Review

Isotachophoretic analysis of inorganic ions

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Abstract

Capillary isotachophoresis is frequently used in analytical practice for the determination of inorganic ions in various matrices. Proper selection of the separation conditions enables one to attain the maximum ratio of effective mobilities of the individual components of a mixture under analysis, and thus their mutual separation. This article examines possibilities of how to differentiate the effective mobilities of inorganic ions along with their use for the analysis of real samples. © 1999 Elsevier Science B.V. All rights reserved.

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Contents

1. Introduction

Capillary isotachophoresis (ITP) is one of the electromigration separation methods capable of analysing mixtures of ionic substances. At present the use of ITP is receding due to the rapid development of capillary zone electrophoresis (CZE). The principle of species separation by both methods is similar, but, however, they differ in the conditions under which the separation takes place and the final state reached after completion of separation. Thus CZE is characterised by a high separation efficiency (10^5–10^7 theoretical plates per m), the use of very small amounts of samples (pl, nl) and short duration of the analysis (1 to 10 min). On the other hand, the small sample volumes introduced (not greater than 10 nl) are connected with low separation capacity, and hence with decreased resolution of analytes in

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the presence of the macrocomponents, the concentration of components under analysis must be within the range of one order. Contrary to this, ITP exerts good preconcentration capability along with high separation capacity. Micro- and macrocomponents may be separated at ratios from 1:100 to 1:1000, and sample volumes of 0.1–100 μl may be loaded. Owing to the preconcentration capabilities ITP is a very suitable technique in cases when the analyte concentration in a sample is very low.

The high separation efficiency of CZE at the analysis of multi-component mixtures can lead (with high probability) to the formation of mixed zones and therefore to "peak overlaps". While ITP mainly uses conduction detectors (the length of zones are the evaluated quantitative parameters), in CZE these are rarely used. Its main detection method is based on the UV light absorption (photometry) and the quantitative parameter to be evaluated is the area under a peak. Since inorganic ions exert low absorption in UV region, their analysis by CZE requires indirect photometric detection.

Detection limits for both methods are very low $(5 \cdot 10^{-9} – 10^{-5}\ M)$ depending on the detection systems used and the properties of samples analysed. ITP and CZE are the main separation techniques for chemical analyses.

The goal of this review is to offer a brief insight into the isotachophoretic application possibilities in the field of inorganic analysis.

2. Separation of inorganic anions

2.1. Separation principles

Inorganic anions may be separated on the basis of different mobilities of their solvates in a suitable solvent, or utilising the differences in their pK values [1]. A frequent case is the use of complex forming equilibria, i.e., the different stabilities of complexes with a suitable cation [1]. An effect of the counterion charge is also often used there. Although the majority of published papers describe the use of aqueous solutions for the electrolyte systems, in certain cases the use of organic solvents enabled one to attain better differentiation mediated by influencing the absolute mobilities of anions. The use of

mixed solvents for ITP separations is restricted not only by the material of a separation unit, but mainly by the requirement that the ionic substances have to be sufficiently soluble in a given medium.

Treatment of the effective mobilities of ions under separation via changing the acid–base equilibria is frequently used for the separation of anions of weak acids in a mixture. But if a compound is not fully dissociated and distributed into several ionic forms, then each of these forms differ in their migration rates, i.e., their mobilities. Therefore one cannot expect that ITP (and all other separation methods where the process continuously disturbs the establishing of acid–base equilibria) may serve for the direct determination of the individual acid–base forms. Here, all the ionic forms of an acid might migrate in one zone with an effective mobility given by actual mobilities of its individual ionic species and their mass distribution. Thus if we want to know the resulting rate of migration of a substance, it is necessary to consider the kinetics, i.e., the rate of establishing the equilibria among individual ionic forms and its changes with those of external conditions. In principle the two boundary cases may be expected: establishment of the equilibria of mutually bonded ionic forms is slow (kinetically stable equilibria) and an acid of such kinetic profile should migrate as separated ionic forms (corresponding zones). When equilibria are changing rapidly (kinetically labile equilibria – second case), then all the ionic forms created would migrate as one homogeneous unity (zone). The most important optimising tool in ITP is the pH value. It controls the dissociation degree of an analyte in its zone and thus its resulting effective mobility. Using a suitably selected pH range it is possible to separate the anions of weak acids according to their pK values. The use of pH adjustment to optimise the separation conditions for the anions of strong acids is restricted, here is better to use the complex-forming equilibria.

