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Applications of ion chromatography in cane sugar research and process problems

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Abstract

Ion chromatography (IC) offers the sugar technologist a simple, reliable technique for the simultaneous separation and determination of inorganic and organic ions in complex process mixtures. Identification and measurement of ions present in sugar liquors are important factors in understanding and maximising sugar recovery. Choice of IC column packing, eluent composition and pH, and detection mode (suppressed and non-suppressed) are shown to be useful variables when analysing sugar factory products, especially the multivalent ions such as phosphate and organic acids (aconitic and oxalic acid). The IC methods show good agreement with conventional analysis methods (potentiometric titration, atomic emission and absorption). IC also produced excellent repeatability and recovery from these matrices. Examples of the application of IC analysis in applied sugar research and processing problems include clarification studies, degradation of molasses, sugar solution colour removal and factory process problems.

Keywords: Sugar cane; *Saccharum officinarum*; Process monitoring; Inorganic anions; Inorganic cations; Organic acids

1. Introduction

The soluble non-sugars extracted from sugar cane (*Saccharum officinarum*) are commonly referred to as ash; this ash is composed of both inorganic and ionic organic material. The nature and concentration of this material affect the purification process and subsequent recovery and quality of the resulting sugar. Variations in ash composition are related to cane variety, soil types, climatic conditions and fertilizer, irrigation and harvesting practices [1].

Inorganic ions present in ash include potassium, calcium, magnesium, chloride and sulphate. Phosphate is an important process chemical but is only present in minor quantities. Organic acids constitute a significant proportion of the ionic organic non-sugars. Acids identified in cane juice include citric, malic, succinic, fumaric, lactic, oxalic, acetic, formic, itaconic and aconitic acid (1-propene-1,2,3-tricarboxylic acid). Most are present at relatively low concentrations as normal metabolic products. Aconitic acid is unusually abundant and responsible for most of the titratable acidity and resultant buffering capacity of the expressed juice [2]. It has been implicated in the formation of false grain, scale and gassing reactions, all of which can lead to process inefficiencies [3–5]. Lactic acid is used as an indicator of both microbial contamination and chemical degradation of sugar [6].

Southern African sugar mills operate as continuous process plants (as opposed to batch processes) requiring numerous samples to identify baseline conditions and subsequent problem areas. Analysis of large numbers of samples by classical methods would be time-consuming and both labour and

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apparatus intensive. Furthermore, other species present in process juices can make some analyses difficult, e.g. colourometric phosphate analysis is prone to interference from silicates and colour bodies.

Chromatographic methods are routinely used in sugar laboratories for the analysis of sugars and other compounds. LC methods based on cation-exchange and reversed-phase stationary phases use refractive index (RI) detection, whilst pulsed amperometric detection techniques are combined with anion-exchange separation [7–11]. The use of suppressed ion chromatography (IC) for the non-routine determination of anions and cations in sugar mill products is well documented [12–17]. Areas of study included white sugar turbidity, scale identification, sugar degradation in beet extraction and identification of process control parameters. Separation difficulties were overcome by the use of gradient elution or column selectivity.

This paper describes the versatility of combining UV, RI and conductivity detection with ion-exclusion, suppressed and non-suppressed IC in addressing sugar factory research and process problems. Examples from both areas are described.

2. Experimental

2.1. Apparatus

A Metrohm 761 Compact IC system (Herisau, Switzerland) was used in this study. It consists of a double piston pump, pulsation damper, manual injection valve, suppressor and associated two-channel peristaltic pump and thermostated conductivity detector. All the components are contained inside an insulated housing to provide thermally stable conditions. Samples were injected using an SGE LS-3200 ALS (20-μl loop) (Victoria, Australia). Metrohm IC-Net 1.1 software was used to control the hardware. The system can be used in both suppressed and non-suppressed modes. As required a Linear 206PHD variable-wavelength UV detector (210 nm) (Reno, NV, USA) and/or an ERMA ERC-7512 refractive index detector (Tokyo, Japan) was/were attached to the 761 IC system. An HP 3396 integrator (Hewlett-Packard, Avondale, PA, USA) was attached to process the output signals from these detectors. UV or RI chromatograms were stored on disk using HP Peak 96 Information Manager software.

Eluent pH was measured with a Crison micropH2001 pH meter (Barcelona, Spain) and used in conjunction with a Mettler Toledo InLab 412 pH electrode (Herisau, Switzerland). This was standardised before use with pH 7 and 4 buffers. A Metrohm 665 Dosimat and silver electrode were used for potentiometric chloride titrations.

2.2. Reagents

All eluents and buffer solutions were prepared from Merck GR reagents (Darmstadt, Germany) (phthalic acid, sodium hydrogencarbonate, sodium carbonate, *para*-hydroxybenzoic acid (pHBA), tris(hydroxymethyl)aminomethane (Tris)). Standard stock solutions of anions and cations (1000 mg/l) were made from analytical reagent-grade reagents (sodium chloride, potassium dihydrogenphosphate, sodium sulphate, potassium nitrate, potassium oxalate). Chromatographically pure *trans*-aconitic acid (Riedel-de Haën, Seelze, Germany) and *cis*-aconitic acid (96%, Sigma, St. Louis, MO, USA) were used to prepare stock solutions of these acids which were stored frozen to inhibit isomerisation. Appropriate dilutions of the stock solutions were made to give the required standards.

