New leading electrolyte for the direct determination of chloride and other anions in analytical isotachophoresis

Th. Meissner[a,c], F. Eisenbeiss[b,*], B. Jastorff[c]

[a]*J+M, Robert-Bosch-Str. 83, D-73431 Aalen, Germany*
[b]*Merck KGaA, SLP, Frankfurter Str. 250, D-64271 Darmstadt, Germany*
[c]*Zentrum für Umweltforschung und Umwelttechnologie (UFT), Universität Bremen, Postfach 330440, D-28334 Bremen, Germany*

Abstract

In a number of experiments it was shown that the dithionate ion possesses a higher effective mobility than the chloride ion in aqueous solution, thus enabling the direct and simultaneous isotachophoretic determination of chloride and other anions. Using an acid–base titration, we found only one pK_a value for dithionic acid, which is in contrast to the two pK_a values stated in the literature. Based on this pK_a value, theoretical calculations and the experimentally observed effective mobility of the dithionate ion indicate a higher effective mobility compared to the chloride ion from pH 3. Taking into account the physico–chemical properties of the dithionate, its unrestricted use as isotachophoretic leading ion was confirmed. Based on the dithionate ion, new electrolyte systems for the determination of chloride were used. One system was optimised for the determination of chloride and other low-molecular-mass anions and applied to the analysis of waste water and drinking water. The water samples were analysed in parallel by ion chromatography and compared with the isotachophoretic results. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Isotachophoresis; Water analysis; Environmental analysis; Buffer composition; Chloride; Organic acids; Inorganic anions

1. Introduction

Capillary isotachophoresis (ITP) is a powerful tool for the analysis of ionic compounds in various matrices [1,2].

One of the main disadvantages of using ITP is the poor performance obtained in the determination of chloride. In general, the chloride ion is the leading ion in the anionic mode of ITP. This means, however, that chloride can only be determined indirectly by comparing the prolongation of the leading zone (chloride) to the leading zone in a run without chloride in the sample. Of course, this procedure restricts the minimal concentration that can be detected as well as the reproducibility.

Several attempts have been made to solve this problem. Ions with a theoretical higher mobility than the chloride ion have been investigated. Experimentally, it was obvious that such ions, e.g. chromate, hexacyanoferrate II and hexacyanoferrate III do not possess a higher effective mobility due to incomplete dissociation and the influence of ionic strength [3]. Although the use of the hydroxide ion (OH^-) as the leading ion has been reported [4], its use is not of advantage. No buffer capacity and the pH of 11–12 (CO_2 absorption) are in connection with OH^- as a leading electrolyte.

Bocek et al. were able to separate the halides chloride, bromide and iodide as well as the sulphate

---

*Corresponding author. Tel.: +49-6151-72-2449; Fax: +49-6151-72 6559.

using cadmium nitrate as the leading electrolyte [3]. The separation is based on complex formation of cadmium with the halides.

From a practical point of view the use of cadmium nitrate has a number of disadvantages: (1) no wide variation of the pH value, (2) no buffer capacity, (3) toxicity of the Cd^{2+}, and (4) no determination of nitrate, as it acts as the leading ion.

It is the purpose of this paper to present a new leading electrolyte in ITP based on the dithionate ion. The new leading electrolyte was investigated theoretically and experimentally with regard to the direct and simultaneous determination of chloride and other ions in analytical isotachophoresis.

2. Experimental

2.1. Instrumentation

The isotachophoretic instrument Ita Chrom EA 101 (J&M, Aalen, Germany) was used in the column-coupling mode. The first capillary, made of fluorinated ethylene–propylene polymer (FEP), had a length of 9 cm with an I.D. of 800 μm; the second, consisting of the same material, had a length of 16 cm but with an I.D. of 300 μm. Both columns were fitted with an on-column conductivity detector; additionally, the second column was equipped with a UV absorbance detector. The capillary tubes were placed in compartments made of plexiglas, which allowed the heat generated by the passage of current to be dissipated. Samples of 30 μl were injected with the aid of a sample valve.

For data evaluation and processing, ITP-WIN 2.21 software was used.