The kinetics of complex-formation equilibria is of principal importance, as in the case of acid–base ones. Thus the kinetically labile complex-formation equilibria are there preferred, when the rate of equilibrium establishment is higher than that of migration of ions. The differences in effective mobilities of the anions are caused by the complex formation with cations present in a leading elec-

trolyte. Since the separation effect depends on that complexation, the separation is related to the complex constants stabilities.

Differences in effective mobilities may be influenced by action of the charge of an counter-ion as well. A braking effect of the ionic atmosphere increases with the charge of ions moving in opposite direction to that of ions to be separated. Electrostatic interactions are strong mainly among the polyvalent ions and counter-ions. In general it should be stated, that due to the electrophoretic and relaxation effect the higher charge of a counter-ion preferably slows down the separated anions with higher charge. By suitable selection of a counter-ion there may be positively influenced differences in effective mobilities of the anions under separation and thus the desired differentiation mainly in a region, where the separated anions are almost fully dissociated, is reached.

2.2. Examples of the isotachophoretic analysis of inorganic anions

Perhaps the first report on the isotachphoretic analysis of inorganic anions was published by Eeveraerts et al. [1], where the separation of sulphates, chlorates and chromates in an operating system consisting of histidine/histidine hydrochloride (leading electrolyte, pH=6) and 2-(*N*-morpholino)ethanesulphic acid (MES) as the terminating electrolyte, is described. Separation according to p*K* values should be useful by using thermometric detection. Boček et al. [2] described the determination of sulphates and chlorides in mineral waters, using $2 \cdot 10$ m*M* Cd(NO$_3$)$_2$ as the leading electrolyte and 10 m*M* citric acid as the terminating electrolyte. Since in this case the anions belong to the strong acids, the differentiation of their mobilities was provided by the complex formation equilibria with Cd ion, the leading anion was nitrate one. Chlorides, bromides, iodides and fluorides were analysed in methanol using a thermometric detector [1]. For experiments with anionic species in methanol was used Tris and 10 m*M* hydrochloric acid in methanol as the leading electrolyte. There was used a combination of the separation based on p*K* values and that based on mobilities. Other authors also succeeded in the separation of halogenides in methanolic medium

[3]. The separation of Cl$^-$, Br$^-$ and I$^-$ can also be achieved by addition of cyclodextrin into the leading electrolyte [4]. Bromides and iodides were determined simultaneously by Fukushi and Hiiro [5]. The separation principle there was based on ion-pairing equilibria between tetradecyldimethyl-benzylammonium ions and these anions in the leading electrolyte.

The same system of electrolytes as in Ref. [1] was used by Ryšlavý et al. [6] for the determination of sulphates and chlorides. With regard to the composition of surface waters, Zelenský et al. [7] worked out an operating system for simultaneous determination of chlorides, nitrites, nitrates, phosphates, sulphates and fluorides. The effective mobilities of macrocomponents formed by nitrate, chloride and sulphate anions were differentiated by the addition of a complexing counter-ion of 1,3-bis[tris-(hydroxymethyl)methylamino]propane (BTP). The authors have used column-coupling capillary ITP with different composition of the leading electrolytes in both capillaries. Macrocomponents were analysed in a pre-separation capillary using 8 m*M* HCl, β-alanine, and 0.1% hydroxyethylcellulose (HEC) at pH=3.55 as the leading electrolyte. Microcomponents were analysed in an analytical capillary with the leading electrolyte consisting of the same chemicals as previously but the amount of HCl was 1 m*M*. Two m*M* citric acid (with pH of approx. 3) was the terminating electrolyte. Detection limits for constituents that are present in river water at lower concentrations (NO$_3^-$, F$^-$ and PO$_4^{3-}$) were in the range of 30–60 pmol.