2.3. Columns and eluents

2.3.1. Anions—suppressed system

Column: Metrosep Anion Dual 1 glass cartridge (installed in glass cartridge holder) (Herisau, Switzerland) (150 mm×3.0 mm, spherical hydroxyethyl methacrylate with quaternary ammonium groups), at room temperature. Eluent: 2.5 m*M* Na_2CO_3–2.4 m*M* $NaHCO_3$, 0.5 ml/min.

2.3.2. Anions—non-suppressed system 1

Column: Metrosep Anion Dual 1 glass cartridge (installed in glass cartridge holder) (150 mm×3.0 mm, spherical hydroxyethyl methacrylate with quaternary ammonium groups), at room temperature. Eluent: 8.0 m*M* phthalic acid −2% acetonitrile; pH 4.25 with Tris, 0.5 ml/min.

Table 1
Dilutions used for suppressed and non-suppressed ion chromatography analysis of sugar factory samples

Sample type	Anions (g/200 ml)		Cations (g/100 ml), non-suppressed
	Non-suppressed	Suppressed	
DAC[a]	8.0	4.0	8.0
MJ and CJ[b]	4.0	2.0	4.0
Syrups	0.7	0.3	0.7
Final molasses	0.2	0.1	0.2–500
Refinery jets	20.0		20.0
Raw sugar		5.0	10.0

[a] DAC, direct analysis of cane juice.
[b] MJ, mixed juice; CJ, clear juice.

2.3.3. Anions—non-suppressed system 2

Column: Hamilton PRP-X100 anion-exchange column (Reno, NV, USA) (150 mm×4.6 mm, poly-(styrene–divinylbenzene)trimethylammonium exchanger), at room temperature. Eluent: 4 m*M* *p*-hydroxybenzoic acid–2.5% methanol, pH 8.5, 1.0 ml/min.

2.3.4. Cations—non-suppressed system

Column: Metrosep Cation 1–2 (125 mm×4.0 mm, spherical silica gel with polybutadiene maleic acid groups), at room temperature. Eluent: 8 m*M* tartaric acid, 1.0 ml/min.

2.3.5. Organic acids—ion-exclusion system

Columns: Bio-Rad HPX-87H (Richmond, CA, USA) (35 °C) and Phenomenex Rezex ROA Organic acid (Torrence, CA, USA) (75 °C) (both 300 mm× 7.8 mm, sulphonated styrene–divinylbenzene). Eluent: 7.5 m*M* H_2SO_4, 0.5 ml/min.

2.4. Sample preparation

Samples for ion analysis were diluted with water (Table 1), filtered (0.45 μm) and injected (20 μl). Isolation of organic acids by solid-phase extraction (SPE) for ion-exclusion analysis was achieved as described previously [18]. The SPE and associated chromatographic method development are described elsewhere [19].

3. Results and discussion

3.1. Anions: linearity, repeatability, recovery and minimum detection limit

3.1.1. Non-suppressed system

A *para*-hydroxybenzoic acid eluent (pH 8.5; background conductivity of ~300 μS/cm) was used to evaluate these method parameters.

(i) The system was linear over a wide range of concentrations for chloride, phosphate, nitrate and sulphate (Table 2). These results are considered acceptable for the range covered.

(ii) The precision of the method was checked by repeatedly injecting a suitably diluted molasses sample. RSD values for chloride and sulphate were 0.6 and 1.4%, respectively ($n=10$). Molasses was chosen as it can be considered the most complex of all sugar factory streams.

(iii) Recovery experiments were employed to evaluate the method quantitatively. Known amounts

Table 2
Linearity regression data for the non-suppressed analysis of selected anions in the range 0.5–100 mg/l

Ion	Slope	R^2	Standard error of estimation
Chloride	0.49±0.002	0.999	0.16
Nitrate	0.24±0.005	0.999	0.40
Phosphate	0.21±0.006	0.997	0.49
Sulphate	0.50±0.010	0.998	0.41

Injection volume was 20 μl; $n=7$.

of chloride, phosphate and sulphate were added to final molasses. Recovery of the added ions was calculated from the initial and final analyses (Table 3) and found acceptable for all ions other than phosphate spiked at 2 and 3 mg/l. The initial concentration of phosphate in diluted molasses is ~1 mg/l, which is close to the minimum detection limit, resulting in small peaks. Reproducible integration of the peak in the background conductivity is difficult. As the area of the peak increases with increasing phosphate concentration this problem diminishes. The poor sensitivity of the non-suppressed technique for phosphate contributes to this problem.