2.2. Chemicals

The following chemicals were used: citric acid, tartaric acid, magnesium acetate, 6-aminocaproic acid (all analytical reagent grade), and β-alanine, creatinine and histidine (all for biochemistry), all from Merck (Darmstadt, Germany); 1,3-bis-[tris(hydroxymethyl)methylamino]propane BTP (BioChemika) from Fluka (Buchs, Switzerland); purified methylhydroxyethylcellulose 1% stock solution from Comenius University, (Bratislava, Slovak

Republic). The 98% sodium dithionate was supplied by Pfaltz and Bauer (Waterburg, USA). Anion standard solutions of chloride, nitrate, sulphate, fluoride and phosphate of 1000 mg l^{-1} were obtained from Merck; all other standard solutions were prepared from the sodium salts of the same concentration. All solutions, electrolytes and standards were produced using ultra pure water from a Seral PRO 90 C system (Seral, Ransbach–Baumbach, Germany) with a conductivity <0.1 μS/cm.

3. Results and discussion

3.1. Calculation and determination of μ_{eff}

The absolute mobility (μ_0) is the mobility of the relevant ion at infinite dilution in aqueous solution. The absolute mobility can be predicted from the absolute ionic equivalent conductance (λ_0).

$$\mu_0 = \lambda_0 / F \tag{1}$$

where F is the Faraday constant.

The λ_0 value for a number of ions can be found in the literature [5,6]; surprisingly high values were listed in the cited literature for the dithionate ion (93×10^{-4} m^{2}S/mol).

The effective mobility (μ_{eff}) of the analytes is the key physico–chemical property in ITP and CE. It depends on the degree of dissociation of the analyte and the ionic strength of the electrolyte solution in accordance with the Debye–Hückel–Onsager relationship.

We calculated the μ_{eff} of the dithionate and chloride ions with the help of an equation proposed by Friedl et al. [7].

$$\mu_{eff} = \mu_0 \cdot \alpha \cdot k \tag{2}$$

where α is the degree of dissociation and k is a correction factor representing the influence of the ionic strength I. The factor k is expressed by an empirical equation which consist of two variables: the ionic strength of the buffer and the charge number of the analyte [7]. The complete equation used for the calculation was:

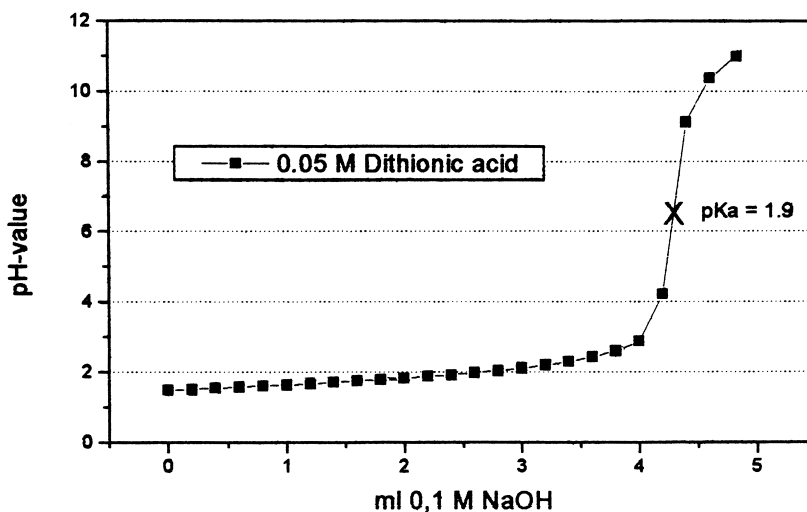$$\mu_{eff} = \mu_0 \cdot \frac{1}{1 + 10^{pKa - pH}} \cdot 10^{-0.77\sqrt{I} \cdot z} \tag{3}$$

Fig. 1. Titration curve of dithionic acid.

In order to obtain the pK_a values of the dithionic acid, an acid–base titration was performed. Fig. 1 shows the typical titration curve of a strong acid with a strong base; surprisingly, only one pK_a value for the divalent acid can be recognised. This pK_a value is 1.9.

This unusual behaviour of a divalent acid can only be explained by the high symmetrical structure of the dithionate ion. Both SO_3 groups are symmetrically connected via a ternary symmetry axis [8]. Based on this data and a leading electrolyte concentration of 5 mmol/l, the μ_{eff} was calculated as a function of pH value according to Eq. (3).

