Journal of Chromatography, 320 (1985) 199–203
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,297

ISOTACHOPHORETIC DETERMINATION OF ANIONIC AND CATIONIC SPECIES IN WELL AND SURFACE WATERS

JIŘÍ VACÍK* and IVA MUSELASOVÁ

Department of Physical Chemistry, Faculty of Sciences, Charles University, Albertov 2030, CS-128 40 Prague 2 (Czechoslovakia)

SUMMARY

Electrolyte systems and the conditions for the isotachophoretic determination of anions (Cl^-, NO_3^-, SO_4^{2-}) and cations (K^+, Na^+, Ca^{2+}, Mg^{2+}) in well and surface waters are described. The results of isotachophoretic determinations on practical samples are compared with those obtained by classical methods.

INTRODUCTION

The analysis of waters by classical methods is tedious and time consuming because of the large number of components to be determined. Isotachophoretic (ITP) determinations of anions in waters have been described[1–3]. Chloride and sulphate alone have been determined with nitrate as the leading ion[1]. The simultaneous determination of chloride, nitrate and sulphate ions has been described[2,3]; however, as chloride was used as the leading ion, its content in the sample was only determined from the lengthening of the time elapsed between the beginning of the experiment and the passage of the first zone through the detector. The reproducibility of the results thus obtained for chloride was poorer than with the other test anions. The determination of chloride, nitrate and sulphate using zone electrophoresis in an ITP apparatus has been reported[4].

Electrolyte systems for the separation of various mixtures of cations have been established[5] and a separation of alkali metal cations has been described[6]. However, no described system permits the simultaneous determination of potassium, sodium, calcium and magnesium cations in a single experiment.

The range of ions to be determined in this work was dictated by the requirements of the Research Institute for Water Treatment in Pargue and consisted of the basic ions (except HCO_3^-) contained in all surface and well waters. For the simultaneous determination of these anions in a single experiment, calcium hydroxide was chosen as the leading electrolyte, as the hydroxyl ions are suitable leading ions. The use of Ca^{2+} counter ions leads to such a decrease in the effective mobility of sulphate (owing to the kinetically labile complex of Ca^{2+} with sulphate) that sulphate can be readily separated from chloride and nitrate. This influence on the effective mobility of sulphate in the determination of nitrate, sulphate and phosphate in artificial fer-

0021-9673/85/$03.30

tilizers (with $CaCl_2$ as the leading electrolyte) has been described[7].

The formation of kinetically labile complexes between the separated ions and counter ions[8–10] has also been used to separate sodium and magnesium ions. It has been found that the N-oxide of nitrilotrismethylenephosphonium acid (H_6L) is a suitable leading electrolyte, with which Mg^{2+} and also Ca^{2+} form various complexes depending on the pH and whose hydroxonium ions act as the leading ions. In the pH range 5.5–7.0, complexes of the type MgL^{4-}, $MgHL^{3-}$ and $CaHL^{3-}$ are formed. Owing to the formation of these complexes, the effective mobilities of calcium and magnesium ions decreases in such a way that K^+, Na^+, Ca^{2+} and Mg^{2+} form four independent, well separated zones.

EXPERIMENTAL

The experiments were carried out on an apparatus with a contact conductivity detector and a *ca.* 35 cm × 0.45 mm I.D. capillary.

Separation of anions

The electrolyte system for the separation of the anions contained calcium hydroxide (prepared by dissolution of CaO in water) at a concentration of $5 \cdot 10^{-3}$ mol dm^{-3} as the leading electrolyte and formic acid at a concentration of $1 \cdot 10^{-2}$ mol dm^{-3} as the terminating electrolyte. Boiled redistilled water was used for the preparation of all the solutions. A current of 50 μA was selected for optimal separation and detection of the ions. To shorten the analysis time, a current of 100 μA was applied during the initial 10 min of the experiment, however. The separation experiments on water samples were evaluated using calibration graphs obtained in the concentration range $2 \cdot 10^{-4}$–$4 \cdot 10^{-3}$ mol dm^{-3}. The zone lengths were evaluated relative to the length of the zone of an internal standard (potassium chromate of a concentration of $2.5 \cdot 10^{-4}$ mol dm^{-3}). An amount of 5 μl was usually injected; a sample of 7.5 μl was used with waters containing some of the test components at a concentration of less than $2 \cdot 10^{-4}$ mol dm^{-3}. One experiment took approximately 17 min.