(iv) A minimum detection limit was determined by injecting consecutively more dilute solutions of chloride, phosphate and sulphate. The minimum detection was calculated at a signal-to-noise ratio of 3. For a 20-μl injection it was found to be 0.1 mg/l for chloride, 0.8 mg/l for phosphate and less than 0.2 mg/l for sulphate in solution.

3.1.2. Suppressed system

A carbonate–hydrogencarbonate eluent was used with suppression (background conductivity of ~17 μS/cm) to evaluate linearity, repeatability and recovery.

(i) The system was found to be non-linear when used across a wide range of concentrations. This non-linearity of the calibration plot in suppressed IC is a well documented effect [20]. As the sample concentration decreases, the slope approaches a limiting value (h_{lim}), whilst at higher concentrations of solute, the slope approaches a different limiting value (h'_{lim}). Two regression lines can be calculated from 0.1 to 5 mg/l and from 5 to 20 mg/l chloride. The breakpoint in the slope has been ascribed to the effect of hydrogen ions in the sample band affecting ionisation and resulting in non-gaussian peak shapes, especially at low concentrations. Care must therefore be taken when analysing samples at concentrations not bracketed by a range of standards. The calibration range was limited to 0.5–5 mg/l for phosphate and 5–20 mg/l for chloride and sulphate to overcome this effect (Table 4). If the entire range was to be used, a polynomial regression would be required to fit the data.

Table 4
Linearity regression data for the suppressed analysis of selected anions

Ion	Range (mg/l)	Slope	R^2	Standard error of estimation
Chloride	5–20	21.4±0.347	0.999	4.13
Phosphate	0.5–5	4.32±0.038	0.999	0.16
Sulphate	5–20	5.87±0.032	0.999	0.42

Injection volume was 20 μl; $n=7$.

(ii) The precision of the method was checked by repeatedly injecting a suitably diluted molasses sample. RSD values for chloride, phosphate and sulphate were 0.5, 4.7 and 0.5%, respectively ($n=$

Table 3
Recovery of chloride, phosphate and sulphate added to diluted final molasses and analysed by non-suppressed ion chromatography

Chloride			Phosphate			Sulphate		
Added (mg/l)	Recovered (mg/l)	Recovery (%)	Added (mg/l)	Recovered (mg/l)	Recovery (%)	Added (mg/l)	Recovered (mg/l)	Recovery (%)
2.1	2.2	105	2.0	4.2	210	0.9	0.9	100
3.2	3.4	106	3.0	4.3	143	1.4	1.3	93
4.2	4.4	105	4.0	4.4	110	1.8	1.8	100
5.3	5.4	102	5.0	5.4	108	2.3	2.3	100
6.4	6.4	100	6.0	6.3	105	2.7	2.9	107
7.4	7.6	103	7.1	7.6	107	3.2	3.2	100
8.5	8.5	100	8.1	9.2	114	3.7	3.5	95
9.5	9.6	101	9.1	9.9	109	4.1	4.0	98
10.6	10.6	100	10.1	10.1	100	4.6	4.6	100
Average recovery (%)		102			112			99
SD (%)		2.3			12.3			3.7
RSD (%)		2.2			10.9			3.7

10). Molasses was chosen as it can be considered the most complex of all sugar factory streams.

(iii) Recovery experiments were employed to quantitatively evaluate the method. Known amounts of chloride, phosphate and sulphate were added to a sucrose solution and the recovery of the added ions was calculated (Table 5). The average recovery was found acceptable provided recoveries were calculated in the calibration range.

(iv) A minimum detection limit was determined for the method for chloride, phosphate and sulphate. For a 20-μl injection, it was found to be less than 0.05 mg/l for chloride and phosphate and less than 0.08 mg/l for sulphate in solution. It can be seen that the suppressed system has lower detection limits than the non-suppressed system, especially for phosphate, which is an important anion in factory streams. However, the system does not afford the same flexibility of eluent pH adjustment to monitor ions of particular interest.

3.2. Cations: linearity, repeatability and recovery

A tartaric acid eluent (pH 3.0; background conductivity of ~700 μS/cm) was used to evaluate these method parameters.

(i) The system was linear over a wide range of concentrations for sodium, potassium, calcium and magnesium (Table 6). These results are considered acceptable for the range covered.

Table 6
Linearity regression data for the non-suppressed analysis of selected cations in the range 0.5–20 mg/l

Ion	Slope	R^2	Standard error of estimation
Sodium	3.26±0.02	0.999	0.36
Potassium	1.61±0.02	0.999	0.33
Calcium	2.43±0.04	0.999	0.65
Magnesium	5.72±0.12	0.998	2.04

Injection volume was 20 μl; $n=6$.

(ii) The precision of the method was checked by repeatedly injecting a suitably diluted mixed juice sample. RSD values for sodium, potassium, magnesium and calcium were 2.4, 1.0, 2.0 and 4.9%, respectively ($n=10$). A mixed juice sample stream was chosen as it contains all the common cations. Other process solutions are either enriched or deficient in some of the ions.

