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UV spectrophotometric detection in the ion chromatographic analysis of alkali and alkaline earth metal and ammonium cations

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ABSTRACT

A spectrophotometric detection procedure for the high-performance ion chromatographic determination of alkali and alkaline earth metal and ammonium cations, after chemical suppression of the eluent, is proposed. Measurements at 200 nm revealed the presence of hydroxide ions, which bear a stoichiometric relationship with the eluted M^{n+} cations. The detection limits and sensitivities were similar to those obtained by the usual conductivity method. The suggested procedure, when tested in the analysis of samples of ammonium cations, gave responses dependent also on the pH of the suppressed solution and relative pK_a values. Fitting of the calibration graphs by means of a non-linear regression routine also allows the determination of the equilibrium constants of the cations.

INTRODUCTION

Ion chromatography (IC) can be a powerful analytical tool for the analysis of ionic and ionizable species [1] if the appropriate column, eluent composition and detector are selected. In analyses for alkali and akaline earth metal and ammonium cations, suppressed conductivity detection is generally adopted whereas a UV–VIS detector is the best choice for absorbing species. However, the demand for "universal" detectors, with a resolution set by the column, required an extension of the range of applicability of available detectors. As chromatographic measurements of akali metal ions using suppressed conductimetric and spectrophotometric detectors connected in series show correlated peaks, attention was devoted to verifying whether UV detection at 200 nm, with suppression of the usual hydrochloric acid eluent, would be a successful alternative for the detection of monovalent and divalent cations. The investigation was also based on the circumstance that the UV absorbance of an aqueous alkaline solution is higher than that of a neutral solution [2,3].

EXPERIMENTAL

Chemicals

All chemicals were of analytical-reagent grade. Demineralized water was passed through a Millipore GS (cartridge 0.22 μm) for final purification and deaerated with helium. Standard solutions of the different cations were prepared by dissolving weighed amounts of the corresponding chloride in water. An ammonium standard solution was prepared from the sulphate [4] and an *n*-propylammonium standard solution from a weighed amount of the corresponding amine. Tetrabutylammonium hydroxide (TBAOH) 30-hydrate (>99%) from Fluka and 40% aqueous TBAOH from Aldrich were used to prepare regenerating solutions.

Apparatus and procedure

A Waters ActIon Analyzer ion chromatograph equipped with a 20-μl sample loop was used. Chromatograms were recorded with a Hewlett-Packard Model 7090A digital plotter and a Spectra-Physics SP4270 integrator. The column, obtained from Dionex, was a CS3 (250 mm × 4 mm I.D.) in conjunction with a CG3 (50 mm × 4 mm I.D.) guard column. The suppression device was Dionex CMMS. A Knauer Model SP87 variable-wavelength UV–VIS detector was employed. Preliminary UV spectra were recorded with a Perkin-Elmer Model Lambda 5 spectrophotometer. In the chromatographic tests the eluent solutions were 25 mM HCl–0.25 mM diaminopropionic acid (DAP) aqueous solution for monovalent cations and 48 mM HCl–8 mM DAP aqueous solution for doubly charged cations. To regenerate the anion micromembrane suppressor 0.05 and 0.1 M TBAOH solutions for monovalent and divalent cations were used, respectively, at a flow-rate of 3 ml/min. For pH measurements a Metrohm Model 654 pH meter was used. The simplex algorithm, as a non-linear regression method, was written in FORTRAN 77 and run under the DOS 3.3 operating system on an IGS (CPU i80286) personal computer equipped with an i80287 numerical processor. All plots were made using an HP Model 7090A digital plotter.

RESULTS AND DISCUSSION

Basic considerations

Suppressed conductimetric detection is based on the fact that the cation micromembrane suppressor effects chemical elimination of eluent H^+ ions as the Cl^- counter ion is replaced with OH^-, which neutralizes H^+, whereas an M^{n+} cation only exchanges its counter ion and consequently passes through the detector as $M^{n+} + nOH^-$. This excess of OH^- is measured by the conductimetric detector [1].

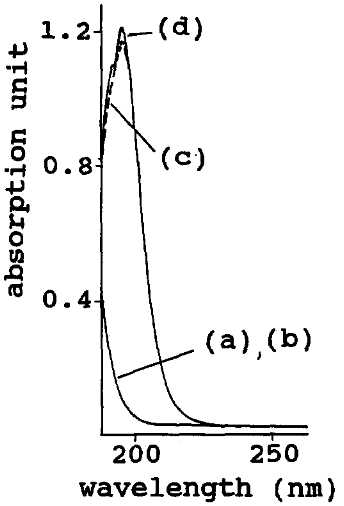

Fig. 1. UV spectra of (a) 10^{-3} M HCl, (b) 10^{-3} M KCl, (c) 10^{-3} M KOH and (d) 10^{-3} M KOH–10^{-3} M KCl.