Separation of cations

For the separation of the cations, H_6L was used at a concentration of $2 \cdot 10^{-3}$ mol dm^{-3} (pH = 2.40) as the leading electrolyte and creatinine at a concentration of $4 \cdot 10^{-3}$ mol dm^{-3} as the terminating electrolyte. The H_6L used was prepared according to the literature[11,12]. Although triply distilled water, purified further on a cation-exchange column, was used for the preparation of the solutions, zones of some test cations, originating from the solutions of the leading and terminating electrolytes, were recorded. The zone lengths for these "impurities" were checked several times a day and were corrected for in the evaluation of the results. The initial current, 80 μA, was decreased to 20 μA after 8 min. The sample volume was 2 μl and no internal standard was used. The calibration graphs were measured in the range from $1 \cdot 10^{-4}$ mol dm^{-3} (for K^+ from $5 \cdot 10^{-5}$ mol dm^{-3}) to $3 \cdot 10^{-3}$ mol dm^{-3}. One experiment took *ca.* 20 min.

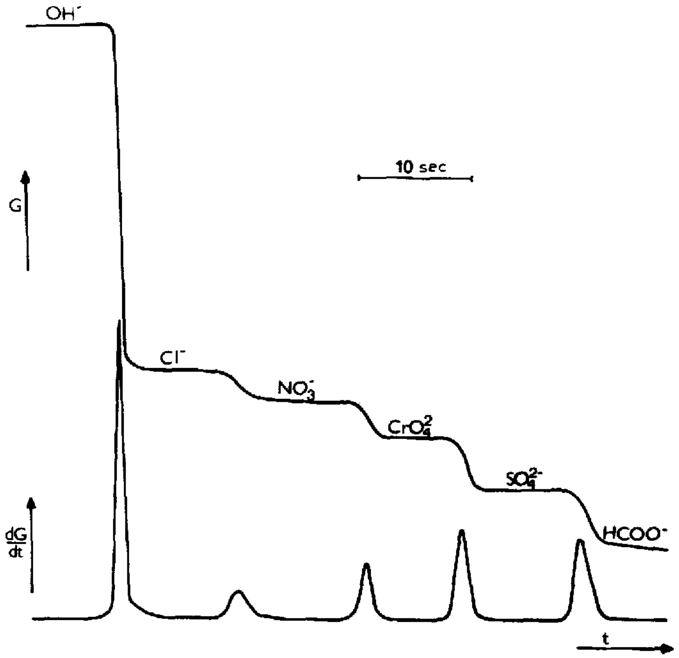

Fig. 1. Isotachopherogram of a mixture of anions. t = time; G = response of the conductivity detector; dG/dt = time derivative of the conductivity detector response.

RESULTS

A typical isotachopherogram of a mixture of the anions is shown in Fig. 1. The results for five different waters are given in Table I. The results of the determination of the anions by isotachophoresis are compared in Table II with those obtained by classical methods at the Research Institute for Water Treatment; chloride and sulphate were determined titrimetrically and nitrate photometrically, after reaction with sodium salicylate, potassium and sodium were determined by flame photometry and magnesium and calcium ions were titrated chelatometrically.

TABLE I

DETERMINATION OF ANIONS IN WATERS

1,2,3 = Potable waters; 4,5 = river waters; c = concentration in mol dm^{-3}; s = relative standard deviation of the concentration.

Sample No.	*Cl^-*		*NO_3^-*		*SO_4^{2-}*	
	$c \times 10^4$	*s(%)*	*$c \times 10^4$*	*s(%)*	*$c \times 10^4$*	*s(%)*
1	7.24	2.1	3.66	1.2	5.63	1.5
2	5.62	2.8	1.65	4.2	3.82	0.9
3	7.66	2.1	1.56	7.0	6.36	0.7
4	6.97	1.7	3.62	1.4	5.82	1.0
5	3.23	3.7	1.69	5.9	3.84	0.6