(iii) Recovery experiments were employed to evaluate the method quantitatively. Known amounts of potassium, calcium and magnesium were added to final molasses. Recovery of the added ions was calculated from the initial and final analyses (Table 7) and found acceptable for all ions.

Table 5
Recovery of chloride, phosphate and sulphate added to diluted first boiling sugar and analysed by suppressed ion chromatography

Added ion (mg/l)	Chloride		Phosphate		Sulphate	
	Found (mg/l)	Recovery (%)	Found (mg/l)	Recovery (%)	Found (mg/l)	Recovery (%)
0.5	0.7	130	0.5	100	0.7	144
1.0	1.4	137	1.0	99	1.2	117
2.0	2.2	112	2.0	99	2.2	109
5.0	4.8	98	5.0	100	5.1	102
8.0	7.9	99	8.0	100	8.1	101
10.0	10.2	102	10.2	102	10.1	101
12.0	11.9	99	12.1	101	12.0	100
15.0	15.3	102	15.5	103	15.1	101
20.0	20.6	102	21.0	105	20.35	101
Average recovery (%)[a]		100.6		99.6		100.9
SD (%)		1.9		0.7		0.6
RSD (%)		1.8		0.7		0.6

[a] Chloride recoveries calculated from 5 to 20 mg/l, phosphate from 0.5 to 8.0 mg/l and sulphate from 5 to 20 mg/l due to non-linearity of calibration (see text).

Table 7
Recovery of potassium, calcium and magnesium added to diluted final molasses and analysed by ion chromatography

Potassium			Calcium			Magnesium		
Added (mg/l)	Recovered (mg/l)	Recovery (%)	Added (mg/l)	Recovered (mg/l)	Recovery (%)	Added (mg/l)	Recovered (mg/l)	Recovery (%)
2.1	2.2	104.7	1.8	2.0	111.1	2.2	2.1	95.5
4.2	4.2	100.0	3.6	3.9	108.3	4.4	4.3	97.7
6.3	6.4	101.6	5.4	5.5	102.6	6.6	6.5	98.5
8.4	8.3	98.9	7.2	7.3	101.4	8.8	8.9	101.1
10.5	10.6	100.9	9.0	8.9	98.9	11.0	10.9	99.1
Average recovery (%)		101.2			104.5			98.4
SD (%)		2.2			5.1			2.0
RSD (%)		2.2			4.8			2.1

3.3. Comparison of IC technique with other chemical techniques

Sugar technologists are reticent to embrace newer techniques without comparison with traditional techniques. A small comparative study was made for chloride, phosphate, potassium, calcium and magnesium. A series of raw sugar samples was analysed for chloride using suppressed IC and potentiometric argentimetric titration. Phosphate was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) and suppressed IC on a series of juices from a varietal trial. The cations were measured by atomic absorption spectrometry (AAS) and non-suppressed IC on a series of juices from a clarification study. The results obtained are shown in Tables 8–10. There is good correlation with statistical analysis of the data showing no significant difference between the techniques.

3.4. Effect of eluent composition and pH

Polyvalent anions present in sugar solutions such as phosphate, aconitic and oxalic acid dissociate in multiple steps. The fraction of the ionic species for any particular polyvalent anion present in solution as a function of pH can be calculated. Both phosphoric and aconitic acid have three dissociation constants (phosphoric acid pK_1 2.23, pK_2 7.21, pK_3 12.32 [21], aconitic acid pK_1 2.99, pK_2 4.18, pK_3 6.11 [22]). At pH 4.3, all of the soluble phosphate present in a juice or molasses sample has an approximate charge of -1. It will therefore elute early in the chromatogram and cannot be easily analysed (Fig. 1a). At pH 8.5 or greater, the phosphate present has an approximate charge of -2 and will be well retained on the ion-exchange column, eluting after the singly charged ions (Fig. 1b). By contrast, ~65% of the aconitic acid in solution has an approximate charge of -2 at pH 4.3 and an approximate charge of -3 at pH 8.5. Thus it is well retained at pH 4.3 (Fig. 1a), whilst taking an inordinate length of time to elute from the column at pH 8 or greater and will not be seen. A similar reasoning applies to oxalic acid in that it can be seen after the sulphate at a pH greater

Table 8
Comparison of chloride concentrations in raw sugar by potentiometric titration and suppressed ion chromatography (IC)

Sample	Chloride (mg/l)	
	Potentiometric	IC
A	263	265
B	132	131
C	103	102
D	130	131
E	83	87
F	249	250
G	148	155
H	102	103
I	124	117
J	226	225
K	119	123
L	264	261
Average	162	163
Minimum	83	87
Maximum	264	265
SD	68	68

Table 9
Comparison of phosphate concentrations in mixed juice by ICP-AES and suppressed IC

Sample	Phosphate as PO_4 (mg/l)	
	ICP-AES	IC
A	77	80
B	46	50
C	79	85
D	85	89
E	57	58
F	49	54
G	44	51
H	90	79
I	76	69
J	49	50
Average	65	67
Minimum	44	50
Maximum	90	89
SD	18	16

than 6 as the divalent ion (Fig. 1b), but not at pH 4 as the monovalent ion (Fig. 1a). Eluent pH therefore has a profound effect on retention of polyvalent ions and can be used to increase the separation and selectivity of the technique. Generally when analysing sugar solutions, phosphate and oxalate will be separated from chloride and sulphate using a high pH eluent, whilst a lower pH eluent is used to analyse for aconitic acid in the presence of chloride and sulphate.