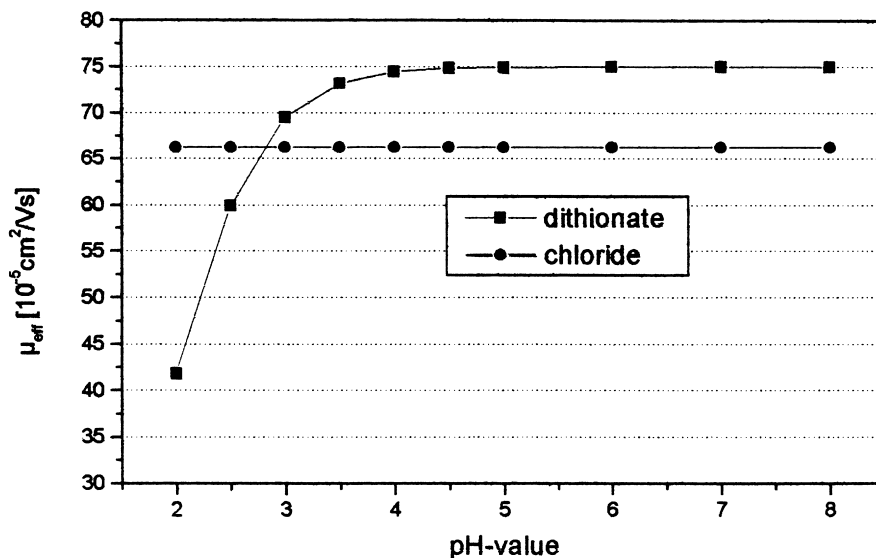Fig. 2 indicates a higher effective mobility of the

Fig. 2. Calculated μ_{eff} of chloride and dithionate ($pK_a = 1.9$).

dithionate compared to the chloride ion starting from a pH value of 3. This was checked experimentally while performing istoachophoretic separations on different inorganic anions with dithionate-based leading electrolytes at different pH values.

The isotachopherograms obtained (Fig. 3) were in agreement with the above-mentioned results.

Fig. 3 illustrates that, beginning from a pH of about 3, the direct isotachophoretic analysis of chloride is possible. Consequently, from a pH of 3, the dithionate possesses a higher effective mobility than the chloride ion.

With the $S_2O_6^{2-}$ ion, a potential leading ion is now available for the first time which is highly mobile in aqueous solution at concentrations commonly used in ITP.

3.2. Stability test

However, in addition to its mobility, the physical–

chemical properties of the new leading ion have also to be considered. The aqueous solution of dithionic acid is clear and shows no absorbance in the wavelength range 220–400 nm. Moreover, the solution is not oxidisable and/or reducible on Pt electrodes [9].

Dithionic acid is known for its instability in more concentrated solution.

$$H_2S_2O_6 \rightarrow H_2SO_4 + SO_2$$
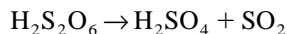
A solution of 240 mmol l^{-1} decays at 25°C in 40 days to 3% [9]. For this reason, we performed a long-term stability test with the aim of evaluating the long-term use of a leading electrolyte based on the dithionate ion. Fig. 4 shows the isotachopherogram of a test mixture and the leading electrolyte system used. This leading electrolyte was used for 28 days, whereby it was stored in a refrigerator at 4°C for the entire period.
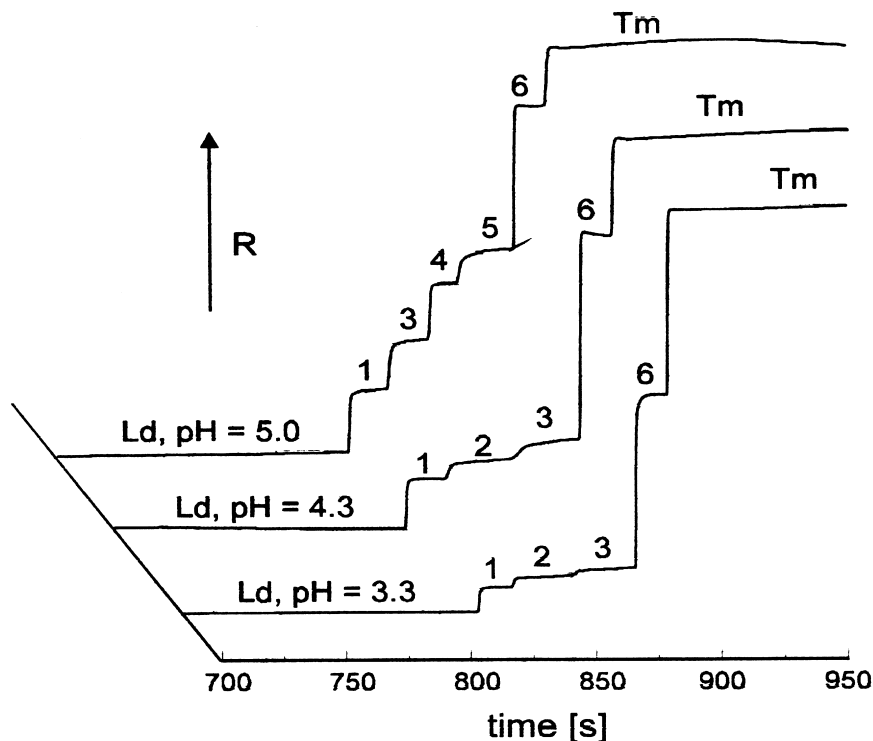
Table 1 shows the mean values of 7 measure-