Vacík and Muselasová [8] used 5 m*M* Ca(OH)$_2$ as the leading electrolyte and 10 m*M* formic acid as terminating one for the analysis of sulphates and nitrates in waters. These anions were similarly analysed by other authors [9,10]. Sulphates in mixture with fluorides and Fe^{2+} and Al^{3+} (these cations were in the form of anionic complexes with diethylenetriaminopentaacetic acid) were determined in raw phosphoric acid [11].

Kaniansky et al. [12] have analysed rainfall water using the leading electrolyte composed of histidine and MgCl$_2$ (pH=6) and the terminating one made of histidine and acetic acid (pH=5). Matějovič and Polonský [13] have been determining sulphates in aqueous extracts of a plant material. Their leading

electrolyte contained β-alanine and magnesium chloride, and citric acid served as the terminating electrolyte.

Pei and Vonderschmitt have analysed sulphates in urine without pretreatment of a sample [14]. The leading electrolyte used there was composed of nitric acid, cadmium nitrate and β-alanine (pH=3.0), the terminating one contained caproic acid. In similar manner it is possible to determine the sulphates also in the samples obtained from plant material after mineralisation. Křivánková and Boček [15] have analysed cooling and waste waters from the nuclear power plants in order to determine the chlorides, sulphates, nitrates, phosphates, fluorides, oxalates, and citrates. Tatsuhara [16] has dealt with simultaneous determination of sulphates and sulphites. To retard the sulphates against chlorides (being the leading anions) he used an addition of acetone into the leading electrolyte, which was afterwards composed of 10 mM histidinium chloride and 30% of acetone (pH=4), the terminating electrolyte was 10 mM caproic acid (pH=3.5).

Yagi et al. have been determining $S_2O_3^{2-}$, SO_4^{2-}, and SO_3^{2-} contained as impurities in Na_2S [17]. The electrolyte system was formed of water–acetone (1:1) with 0.5 mM HCl and 10 mM histidine (leading electrolyte), and 10 mM sodium acetate (terminating electrolyte). Fukushi and Hiiro in several papers have been dealing with the determination of inorganic anions in sea water. In systems of the leading (10 mM HCl, histidine, 0.1% of Triton X-100, pH=4.0) and terminating electrolyte (10 mM hexanoic acid) they have determined fluorides [18]. In the same systems they have been analysing tripolyphosphates, pyrophosphates and orthophosphates [19]. Further they have used the system of the leading electrolyte containing 5 mM of perchloric acid, methanol and Tris, and 10 mM sodium fluoride as the terminating electrolyte for the determination of bromides [20]. Five mM NaOH with 0.1% hydroxypropyl-methylcellulose as the leading and 10 mM sodium acetate as terminating electrolyte was used by these authors at the analysis of sulphides [21]. In all cases the authors before the main analysis have used more or less complicated pretreatment, sometimes a preconcentration was necessary.

Influence of poly(vinylpyrrolidone) (PVP) on isotachophoretic separation of eighteen inorganic anions in aqueous electrolyte was investigated by Madajová et al. [22]. The polymer (added to the leading electrolyte) was found to influence selectively the effective mobilities of some anions from this series. In some instances the resulting differences in these separation characteristics provided the isotachophoretic separations, not feasible in ordinary aqueous electrolyte systems. In the article the effective mobilities of AsO_4^{3-}, PO_4^{3-}, CrO_4^{2-} SeO_3^{2-}, $P_2O_7^{4-}$, ClO_3^-, SCN^-, BrO_3^-, F^-, I^-, ClO_4^-, NO_3^-, SO_4^{2-}, NO_2^-, $S_2O_3^{2-}$, Br^- and Cl^- were studied in operating systems of the leading electrolyte containing 10 mM histidinium chloride, 0.2% HEC, 0–10% PVP (pH=6), and the terminating one consisting of MES and histidine (pH of approx. 6).