The elution order of the divalent cations can be interchanged by the addition of a complexing agent such as dipicolinic acid to the tartaric acid (4 m*M* tartaric acid–1 m*M* dipicolinic acid). The modifier forms a non-stochiometric complex with calcium to produce an approximate +1.5 charge, thus eluting earlier than magnesium. Separation can be accelerated by omission of the dipicolinic acid with a loss of divalent ion resolution (Fig. 2).

3.5. Factory samples

3.5.1. Clarification project

Clarification is the process of taking extracted cane juice (mixed juice, MJ) and adjusting to pH 7 with lime. Two benefits arise from this process. Firstly, sucrose inversion is minimised throughout the later processes. Secondly, the natural or added phosphate present in the juice reacts with the calcium in the lime to produce a precipitate of insoluble calcium phosphate which traps colloidal material and colour bodies. The resultant solution is known as clear juice (CJ). IC has been used in clarification studies to monitor the efficiency of phosphate removal and the effect of inclusion of sugarcane tops and trash on the ash values (Table 11). Samples 1–4 are from clean, fresh cane whilst addition of tops and trash introduces more soluble ash into the MJ (samples 5–9). These include chloride and sulphate

Table 10
Comparison of potassium, calcium and magnesium in mixed juice by AAS and non-suppressed IC

Sample	Potassium (mg/l)		Calcium (mg/l)		Magnesium (mg/l)	
	AAS	IC	AAS	IC	AAS	IC
A	760	757	195	196	115	114
B	750	880	170	185	120	108
C	754	670	200	198	125	126
D	726	720	180	193	120	127
E	1724	1610	415	474	220	243
F	1745	1720	459	420	230	240
G	1607	1538	345	359	256	254
H	1812	1760	430	469	250	265
I	803	785	258	265	174	147
J	771	755	268	266	165	128
Average	1145	1120	292	303	178	175
Minimum	750	670	170	185	115	108
Maximum	1812	1760	430	474	256	265
SD	499	469	112	118	57	66