The role of OH^- ions in also producing an absorption peak can be seen from the UV spectra for 10^{-3} M KCl, 10^{-3} M HCl, 10^{-3} M KOH and 10^{-3} M KCl–10^{-3} M KOH aqueous solutions reported in Fig. 1. The spectra of KCl and HCl solutions coincide with a low absorbance, because only the Cl^- ion weakly absorbs, whereas the absorbances of KOH and KOH–KCl solutions are higher owing to the presence of OH^- and are slightly different from each other because of the small contribution of the Cl^- ion. Also, the absorbances of equimolar solutions of monovalent cation hydroxides are identical whereas those of divalent ions are twice as high. These findings suggest the possibility of utilizing the spectrophotometric detector at 200 nm in place of the usual conductimetric detector for quantitative high-performance IC analyses.

As the highest signal for both the conductimetric and spectrophotometric detection modes is obtained when the excess of OH^- is a maximum, the suppression step must be optimized by varying the flow-rate of the regenerating solution. Two aspects of the suppressor device have to be taken into account: the finite rate of regeneration of the membrane suppressor and the permeation of the regenerating solution through the porous membrane. The regeneration is no longer quantitative when both the

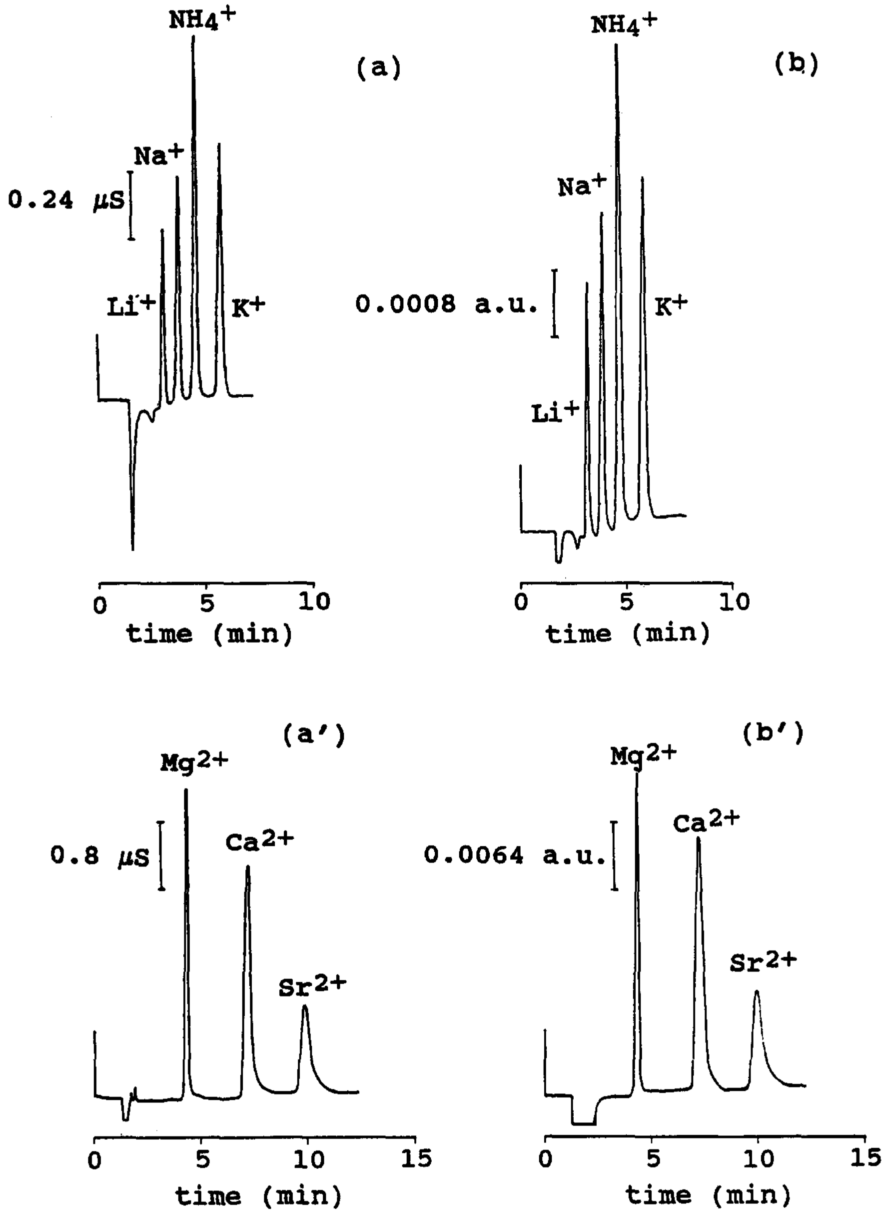

Fig. 2. IC responses of various monovalent and divalent cations with (a and a′) the suppressed conductivity detection and (b and b′) the suppressed spectrophotometric detection at 200 nm. Chromatographic conditions: flow-rate, 1 ml/min; sample loop, 20 μl; column, Dionex CS3 plus a CG3 guard column; mobile phase, (a) and (b) 25 m*M* HCl–0.25 m*M* DAP in water, (a′) and (b′), 48 m*M* HCl–8 m*M* DAP in water. Cation concentrations: Li^+, 0.1; Na^+, 0.4; NH_4^+, 4; K^+, 1; Mg^{2+}, 2; Ca^{2+}, 4; Sr^{2+}, 6 mg/l.

flow-rate and concentration are too low, whereas permeation occurs when they are too high so that suitable values of concentration and flow-rate must be selected.

Alkali and alkaline earth metal cations

Fig. 2 shows the chromatograms of monovalent and divalent cations detected with the conductimetric detector (a,a′) in comparison with those

TABLE I

DETECTION LIMITS CALCULATED AS PEAK HEIGHTS EQUAL TO THREE TIMES THE STANDARD DEVIATION OF THE BASELINE NOISE FOR DIFFERENT MONOVALENT AND DIVALENT CATIONS