3. Separation of inorganic cations

3.1. Separation principles

For the separation of cations the same principle as that of anions is utilised, i.e., the differences in absolute mobilities of individual cations due to their different masses and charges. Solvation of cations in aqueous media plays more important role than that in the case of anions [1]. Normally, the migrating ions there are surrounded by the ions bearing opposite charge (ionic atmosphere), which has a braking effect on the migration of ions under separation. Actual mobilities of solvated ions in this case may be controlled by means of the electrophoretic and relaxation effect. Action of both effects increases with the charge of both ion and counter-ion, with decreasing dielectric constant of a solvent and increasing concentration of an electrolyte. The values of absolute mobilities may be varied in desired direction by suitable selection of the solvent, based mainly on different solvation abilities.

Very frequent is the use of different complex formation abilities of metal cations [1]. In this case it is possible to separate either the cationic complexes of metal complexes with a suitable ligand present in the leading electrolyte (because the effective mobilities are in relationship with the stability constants of corresponding complexes). There are important two requirements: the complex formation equilibria

among individual complex species should be kinet-ically labile and their ionic form have to bear positive charge. In some cases an excess of suitable complexing agent is added to a sample with cations, which are then separated as corresponding anionic complexes (chelates). This approach usually requires to work at elevated pH in order to prevent the loses of analysed material due to the decomposition of a chelate during the migration. This way of separation is convenient at the ITP analyses of metals in mixtures, in which we simultaneously need to ana-lyse anionic components.

Similarly, as with isotachophoretic separation of anions, the effect of charge of a counter-ion is utilised here [1]. This counter-ion must be an anion of weak acid, whose pK value is numerically close to the desired pH value of the leading electrolyte. Changes of the effective mobilities of cations can also be attained by changing their degree of dissocia-tion, attainable by proper pH adjustment of the leading electrolyte. But in case of inorganic cations this way of influencing the cation effective mobilities is not used much.

3.2. Examples of the isotachophoretic analysis of inorganic cations

Everaerts et al. [1] described some operating systems enabling the separation of cation mixtures. Thus in the operating system composed of 10 mM HCl (leading electrolyte) and 10 mM Tris (termi-nating electrolyte) there were separated Tl, La, Ca, Fe^{II}, Cd, and Li. The leading electrolyte 10 mM CH$_3$COOK adjusted to pH=5.4 by adding acetic acid, and 10 mM Tris as the terminating electrolyte was used for the separation of a mixture containing Ba, Ca, Na, Ni, Cd and Pb. The most important of those are Pb, Ce, La and Cr, which are all polyvalent ions. Further, these authors have separated a mixture containing K, Ba, Ca, Na, Ni, Mn and Cu in the following system: leading electrolyte was 10 mM KOH adjusted to pH=6.4 by adding cacodylic acid, and terminating electrolyte was 10 mM Tris. In all cases the thermometric detector was used.

The most frequent separation of cations by ITP is the achieved by the use of complex forming equilib-ria with negatively charged ligands or electroneutral ones. Thus, equimolar mixtures of 14 lanthanide ions

have been separated and determined simultaneously using complex forming equilibria between 2-hy-droxyisobutyric acid (HIBA) and these ions [23,24]. The relative standard deviations (RSDs) of simulta-neous determinations of 5 nmol of lanthanides were 1.2–1.5%. Leading electrolyte was formed by 27 mM KOH, 15 mM HIBA, acetic acid and 0.0025% PVA (pH=4.92), the terminating electrolyte con-tained β-alanine and acetic acid (pH=4.00).