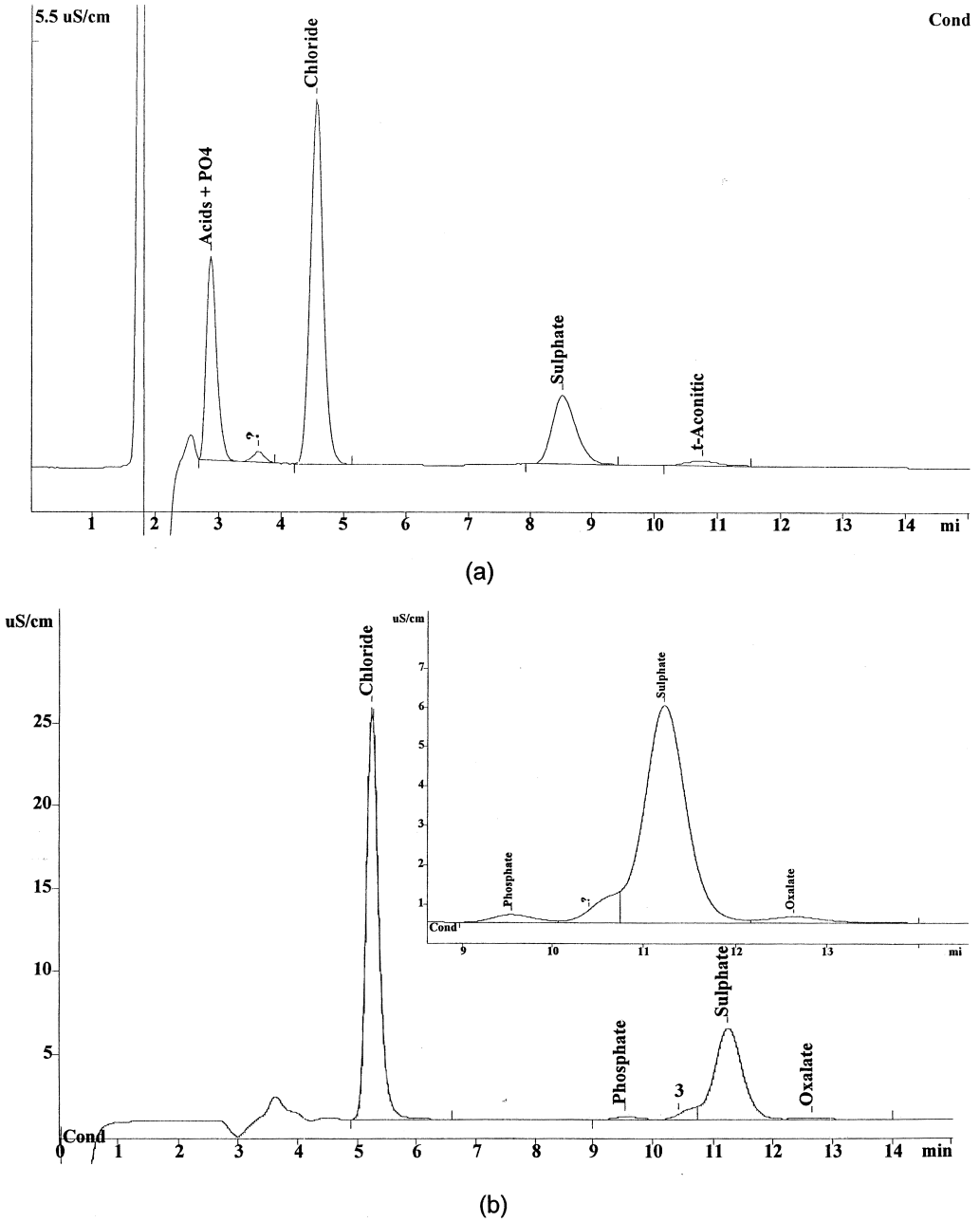

Fig. 1. Chromatogram of anions present in molasses: (a) non-suppressed at pH 4.3; (b) suppressed. Insert shows minor components phosphate, oxalate and an unknown. Chromatographic conditions are described in the text.

(approximately twice as much), as well as aconitic (approximately three times more) and oxalic acids. Increased levels of both acids require more lime for neutralisation leading to increased ash in the clear juice and subsequent lower sucrose recovery. This can be seen in the increased calcium levels reported for the CJ (samples 5–9). An increased level of aconitic acid with the inclusion of tops and trash is a