Regenerating concentration, 0.05 and 0.1 *M* TBAOH for singly and doubly charged cations, respectively. Chromatographic conditions as in Fig. 2.

Ion	Detection limit (μg/l)	
	UV detection	Conductimetric detection
Li^+	0.97	0.94
Na^+	1.25	1.22
NH_4^+	2.1	2.0
$C_3H_{10}N^+$	5.4	6.0
K^+	6.81	6.12
Mg^{2+}	3.69	6.39
Ca^{2+}	9.99	16.89
Sr^{2+}	19.38	66.60

recorded with the spectrophotometric detector (b,b′). Table I reports the detection limits calculated as peak heights equal to three times the standard deviation of the baseline noise. Both monovalent and divalent cations, with the exception of ammonium ions, exhibit a linear range of response up to 10^{-3} *M*.

The fact that the detection process always involves the measurement of the excess of OH^- generated by the replacement of the counter ion makes it possible, in principle, to use a single calibration graph whatever the cation to be analysed. In this particular instance peak areas must be used in place of peak heights, as the peak height depends on the retention time of the eluted species, and the proper ratio M^{n+}/OH^- has to be taken into account.

Ammonium cations

In the determination of ammonium ions, even if a strict relationship between spectrophotometric and conductimetric detection holds, some drawbacks can arise owing to the weakness of the conjugated bases. The OH^- ions generated in the suppression step react with the ammonium ion to reach an equilibrium concentration, so generating a downward curvature of the calibration line. This curvature depends on the equilibrium constant of the weak base and on the pH of the eluent solution after the suppression in the absence of the analyte. The pH, in fact, assumes different values, higher than 7, depending on the purity of the regenerating agent used for the membrane suppressor as a consequence of the "slip" of the regenerating solution, aqueous TBAOH solution, through the membrane. Dedicated ion chromatographic analyses of collected eluent samples revealed the presence of Na^+ and K^+ impurities coming from the TBAOH. These impurities are responsible for the pH value higher than 7 as they pass through the micromembrane together with their OH^- counter ion. This drawback can be

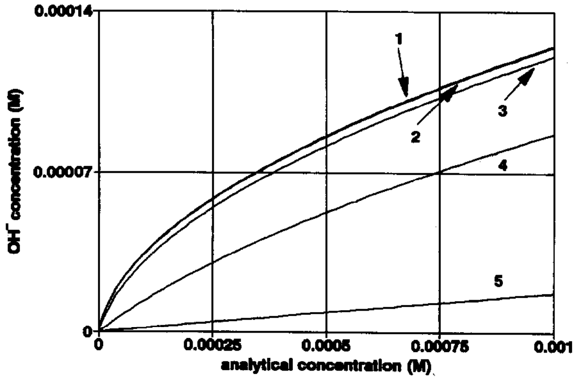

Fig. 3. Theoretical calibration graphs for a weak acid obtained with the model given by eqn. A5 in which $C_{max} = C^0$ for pK_a = 9.25 and $B = 10^{-7}$ (1), 10^{-6} (2), 10^{-5} (3), 10^{-4} (4) and 10^{-3} (5) *M* OH^-.