TABLE II

COMPARISON OF THE RESULTS OF THE DETERMINATION OF ANIONS USING ITP (c_1) WITH THOSE OBTAINED BY CLASSICAL METHODS (c_2)

c_1, c_2 = concentrations in mol dm^{-3}

Sample No.	Cl^-		NO_3^-		SO_4^{2-}	
	$c_1 \times 10^3$	$c_2 \times 10^3$	$c_1 \times 10^3$	$c_2 \times 10^3$	$c_1 \times 10^3$	$c_2 \times 10^3$
1	0.72	0.68	0.37	0.30	0.56	0.65
2	0.56	0.42	0.17	0.15	0.38	0.47
3	0.77	0.67	0.16	0.15	0.64	0.65
4	0.70	0.66	0.36	0.31	0.58	0.64
5	0.32	0.23	0.17	0.06	0.38	0.43

An isotachopherogram of a mixture of the cations is depicted in Fig. 2 and the results are given in Table III. The present results are compared in Table IV with those obtained at the Research Institute for Water Treatment. The electrolyte system used does not allow the separation of NH_4^+ from K^+ ions or the separation of Ba^{2+} from Na^+ ions.

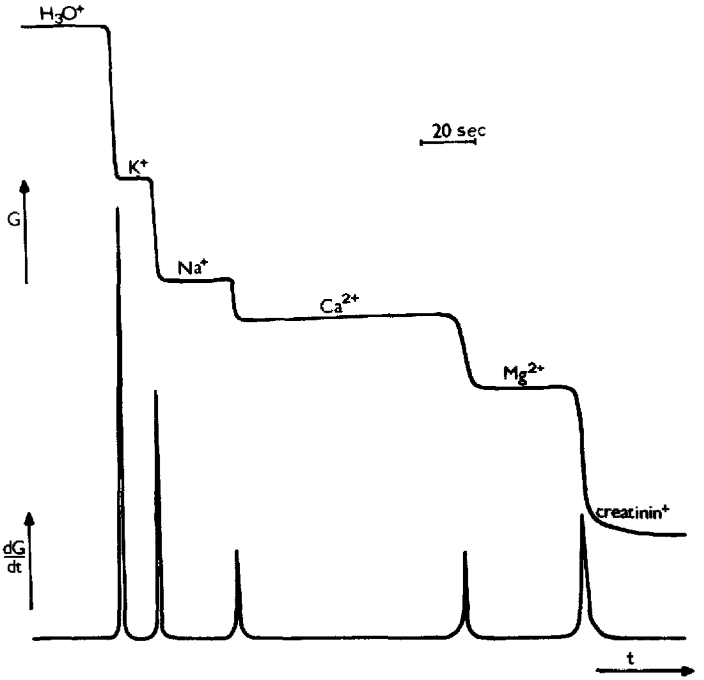

Fig. 2. Isotachopherogram of a mixture of cations. Symbols as in Fig. 1.

TABLE III

DETERMINATION OF CATIONS IN WATERS

1 = Well water; 2,3 = river waters; c = concentration in mol dm^{-3}; s = relative standard deviation of the concentration

Sample No.	K^+		Na^+		Ca^{2+}		Mg^{2+}	
	$c \times 10^4$	$s(\%)$	$c \times 10^4$	$s(\%)$	$c \times 10^4$	$s(\%)$	$c \times 10^4$	$s(\%)$
1	1.01	2.2	17.01	0.8	21.19	0.5	9.06	0.9
2	2.33	1.0	20.60	0.3	11.42	0.6	4.06	0.9
3	0.89	3.0	1.78	1.4	4.38	0.8	1.70	2.5

TABLE IV

COMPARISON OF THE RESULTS OF THE DETERMINATION OF CATIONS BY IPT (c_1) WITH THOSE OBTAINED BY CLASSICAL METHODS (c_2)

c_1, c_2 = concentrations in mol dm^{-3}.

Sample No.	K^+		Na^+		Ca^{2+}		Mg^{2+}	
	$c_1 \times 10^3$	$c_2 \times 10^3$	$c_1 \times 10^3$	$c_2 \times 10^3$	$c_1 \times 10^3$	$c_2 \times 10^3$	$c_1 \times 10^3$	$c_2 \times 10^3$
1	0.10	0.10	1.70	1.64	2.12	1.98	0.91	0.89
2	0.23	0.22	2.06	1.74	1.14	1.11	0.41	0.53
3	0.09	0.04	0.18	0.14	0.44	0.40	0.17	0.20

ACKNOWLEDGEMENTS

Dr. J. Podlaha is thanked for his help with the selection and preparation of a suitable complexing agent for the separation of the cations.

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