2.8% and 3–15%, for retention time and peak area, respectively. Validation of this ultra fast separation vs ion chromatography indicated that the proposed procedure is a valid alternative to the classical one for the analysis of an industrial water sample.^[65]

A very efficient column for simultaneous separation of common inorganic and organic ions was prepared by coating a RP column in two steps, firstly with 5 mM Triton X-100 from 30% acetonitrile and secondly with aqueous 5 mM cetylpyridinium chloride. The eluent was 2 mM sodium perchlorate

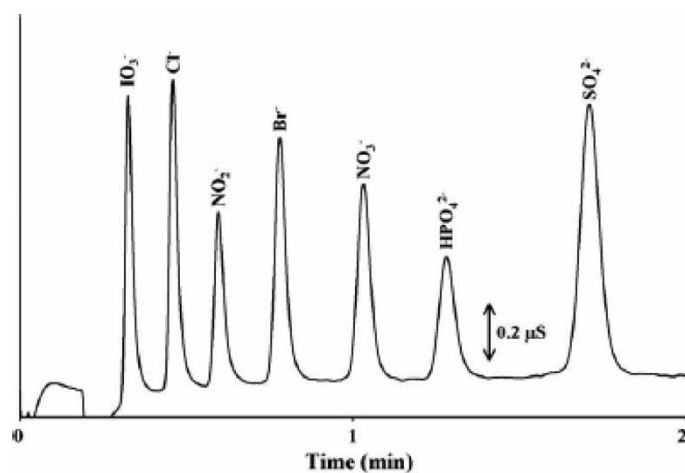


Figure 5. Suppressed anion separation with 4-hydroxybenzoic acid eluent at pH 10.0. Experimental conditions: 2 cm long column, eluent is 4-hydroxybenzoic acid 2.5 mM, 1.0 mL/min, coating solution for pre-column and separation column is DDAB 1 mM in 35% ACN, separation column capacity is 12 $\mu\text{equiv./column}$ (6 $\mu\text{equiv./cm}$), ASR-SULTRAII 2mm suppressor at 40 mA, analyte concentration is 150 μM . Reprinted from ref. [64] with permission from Elsevier.

and direct UV detection at 210 nm was used. The performance data showed an actual average plate number of 86 000 plates/m. The peaks were well shaped with an average asymmetry factor of 1.09. Incorporation of the non-ionic surfactant to in the coating gave sharper peaks and a dramatic reduction of retention times especially for organic anions via reduced hydrophobic interaction between these anions and the RP material.^[66]

Since the main drawback of ODS columns used under IPC to separate anions, compared to anion exchange stationary phases, is their incompatibility with eluents regularly used with conductivity detection, two strategies were devised to overcome this problem.

Firstly the potential of zwitterionic substances as eluents compatible with conductivity detection was investigated because of the very low background conductivities that can be obtained. This strategy resulted in a good separation of inorganic and organic ions with TBA as IPR^[66] and in linear calibration curves for fluoride, chloride, nitrite, bromide, pyruvate, and nitrate, with DLs ranging from 0.075 to 0.15 mg/L (ppm) for the five inorganic anions. The method was operated to determine water-soluble anions in aerosol samples at concentrations as low as 0.3 mg/L.^[67]

Alternatively graphitized carbon packing, which is sintered from carbonic material at a high temperature and shows excellent chemical and physical resistance, was used in the IPC of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , SO_4^- , HPO_4^- and I^- as illustrated in Figure 6. This way suppressed conductivity detection was possible. The alkaline mobile phase was optimized while

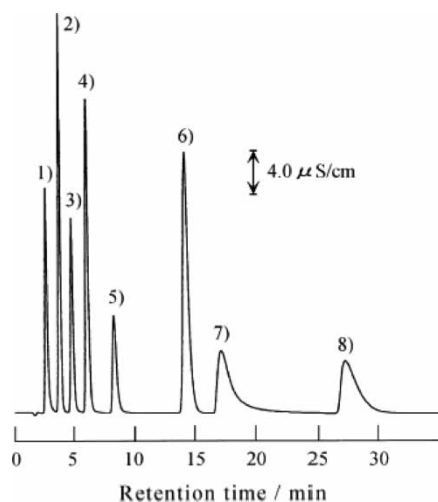


Figure 6. Ion chromatogram of a standard mixture. Eluent: 1 mM TBA–2 mM Na₂CO₃–5% CH₃CN. Ions (μg/ml): 1 = F⁻ (4); 2 = Cl⁻ (8); 3 = NO₂⁻ (8); 4 = Br⁻ (20); 5 = NO₃⁻ (8); 6 = SO₄²⁻ (20); 7 = HPO₄²⁻ (40); 8 = I⁻ (40). Reprinted from ref. [68] with permission from Elsevier.

changing the concentrations of the IPR (TBA) and of the eluting agent (sodium carbonate) with a fixed concentration of acetonitrile. Good resolution was achieved in 30 minutes. Calibration curves were linear with a correlation coefficient of 0.999 or better. For example the lineary range was from 0.5 to 10 $\mu\text{g/mL}$ for F^- , and from 5.0 to 100 $\mu\text{g/mL}$ for HPO_4^- and I^- . The relative standard deviations of peak areas were between 0.2 and 0.9% for 10 repeated measurements. The IPC method was used to determine chloride, bromide and sulfate in pharmaceutical compounds.^[68]

IPC anion separation commonly relies upon ammonium-based IPR. Analytes spanning the Hofmeister series from kosmotropic (iodate, chloride, nitrite) and intermediate (nitrate, bromide) to chaotropic anions (perchlorate, thiocyanate, iodide) allowed the characterization of sulfonium and phosphonium ions that are new IPRs. Significant changes in retention behavior are observed: retention generally increase in the order tributylsulfonium < TBA < tetrabutylphosphonium. Since anion retention is influenced by the kosmotropic/chaotropic character of both the IPR and the anion it is clear that this could allow for much more selective control of the retention factor of a desired anion.^[69]

Interesting application of IPC of common anions in real matrixes were the determination of urinary thiocyanate and nitrate using fast ion-interaction chromatography,^[70] the determination of iodide in urine by ion-pair chromatography with electrochemical detection,^[71] and the measurement of bromate in bottled water by high performance liquid chromatography with post-column flow reactor detection.^[72]

Hyphenation of IPC and ICP-MS equipped with a collision/reaction cell was useful for the analysis of organophosphorus chemical warfare degradation products: ethyl methylphosphonic acid isopropyl methylphosphonic acid, and methylphosphonic acid. IPC, with mobile phase 50 mM ammonium acetate; 2% methanol, 5 mM myristyl trimethylammonium bromide pH 4.85 on a C8 column, offered the best separation thanks to the slight charge differences between the species of interest. This method provides a highly sensitive baseline separation of the three species within 15 min and DLs of less than 263 pg/mL.^[73] Ion-pair extraction and IPC, with tri-*n*-butylamine as IPR, were combined for the determination of phosphoric acid mono- and diesters in municipal wastewater: it was found that even tertiary treatment does not ensure complete removal of these compounds that may probably originate from the microbial hydrolysis of phosphoric acid trimethylesters used as flame retardant. Matrix effects that occur during ESI altered the signal intensity of an analyte in the analysis of real samples and reliable quantification was demonstrated to require standard addition.^[74]

As a concluding remark it has to be underlined that the present author attempted to cover most developments that increased the scope of IPC in the inorganic field during the last decade; a critical trade-off between breadth and depth of applications concerning inorganic analytes and inorganic elements containing compounds was done.

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