Journal of Chromatography, 364 (1986) 189–192
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROMSYMP. 863

DETERMINATION OF NITRATE AND CHLORIDE IONS IN FOOD BY SINGLE-COLUMN ION CHROMATOGRAPHY

J. PENTCHUK, Ü. HALDNA* and K. ILMOJA
Institute of Chemistry, Academy of Sciences of the Estonian SSR, 15 Akadeemia tee, 200026, Tallinn (U.S.S.R.)

SUMMARY

The use of an appropriate eluent for the simultaneous determination of chloride and nitrate ions in vegetables by single-column ion chromatography is described. Different eluents should be used for vegetables having a high nitrate content, *e.g.*, lettuce, field salad and beetroot, and for those having a low nitrate content, *e.g.*, potato, cabbage, carrot and cucumber. For the former an eluent of 1.5 m*M* gluconic acid + 1.5 m*M* boric acid, pH 8.6, is recommended, for the latter, 1.0 m*M* phthalic acid, pH 5.2, is appropriate.

INTRODUCTION

The simultaneous determination of chloride and nitrate ions in vegetables is essential to conform with legal regulations and to meeting quality control requirements. A high chloride content lowers the quality of vegetables, and nitrate may be converted into nitrosamines which have high carcinogenicity.

The separation and determination of inorganic anions including those of chloride and nitrate is now easily carried out by ion chromatography. Conventional colorimetric and titrimetric methods for determination of chloride and nitrate ions in vegetables suffer from such drawbacks as interferences caused by other solutes present, the need for silver salts and for different procedures for the two ions. In this report, the application of single-column ion chromatography to the determination of nitrate and chloride ions in vegetables is described. This enables the instrumentation to be simplified, thereby decreasing its cost and maintenance, and reduces the dead volume as a result of eliminating the suppressor column, thereby increasing efficiency and hence resolution.

The nitrate and chloride content in vegetables varies to a great extent (see Tables I and II). Therefore, a good chromatographic separation of these two ions must be provided even when one of the ions is present in large excess. Moreover, a sufficiently good separation of nitrate and chloride from the organic acids present in vegetables must also be achieved[1].

0021-9673/86/$03.50

EXPERIMENTAL

Apparatus

An IVK-11 ion chromatograph (SKB Academy of Sciences of the Estonian SSR) with a conductivity detector was used. Separation columns (60 mm × 4 mm I.D. or 150 mm × 2 mm I.D.) packed with a BAKC-type ion exchanger[2] were operated at room temperature (20 ± 2°C). The ion exchanger used had a capacity of 0.1 mequiv./g. The sample loop had a volume of 100 μl and the flow-rate was 0.8 ml/min.

Materials

All reagents were of analytical grade (Sojuzkhimreaktiv). Doubly distilled water was used throughout. Two eluents were used. Eluent 1 consisted of 1.5 m*M* gluconic acid and 1.5 m*M* boric acid obtained by dissolving the respective amounts of the acids in water, followed by adjustment of the pH to 8.6 with potassium hydroxide solution. Eluent 2 was phthalic acid solution. Its concentration and pH were varied in the ranges 1–2 m*M* and 4.0–6.5, respectively. The adjustment of pH was carried out as above.

Sample preparation

A 10–50 g vegetable sample was homogenized in a blender. The resulting slurry was filtered through two paper filters. The filtrate was diluted (1:10–1:200) in the eluent used and filtered through a 0.2-μm membrane filter. This solution was injected into the chromatograph.

RESULTS AND DISCUSSION

Samples of a high nitrate content

For vegetables having a high nitrate content, *e.g.*, lettuce, field salad and beetroot, we found that the most suitable eluent is eluent 1. This eluent yields a relative retention, $\alpha_{Cl^-/NO_3^-} = 4$ and a capacity factor, $k'_{Cl^-} = 3.5$[3], see also Fig. 1 and Table I. The detection limits are 0.5 and 4 ppm for chloride and nitrate, respectively.

Samples of a low nitrate content

In the case of vegetables having a low nitrate content, *e.g.*, potato, cabbage, carrot and cucumber, interference from organic acids has frequently been observed; a negative peak due to organic acids is not separated from the chloride peak (Fig. 1B). To overcome this difficulty, the concentration of the phthalate eluent and its pH were varied in the ranges of 1–2 m*M* and 4.0–6.5, respectively. The best results were obtained with 1.0 m*M* phthalate, pH 5.2, which yields $\alpha_{Cl^-/NO_3^-} = 2.4$ and $k' = 1.4$. The chloride and nitrate peaks were well separated from each other and from the system peak, see Fig. 2. The detection limits were 0.2 and 2 ppm for chloride and nitrate, respectively.

Analytical performance

The experimental error depends on the minor components present (especially on the organic acids content), on the dilution of the solution and accuracy of the