Hirokawa and Hashimoto [25] have tested several helping complexing agents for the HIBA electrolyte systems used in ITP separation of 15 rare-earth elements (yttrium and lanthanides with exception of Pm) such as malonic, maleic, tartaric and glycolic acid. The optimised leading electrolyte was a 20 mM ammonia solution containing 20 mM malonic acid and 7.5 mM HIBA (pH=4.8, 2-ethylbutyric acid buffer), the termination electrolyte was a 20 mM carnitine hydrochloride. Complexing 2-hydroxy-isobutyric acid was used as a counter-ion for the successful separation of alkaline earth elements [26], and Ba, Na, Ca, Mg, Mn, Cd, Co, Zn, Ni, Pb and Cu also [27]. These authors [28] have been analysing samples of waters in order to determine Fe^{II}, Cu, Ni, Zn and Al in the operating systems of the following composition: the leading electrolyte was 20 mM Na$^+$(K$^+$), HIBA, acetic acid, the terminating elec-trolyte was 5 mM acetic acid. Hirokawa et al. [28] have separated a mixture of 20 cations in the systems containing NH$_4^+$ as the leading ions, acetate ions (Ac) served as pH buffering counter-ion (pH=4.8). The migration order was as follows: Ba, Sr, Ca, Na, Mg, (Mn, Fe^{II}, Co), Ni, Zn, La, Ce, Cd, Y, Li, Lu, Gd, (Cu, Pb), and Zr^{IV}O, Fe^{III}. In the NH$_4$Ac–HIBA systems a total separation was reached with the following migration order: Ba, Sr, Ca, Na, Mg, Mn, Fe^{II}, Cd, Co, Li, Ni, Zn, La, Pb, Ce, Gd, Cu, Y, Zr^{IV}O and Lu. The zones were fractionated and analysed off-line by particle-induced X-ray emission (PIXE). The recovery of metal cations was 100% with both electrolyte systems, except for Fe^{II} and Zr^{IV}O. The latter forms a hydroxyl complex, while Fe^{II} gave a hydroxyl complex of Fe^{III} – the oxida-tion product of ferrous ions. For these ions the recovery in the NH$_4$Ac–HIBA system was lower than that for the NH$_4$Ac system.

Similarly, the group of 20 metal ions was sepa-rated in the form of kinetically labile complexes with

tartaric acid [29]. Thus, the leading electrolyte was 20 mM ammonia solution buffered by adding the acetic acid (pH=4.8), and the concentration of tartaric acid was varied in the range 0–5 mM. The terminator was 20 mM carnitine hydrochloride solution.

A mixture of Fe^{II} and Fe^{III} was separated by using 1,1-phenantroline as a complex forming agent [30]. The separation was carried out in a conventional electrolyte system for cation analysis. The leading electrolyte was 20 mM ammonia solution buffered with acetic acid (pH=4.8), terminator was β-alanine (pH=3.6). Nakabayashi et al. [31] determined Mn and Zn in waste waters in the form of complexes with diethyldithiocarbamate placed in the leading electrolyte of following composition: 5 mM HCl, 3 mM β-alanine and 45% acetone. The terminating electrolyte was 5 mM disodium salt of EDTA.

Zelenský et al. [32] have been determining the trace concentrations of Cd and Mn in drinking water as kinetically labile complexes with xylenol orange. Their leading electrolyte was composed of 20 mM NH$_4^+$, acetate anions, 0.4 mM xylenol orange, and 0.1% of HEC (pH=5.0), terminator was 1 mM nitric acid (pH=3.0). Using photometric detection, the attained detection limit was as low as 10^{-8} M. This researcher solved a problem of the ITP determination of trace amounts of Cr^{VI} besides the excess of Cr^{III} [33]. The detection limits for Cr^{VI} were in the range 4–5 ppb. Reproducibility of the determinations within the concentration range 10^{-7}–$5 \cdot 10^{-6}$ M was 2–3% or better. The practical utility in the trace determination of Cr^{VI} in drinking and waste water samples seems to be promising.