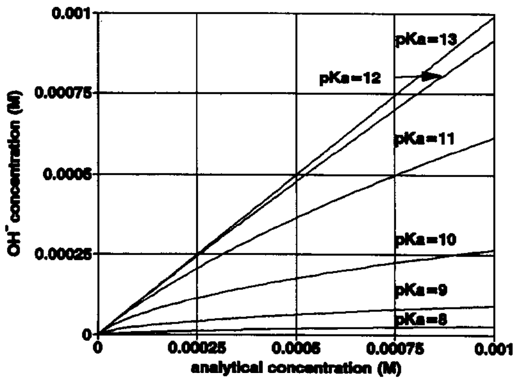

Fig. 4. Theoretical calibration graphs for a weak acid obtained with the model given by the eqn. A5 in which $C_{max} = C^0$ for $B = 10^{-5}$ *M* OH^- and pK_a = 13, 12, 11, 10, 9 and 8.

almost eliminated by using ultra-pure TBAOH solution free from alkali metals, so obtaining a final pH of the eluent solution after the suppression very near to 7 (7.2 in our case).

To clarify the influence of the pK_a values of the eluted species and of different background pH values, several plots of the excess of the OH^- ion *vs.* the analyte concentration were calculated (see Appendix). As the peak height and width depend on particular experimental situations (column, flow-rate, eluent strength), the calculations were carried out using eqn. A5 in which C_{max} was replaced by the analytical concentration C^0. The curves reported in Figs. 3 and 4 show that for a fixed pK_a value, the higher the background pH value the smaller is the curvature with a concomitant lower sensitivity, whereas for a fixed background pH analytes characterized by high pK_a values exhibit good linearity with a sensitivity approaching that of a strong base.

In agreement with the above considerations, the experimental curves in Fig. 5 show that NH_4^+ (pK_a = 9.25), $C_3H_7NH_3^+$ (pK_a = 10.71) and K^+ give progressively higher signals. Further, by using the simplex procedure [5] as a non-linear fitting approach we tried to extract from the experimental curve relative to the NH_4^+ ion the background pH value, the equilibrium constant and the molar absorptivity of OH^- ion (see eqn. A6). Fig. 6 shows the close fit between the calculated and the experimental absorbance values. The estimated parameter values are pH = 7.13, pK_a = 9.32 and ε_{200} = 1018, which are in excellent agreement with the expected values, namely $pH_{exp.}$ = 7.2, pK_a = 9.25 and ε_{200} = 900 (value obtained from our UV spectra). In this connection, it must be pointed out that in the calculation of the parameters some sources of error are undoubtedly present, namely the dynamic character of the measurements, generally not desirable when equilibrium constants are looked for, the inaccurate calculation of the dilution factor $V_{inj}/(\sigma\sqrt{2\pi})$ owing to the inaccuracy of the peak width, $W = 4\sigma$, and the imperfect reproducibility of the peak height. However, the results found demonstrate that at the peak maximum, where the concentration is almost uniform, the equilibrium is effectively reached for short time intervals even if the concentration profile does not follow strictly a Gaussian shape.

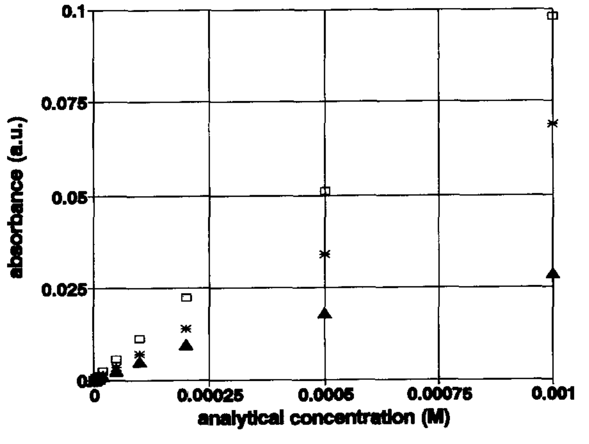

Fig. 5. Experimental calibration graphs for (▲) NH_4^+, (✱) $C_3H_7NH_3^+$ and (□) K^+. Chromatographic conditions as in Fig. 2 for singly charged cations.