Fig. 3. Isotachopherograms with dithionate leading electrolytes at different pH values. Leading electrolyte (Ld): 5 mmol l^{-1} dithionic acid (β-alanine, pH=3.3), (6-aminocaproic acid, pH=4.3), (creatinine, pH=5), 0.1% HMEC, Terminating (Tm): 5 mmol l^{-1} tartaric acid, injection: 30 μl, current: I$_1$=230 μA, I$_2$=30 μA. 1: Chloride, 2: sulphate, 3: nitrate, 4: perchlorate, 5: chlorate, 6: fluoride. R=resistance.
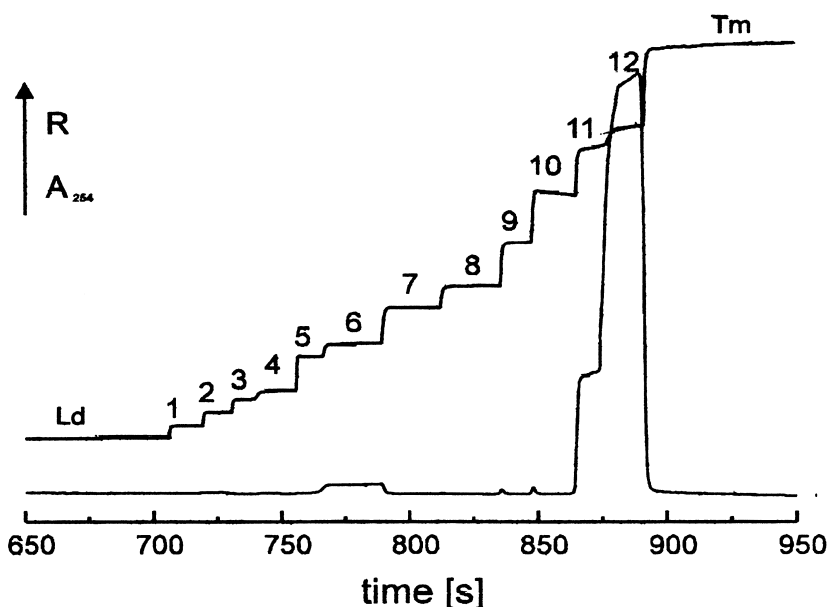
Fig. 4. Isotachopherogram of the test mixture of different anions. Leading electrolyte (Ld): 5 mmol l^{-1} dithionic acid, histidine, pH=6, 0.1% HMEC, Terminating (Tm): 5 mmol l^{-1} glutamic acid, injection: 30 µl, current: I_1=230 µA, I_2=30 µA. 1: Chloride, 2: nitrate, 3: perchlorate, 4: chlorate, 5: fluoride, 6: 2-ketoglutarate, 7: glutarate, 8: adipate, 9: acetate, 10: phosphate, 11: benzoate, 12: 2,4-dinitrophenolate. R=resistance, A$_{254}$=absorption at 254 nm.

ments and the relative standard deviation (R.S.D.) of the relevant anions over the entire period. It can be concluded from Table 1 that there is no systematic drift in the mean values; in fact, normal fluctuation of the mean values is apparent.

The fluctuation of the mean values for all anions is approximately 4%. The exception to this is the benzoate ion, where a maximum fluctuation of 7.5% can be established.

The R.S.D.s of the relevant ions are, in the majority of cases, <3% (except for benzoate).