Boček et al. have dealt with the problem of ITP analysis of cations on a general level [34]. One of the most complicated task at analysis is the separation and determination of alkali and alkaline earth elements. Their mobilities in aqueous solutions are very close each other. Alkali and some of the alkaline earth metal cations were, however, successfully separated in methanolic medium [1,3,28,35,36]. Thus, cations of K, Na, Ca and Mg were separated basing on the labile complex formation with 2 mM N-oxide of nitrilotrismethylenephosphonic acid contained in the leading electrolyte, 4 mM creatinine was the terminating electrolyte [8]. The concentrations of given metals in samples were in the range

0.8–$21.2 \cdot 10^{-4}$ M. Some alkali and alkaline earth metals were separated by means of complexing counter-ions of acids as HIBA [37] and cyclohexane-1,2-diaminotetraacetic acid (CyDTA) [38]. Sulphates as counter-ions were used for the simultaneous determination of K, Na, Li, Ca and Mg in biological tissues [39]. Buben et al. [40] determined K, Na, Mg and Ca in infusion solutions using the electrolyte system of the following composition: 5 mM of sulphuric acid (producing leading ions H$_3$O$^+$), the terminator was 10 mM lithium citrate.

Matsushita et al. [41] described the determination of Ca in the presence of phosphate anions using a leading electrolyte consisting of 10 mM potassium acetate–acetic acid (pH=5.4) and a terminating electrolyte containing 10 mM n-hexanoic acid. It was reported [42], that addition of a polyoxyethylene ether-type surfactant (Triton X-100) to the leading electrolyte enabled one to separate the alkali and some alkaline earth metal cations. Thus, cations of Rb, Na and Ca were determined in a pharmaceutical preparation [43]. A 10 mM solution of ammonium picolinate (pH=5.4) containing 30 mM 18-crown-6 and 0.4% (w/v) of Triton X-100 was used as the leading electrolyte, the termination one was formed by 5 mM acetic acid. ITP, using 2.10 mM potassium citrate as the leading electrolyte (pH=5.0) and magnesium chloride as the terminating one provided suitable method for the simultaneous determination of Ba and Sr in a silica matrix [44]. The full separation of alkaline metals and alkaline earth ones was attained by use of the complexation with 18-crown-6 ether [45,46].

The separation of alkaline earth metal cations in an anionic mode inherit disadvantages (restricted pH range of the separation [47–50] and close effective mobilities of the metal chelates [40]). Authors of [47,48] have separated the EDTA complexes in operating systems where the leading electrolyte was 10 mM HCl, Tris, and 0.5% methyl cellulose (pH=8.5), the terminating electrolyte was 10 mM hexanoic acid. The same authors have separated the alkaline earth metal complexes with EDTA and glycoletherdi-amino-N,N,N',N'-tetraacetic acid (GEDTA) [49].

The separation of K, Na, Li, Ba, Sr, Ca and Mg has been achieved using N-hydroxy-ethyliminodiacetic acid (HIDA) as the complexing

co-counter-ion [51]. Alkali metal cations present in the model mixtures were determined in the concentration range $1–125\cdot10^{-5}$ *M* with the RSD that was in most cases less than 0.1%. Detection limits for individual ions were within $6.4–18.0\cdot10^{-6}$ *M*. The separation of the alkali metals in mineral and drinking water and in the lyophilised blood was carried out as well. The differentiation of effective mobilities of alkali metal and alkaline earth metal cations was solved by influencing the solvation equilibrium by use of a mixed solvent of water–polyethylene glycol (PEG) [52]. PEG retards not only the alkaline earth elements Mg, Ca, Sr, and Ba, but it allows one to resolve the alkali metals Cs, Rb, K, Na and Li. The composition of leading electrolyte was 10 (5, 20) m*M* NH_4^+, acetate ions, PEG, and 0.2% of HEC (pH=5), that of terminating electrolyte was 5 (3) m*M* tetraethyl ammonium perchlorate. At presence of 50% of PEG in the leading electrolyte the migration order is as follows: NH_4^+, Cs, Rb, K, Na, Mg, Ca, Sr, Li and Ba. The operating systems water–PEG were used for the analysis of surface, waste, and mineral water [52], blood [53], urine [52], blood serum [54,55], and infusion solutions [56].

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