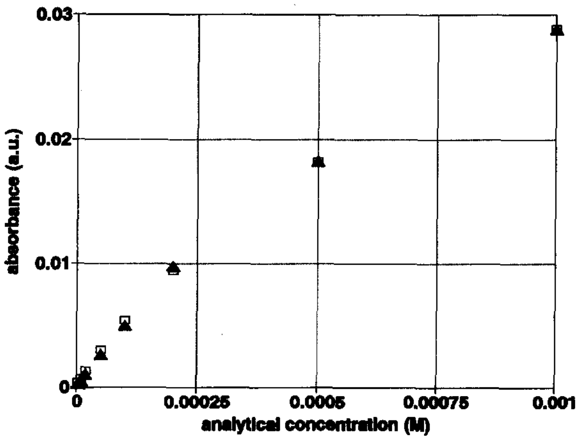

Fig 6. (▲) Experimental calibration graph for NH_4^+ and (□) calibration graph obtained by the simplex method. Values used in the fitting procedure: V_{inj} = sample loop, 20 μl, σ = 0.12 ml, b = 1 cm.

CONCLUSIONS

It has been demonstrated, both theoretically and experimentally, that in the chromatographic determination of cations the conductimetric detector can be replaced, without appreciable loss of sensitivity, with a spectrophotometric detector. The absorbance at 200 nm, even in the absence of a rounded maximum in the spectrum, reveals fairly well the presence of an excess of OH^- ions which are associated with the analyte cations after the suppression step. Therefore, the procedure described can be a suitable way of working when the chromatographic analysis of different species requires the use of more than one detector connected in series or when an ion replacement procedure is adopted [6]. Finally, the fitting procedure for the calibration graph, in addition to confirming the general correctness of our reasoning, indicates an easy way of measuring the pK_a values of the eluted ammonium cations.

ACKNOWLEDGEMENTS

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APPENDIX

Model for calculation of the theoretical calibration graph

Under the hypothesis that the chromatographic peak relative to a generic ammonium ion, NH^+, is Gaussian in shape, it holds that

$$C_{NH^+} = C_{max} \exp\left[-\frac{1}{2}\left(\frac{V_{max} - V}{\sigma}\right)^2\right]$$

where V_{max} is the retention volume and C_{max}, the concentration relative to the peak height, can be expressed as

$$C_{max} = C^0 V_{inj}/(\sigma\sqrt{2\pi})$$

as $C^0 V_{inj}$ is the amount of the analyte taken.

The passage through the membrane suppressor (where all the chloride counter ions are converted and a slight permeation of the regenerating solution can occur) generates OH^- ions with a concentration profile similar to that of NH^+ but modified by the attainment of the following acid–base equilibrium:

$$NH^+ + OH^- \overset{K}{\rightleftharpoons} N + H_2O$$

Among the peak concentrations of all the species involved, the following relationships hold:

$$|NH^+|_0 = C_{max};\ |NH^+| = C_{max} - x \qquad (A1)$$

$$|OH^-|_0 = C_{max} + B;\ |OH^-| = C_{max} + B - x \qquad (A2)$$

$$|N|_0 = 0;\ |N| = x \qquad (A3)$$

The subscripts 0 indicate concentrations before the acid–base equilibrium, B is the concentration of hydroxide permeated (that is, the background) and x is the amount of NH^+ reacted with OH^- as determined by the equilibrium constant K:

$$K = \frac{|N|}{|NH^+||OH^-|} \qquad (A4)$$

As the effective signal is given by the excess of OH^- in respect to the background B, namely $C_{max} - x$, insertion of eqns. A1–A3 in eqn. A4 gives

$$|OH^-|_{exc} = C_{max} - x = -\frac{KB + 1}{2K} + \frac{(K^2B^2 + 1 + 4KC_{max} + 2KB)^{\frac{1}{2}}}{2K} \qquad (A5)$$

Combining the Lambert–Beer relationship, $A_{peak} = \varepsilon b|OH^-|_{exc}$, the molar absorptivity, ε, of OH^- and the optical path, b, the following equation can be derived:

$$A_{peak} = \varepsilon b\left[-\frac{KB + 1}{2K} + \frac{(K^2B^2 + 1 + 4KC_{max} + 2KB)^{\frac{1}{2}}}{2K}\right] \qquad (A6)$$

The unknown parameters ε, B and K can be determined from the experimental measurements of the absorbance by using a non-linear regression algorithm. In particular, a Nelder and Mead four-vertices simplex algorithm, which compares experimental and calculated absorbances for different concentrations of NH^+ injected, was successfully used.

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