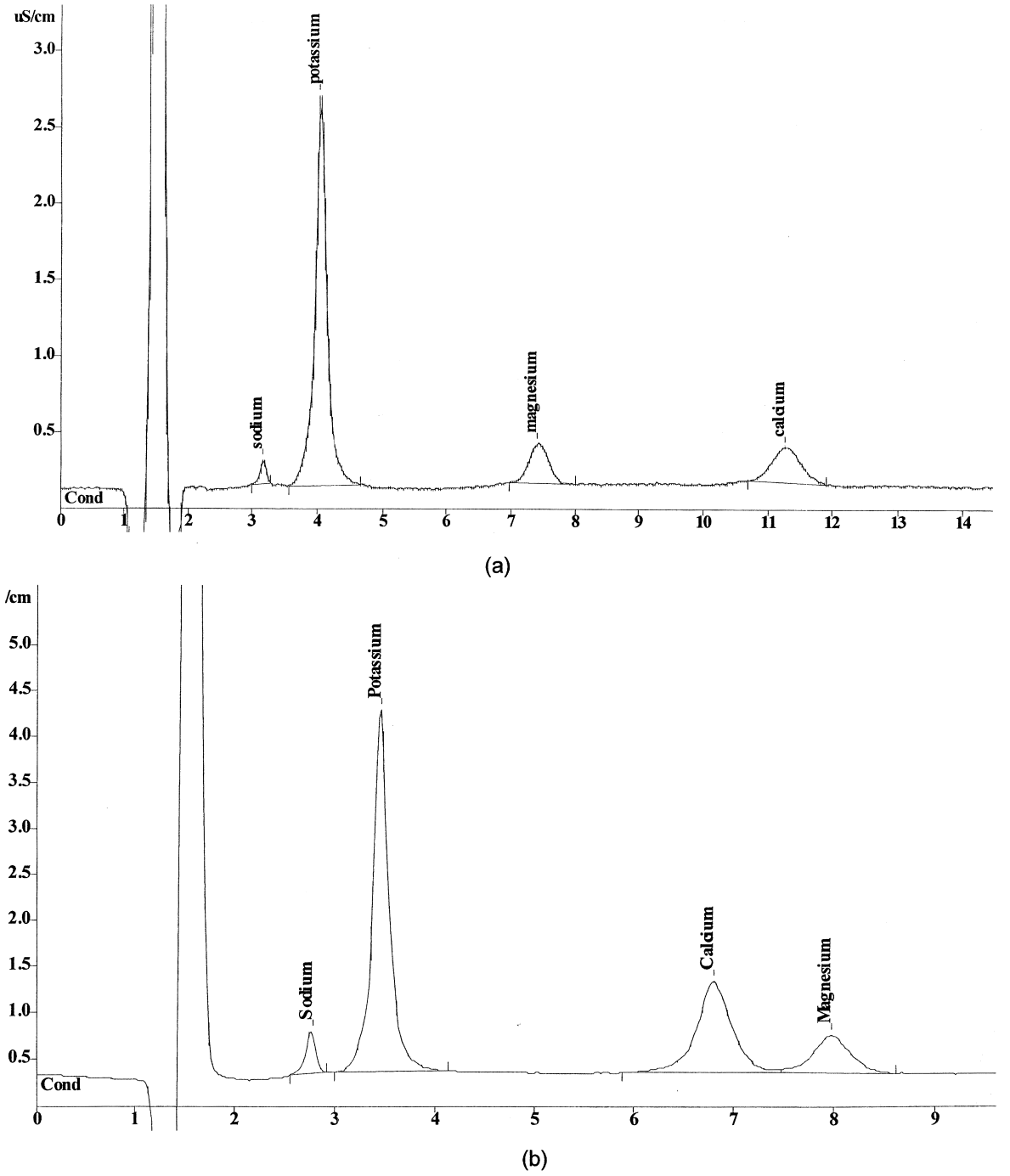

Fig. 2. Separation of sodium (1.1 mg/l), potassium (25.9 mg/l), calcium (5.3 mg/l) and magnesium (4.6 mg/l) in diluted molasses samples using 4 m*M* tartaric acid–1 m*M* dipicolinic acid (a) and 8 m*M* tartaric acid only (b). Note reversal of calcium and magnesium and shorter analysis time.

Table 11
Levels of anions in MJ/CJ clarification trials

Test	Juice	Anions (mg/l)					Cations (mg/l)		
		Chloride	Phosphate	Sulphate	Aconitic	Oxalate	Potassium	Calcium	Magnesium
1	MJ	523	152	415	273	14	685	156	114
	CJ	566	40	452	269	18	757	196	114
2	MJ	507	195	424	154	17	777	121	108
	CJ	528	45	440	272	19	880	185	113
3	MJ	529	173	421	323	16	667	156	126
	CJ	560	55	448	324	14	754	198	133
4	MJ	507	187	428	281	15	659	154	127
	CJ	536	62	451	289	16	726	193	129
5	MJ	1011	270	626	1115	49	1618	336	243
	CJ	1061	108	664	1162	41	1724	474	234
6	MJ	1009	351	644	913	50	1644	337	240
	CJ	1074	94	681	924	53	1745	459	225
7	MJ	1114	334	847	1010	31	1607	359	254
	CJ	1176	77	898	973	45	1662	457	246
8	MJ	1244	510	890	1148	46	1803	374	265
	CJ	1301	63	915	1167	37	1812	469	238
9	MJ	1017	255	677	901	36	1593	351	228
	CJ	1071	48	704	880	25	1625	486	215

consequence of the inclusion of growing regions of the cane. This acid is directly associated with cane growth and metabolism [23]. Phosphate removal can be clearly seen to occur across the clarification stage.

3.5.2. Molasses decomposition

Isomerisation of the *trans*-aconitic acid to the *cis*-aconitic acid isomer has been found to occur across the factory processes. Direct quantitative analysis of the two isomers by ion-exclusion chromatography using RI detection is difficult due to both co-elution with sugars and the amount of sugar present relative to the acid (~200:1). An SPE method has been developed to isolate the acids from sugars and allow analysis by ion exclusion. A dual-column system is used with the columns maintained at different temperatures to achieve separation of most acids present in juices. Recovery is greater than 85% for most of the acids [19]. Both UV and RI detection are used to give both sensitivity and selectivity (Fig. 3). A peak confirmation system has been developed using the UV/RI area ratio and has proved useful in decarboxylation work (see later). This system has been used to monitor the acid profiles of weekly composite MJ entering 15 South African mills throughout the 1998–1999 season (~10 months). Although providing a good, accurate profiling method, it is time consuming—an analysis takes up to 60 min per sample including SPE sample preparation. This study showed that aconitic acid entering the mill was predominately in the trans isomer form and

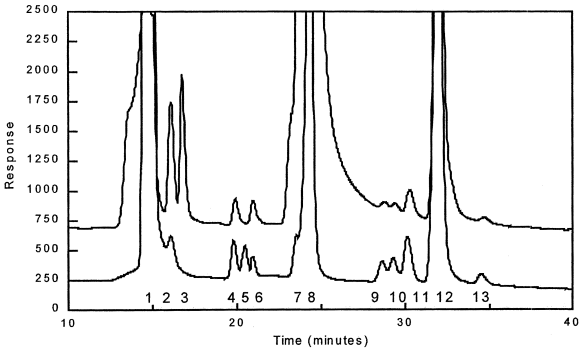

Fig. 3. Ion-exclusion chromatogram of a standard acid mixture showing UV (upper trace) and RI (lower trace) response. Peaks: 1=solvent; 2=oxalic (2.0 mg/l); 3=*cis*-aconitic (18.3 mg/l); 4=citric (3.1 mg/l); 5=phosphoric (2.2 mg/l); 6=tartaric (2.0 mg/l); 7=malic (4.3 mg/l); 8=*trans*-aconitic (37.6 mg/l); 9=succinic (2.8 mg/l); 10=glycollic (3.3 mg/l); 11=lactic (6.6 mg/l); 12=formic (from SPE); 13=acetic (2.6 mg/l) acids. Chromatographic are conditions described in the text.

that ~50% isomerised to the cis form during factory processing [19].