In conclusion, we state that a leading electrolyte

Table 1
Mean values of the zone lengths and R.S.D.s of the long-term stability test

Anion	First day		13th day		20th day		28th day	
	ϕ (s)	R.S.D. (%)	ϕ (s)	R.S.D. (%)	ϕ (s)	R.S.D. (%)	ϕ (s)	R.S.D. (%)
Chloride	12.96	1.7	13.26	2.2	12.86	2.7	13.11	3.0
Nitrate	11.14	1.0	11.19	1.7	11.29	1.6	11.24	1.3
Perchlorate	9.18	1.6	9.14	1.7	9.25	1.3	9.2	1.4
Chlorate	15.33	1.7	15.95	1.8	15.31	0.8	15.34	1.0
Fluoride	10.64	2.6	10.06	1.3	10.24	1.7	10.14	1.7
2-Ketoglutarate	22.08	2.3	21.62	1.3	22.09	1.2	22.73	1.2
Glutarate	21.37	2.6	20.99	0.8	21.51	1.3	21.73	1.5
Adipate	22.58	2.2	22.16	0.8	22.71	1.3	23.16	1.6
Acetate	11.76	2.1	11.49	0.9	11.65	1.8	11.81	1.9
Phosphate	16.27	2.8	15.91	1.5	16.23	1.5	16.59	1.6
Benzoate	9.95	2.9	9.26	2.8	9.91	3.8	9.17	4.8
2,4-Dinitrophenolate	14.96	2.9	15.58	2.1	14.68	1.9	15.04	2.7

ϕ=mean value.

which contains dithionate is stable for at least 4 weeks and can therefore be used without restriction over this period.

Now, for the fist time, a suitable ion, the dithionate ion, exists that can be substituted for the chloride-based leading electrolyte. This now enables the latter to be directly determined.

3.3. Application of the new leading electrolyte

We focused the application of the new leading ion on the determination of chloride and other low-molecular-mass anions in environmental samples.

In previous papers we used a chloride leading electrolyte with BTP added to the electrolyte for the separation of low-molecular-mass anions [10,11]. The complex-forming properties of BTP were used in order to enhance the resolution, especially for the nitrate and sulphate ions.

In connection with the dithionate leading electrolyte, the use of BTP was not of advantage. We found a decrease in the step height difference between the leading ion (dithionate) and the sample ion (chloride) caused by the additive BTP. BTP as a

Table 2
Operational system

	Leading	Terminating
Solvent	Water	Water
Anion	Dithionate	Citrate
Concentration (mmol/l)	5	5
Counter ion	β-Alanine	–
Co-counter ion	1.8 mmol l^{-1} Mg^{2+}	–
Additive	0.1% HMEC	–
pH	3.5	ca. 4

HMEC = hydroxymethyethylcellulose.

divalent cation also interacts with the dithionate ion, thus reducing the effective mobility of the dithionate.

We thus investigated Ca^{2+} and Mg^{2+} salts, both have been used in ITP in the past [12,13].

In this case the mobility of the dithionate is not influenced because the dithionate salts of the mentioned cations are completely soluble in aqueous solution [9].