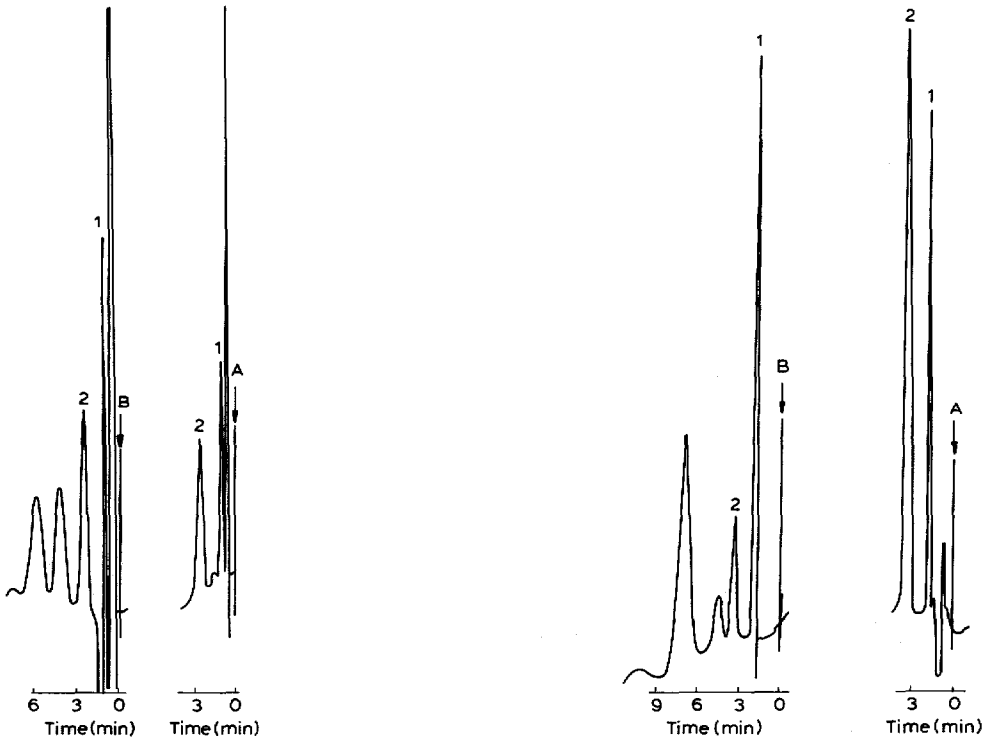

Fig. 1. Chromatograms of a standard mixture (A) (1 = Cl^-, 3 ppm; 2 = NO_3^-, 12 ppm) and of a carrot extract (B), dilution 1:29 (1 = Cl^-, 160 mg/kg; 2 = NO_3^-, 480 mg/kg). Conditions: BAKC-1 anion-exchanger column (25–40 μm, capacity 0.10 mequiv./g), 150 mm × 2 mm I.D., with 1.5 m*M* gluconic acid + 1.5 m*M* boric acid, pH 8.6, as eluent. The flow-rate was 1 ml/min and conductivity detection was used.

Fig. 2. Chromatograms of a standard mixture (A) (1 = Cl^-, 5 ppm; 2 = NO_3^-, 20 ppm) and of a cabbage extract (B), dilution 1:19 (1 = Cl^-, 120 mg/kg; 2 = NO_3^-, 140 mg/kg). Conditions: BAKC-1 anion-exchange column (25–40 μm, capacity 0.10 mequiv./g), 60 mm × 4 mm I.D., with 1 m*M* phthalate, pH 5.2, as eluent. The flow-rate was 0.8 ml/min and conductivity detection was used.

TABLE I

VEGETABLES WITH HIGH NITRATE CONTENTS

A = Ion chromatography; B = ion-selective electrodes; C = colorimetry.

Vegetable	*Chloride (mg/kg)*		*Nitrate (mg/kg)*		
	A	*B*	*A*	*B*	*C*
Lettuce	540	680	1800	2600	1900
	500	600	2600	3100	2700
	460	400	2700	4300	3000
	450	500	1900	3300	2000
	440	600	2300	3200	2400
	440	500	2500	4400	2700
Field salad	1400	1700	4400	3600	4000
	900	1100	3200	2600	2900
	800	1000	2600	2500	2700
Beetroot	300	310	1800	2000	–
	250	260	1400	1300	–
	180	220	1700	1500	–

TABLE II

VEGETABLES WITH LOW NITRATE CONTENTS

Methods as in Table I.

Vegetable	*Chloride (mg/kg)*		*Nitrate (mg/kg)*		
	A	*B*	*A*	*B*	*C*
Potato	450	600	170	120	–
	350	400	110	90	–
	700	800	50	40	–
	800	700	120	80	–
	700	800	40	100	–
	650	850	70	50	–
Cabbage	220	260	240	600	270
	240	280	210	500	190
	110	150	390	600	420
	140	200	600	1100	700
Carrot	160	180	500	600	–
	130	200	220	300	–
	120	110	110	190	–
Cucumber	640	690	360	540	–
	490	600	230	190	–
	400	430	270	290	–
	540	640	120	200	–

dilution procedures. Evaluation of the chromatograms was performed by measuring the peak heights. The calibration plots were linear from 0.2 to 10 ppm for chloride and from 2 to 30 ppm for nitrate. If a calibration plot was used, coefficients of variation, $C.V._{Cl^-} = 0.13$ and $C.V._{NO_3^-} = 0.09$ were obtained. More precise results can be obtained by the method of additions: $C.V._{Cl^-} = 0.05$ and $C.V._{NO_3^-} = 0.03$.

The recoveries were determined by spiking the extract with a known amount of an appropriate standard; for both ions the recoveries were found to be in the range 93–100%.

The results of the ion chromatographic determinations were compared with those obtained by other methods (ion-selective electrodes and colorimetry), see Tables I and II. No statistically significant differences between these methods were observed. However, the results obtained by the ion-selective electrodes have obviously been influenced by the presence of several organic compounds in the vegetables studied[4].

REFERENCES

1 R. J. Bushway, J. L. Bureau and D. F. McGann, *J. Food Sci.*, 49 (1984) 75.
2 Ü. Haldna, R. Palvadre, J. Pentchuk and T. Kleemeier, *J. Chromatogr.*, 350 (1985) 296.
3 J. C. Giddings, *Dynamics of Chromatography*, Part I, Marcel Dekker, New York, 1965.
4 B. Schmidt and G. Schwedt, *Dtsch. Lebensm.-Rundsch.*, 80 (1984) 137.