An isotachopherogram from a low-molecular-mass anionic standard and a blank-run of the electrolyte system are shown in Fig. 5. The ITP system applied is listed in Table 2.
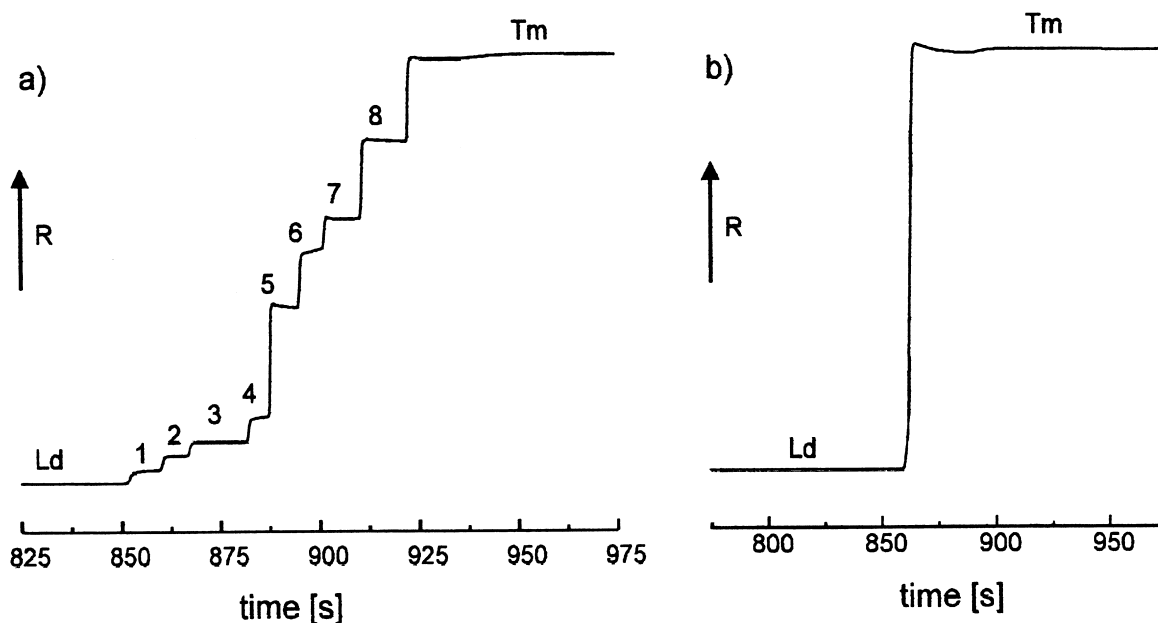

Fig. 5. (a) Isotachopherogram in the second capillary of the separation of a standard anion mixture and (b) a blank-run (terminating injected as sample). The operational system in Table 2 was used. Injection: 30 µl, current: $I_1 = 230$ µA, $I_2 = 30$ µA, 1: Chloride, 2: nitrate, 3: sulphate, 4: nitrite, 5: fluoride, 6: formate, 7: oxalate, 8: phosphate. R = resistance.

The operational system was applied to the analysis of inorganic anions in waste water and drinking water. The waste water was taken from the industrial area of Merck before entering the sewage purification plant. The drinking water was also taken from the Merck KGaA supply. Both samples were analysed in parallel by ion chromatography, using a suitable European standard method (EN ISO 10304) [14].

The waste water sample was diluted 1:1000 prior to analysis by ITP and ion chromatography (IC). The dilution factor for the drinking water was 1:5 for the ITP and 1:10 for the IC.

Fig. 6 illustrates the determination of inorganic anions in waste water and drinking water.

The ions were identified by comparing the RSHs (relative step heights) in the sample with the RSHs in standard solutions and, for confirmation, by adding the appropriate ion to the sample. For quantification, the mean value of three independent measurements were inserted in the already recorded calibration equations.

The quantification in the IC method was performed by using the average peak areas of three

Table 3
Results of the waste water and drinking water analysis with ITP and IC

Anion	Waste water (ppm)		Drinking water (ppm)		
	ITP	IC	ITP	IC	Limiting value[a]
Chloride	1840	1723	37	34	–
Nitrate	–	–	48	44	50
Sulphate	1780	1740	75	73	250

[a] Limiting value European Union.

measurements of anion standards with a concentration of 10 ppm.

The results of both methods are listed in Table 3.

The accuracy of the ITP results can be concluded from Table 3. The results obtained are all within the same degree of magnitude. The value for nitrate in the drinking water sample is high; it is close to the limiting value specified by the European Union.

4. Conclusions

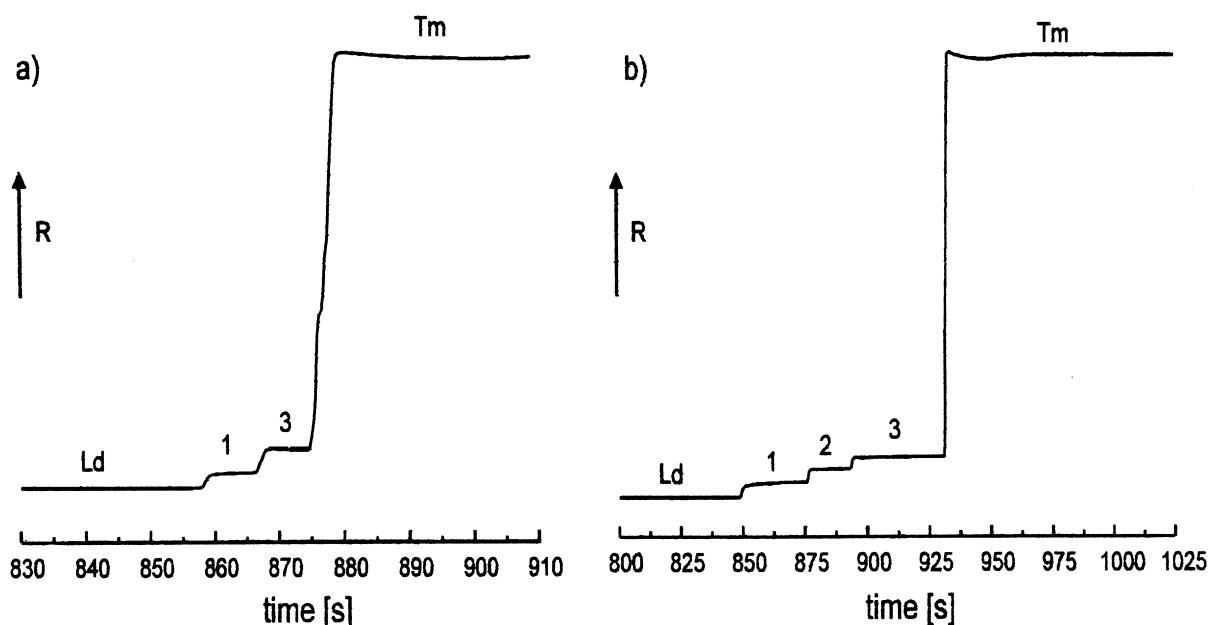One of the main disadvantages associated with

Fig. 6. Isotachopherograms of waste water (a) and drinking water (b) samples. The operational system shown in Table 2 was used. Injection 30 μl, current: $I_1 = 230$ μA, $I_2 = 30$ μA. 1: Chloride, 2: nitrate, 3: sulphate. R=resistance.

analytical ITP has now been eliminated. Now, for the fist time, a suitable ion, the dithionate ion, exists that can be substituted for the chloride-based leading electrolyte. This now enables the latter to be directly determined. The dithionate ion is stable and possesses a higher effective mobility compared to the chloride ion in aqueous solution from pH 3. We demonstrated the application of the new leading ion in the analysis of chloride and other anions in model mixtures and in the determination of inorganic anions in real waste- and drinking water samples. The results obtained for the inorganic anions by ITP were in agreement with those obtained by IC.

The new leading ion offers the opportunity for new application areas in ITP.

References

[1] P. Bocek, M. Deml, P. Gebauer, V. Dolnik, Analytical Isotachophoresesis, VCH, Weinheim, 1988.

[2] F.M. Everaerts, J.L. Becker, T.P.E.M. Verheggen, Isotachophoresesis: Theory, Instrumentation and Applications, Elesevier, Amsterdam, 1976.

[3] P. Bocek, I. Miedziak, M. Deml, J. Janak, J. Chromatogr. 137 (1977) 83–91.

[4] J. Vacik, I. Muselasova, J. Chromatogr. 320 (1985) 199–203.

[5] Landolt Börnstein, Zahlenwerte und Funktionen, Vol II, Teil 7, Springer Verlag, Berlin 1960.

[6] CRC Handbook of Chemistry and Physics, 76th ed., CRC Press, Boca Raton, Florida, 1986.

[7] W. Friedl, J.C. Reijenga, E. Kenndler, J. Chromatogr. A 709 (1995) 163–170.

[8] Hollemann–Wiberg, Lehrbuch der Anorganischen Chemie, Walter de Gruyter, Berlin, New York, 1985.

[9] Gmelin Synthese, No. 9 (1964) 962–1036.

[10] T. Meissner, F. Eisenbeiss, B. Jastorff, Fresenius, J. Anal. Chem. 362 (1998) 459–464.

[11] Th. Meissner, F. Eisenbeiss, B. Jastorff, J. Chromatogr. A 810 (1998) 201–208.

[12] I. Zelensky, V. Zelenska, D. Kaniansky, P. Havasi, V. Lednarova, J. Chromatogr. 294 (1984) 317–327.

[13] D. Kaniansky, I. Zelensky, P. Havasi, M. Cerovsky, J. Chromatogr. 367 (1986) 274–279.

[14] EN ISO 10304 Parts 1 and 2, Bestimmung der gelösten Anionen mittels Ionenchromatographie, Beut Verlag, Berin, 1996.