Molasses is the final mother liquor from which no further sucrose can be crystallised. Exhaustion of the molasses is dependent on reducing sugar concentrations and ash levels. Some ions are melassigenic (molasses forming thereby reducing sucrose recovery) particularly sodium, calcium and magnesium. Molasses is known, under as yet undefined conditions, to gas and foam. The larger volumes occupied by this material decrease factory throughput, placing enormous pressure on process staff. Aconitic acid has been monitored during studies of this phenomenon.

Molasses samples stored at elevated temperatures for extended periods of time were analysed by both non-suppressed (chloride, sulphate and aconitic acid) and suppressed (phosphate) techniques (Table 12). The volume of CO_2 produced was also measured. Isomerisation of the *trans*-aconitic acid to *cis*-aconitic acid is followed by decomposition to itaconic acid and CO_2. This can be followed using ion-exclusion separation with UV detection [19]. A model of isomerisation followed by decarboxylation has been proposed [25] and shows dependence on pH, temperature and ionic strength of the molasses solution. Decarboxylation is a thermal decomposition reaction and occurs at higher temperatures as seen in the results. Molasses gassing is often associated with

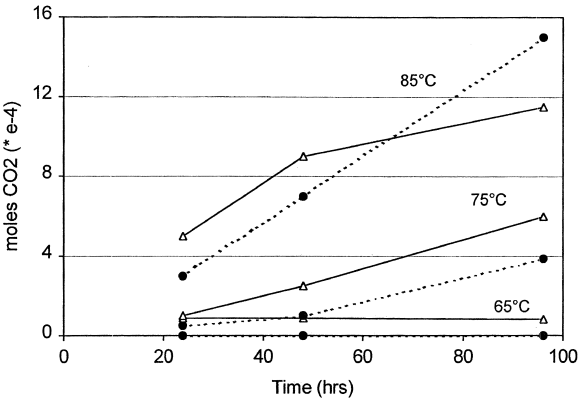

Fig. 4. Comparison of estimated and measured CO_2 gas evolution at 65, 75 and 85 °C (· measured; < estimated from aconitic acid). Details are given in the text.

''Maillard'' type reactions that occur between glucose and amino acids [26]. Measurement of glucose, fructose and sucrose in the samples showed little change in the fructose/glucose ratio, a parameter often used as an indicator. A correlation was found between aconitic acid disappearance and CO_2 gas production (Fig. 4) indicating decarboxylation as the source of CO_2. Decarboxylation of aconitic acid is not the only source of gaseous CO_2 production. Other organic acids present in the molasses can undergo a similar reaction, which may account for

Table 12
Levels of anions during heating trials on final molasses

Temperature (°C)	Heating time (h)	Anion (%)				
		Chloride	Phosphate	Sulphate	Aconitic acid	Oxalic acid (mg/l)
Starting molasses	0	2.03	0.3	2.22	2.36	781
65	24	2.04	0.3	2.26	2.17	738
	48	2.03	0.3	2.30	2.21	514
	75	2.03	0.3	2.34	2.27	478
75	24	2.02	0.3	2.38	2.20	759
	50	2.02	0.3	2.35	1.99	774
	95	2.04	0.3	2.33	1.48	753
85	24	2.03	0.3	2.37	1.61	484
	48	2.04	0.3	2.21	1.08	1803
	96	2.05	0.3	2.22	0.58	1006

the difference in the measured and predicted gas evolution. At 85 °C oxalic acid appears to also be produced. This agrees with the findings that aconitic acid can ultimately form oxalic acid when decomposed [18].

3.5.3. Raw sugar colour removal

Production of a low-coloured cane sugar requires some form of colour removal strategy. Processes utilized include precipitation methods (carbonation and phosphitation), chemical methods (sulphitation and ion exchange) and adsorption methods (granular carbon). Recent research at the Institute and the Malalane mill has shown the viability of using ozone as an aid to colour removal [24]. Concern was raised regarding the possible generation of acidic material due to ozonation of non-sugar compounds. During laboratory trials, the concentrations of organic acids present in a raw sugar solution were monitored (ion-exclusion chromatography) as increasing concentrations of ozone were applied at high doses (Fig. 5). Decreasing concentrations of aconitic acid were followed by an increase in concentrations of smaller acids as more ozone was used. Based on these results, factory trials were conducted at lower concentrations, with substantially no degradation of aconitic acid. The technique has found increasing use in the South African industry based on the success of these trials.

4. Conclusions

Ion chromatography has been shown to be a simple, reliable technique for the simultaneous analysis of both inorganic and organic ions found in sugar streams. Both suppressed, non-suppressed and ion-exclusion techniques have value in solving analysis problems related to sugar processing. Conductivity detection combined with UV and RI has advantages in a research environment. The methods have been shown to be linear, reproducible and comparable to existing methods. The advantages of IC are the ability to simultaneously analyse groups of either anions or cations, the relative speed of analysis and ease of automation. The technique has been successfully applied in the Southern African sugar industry for both research and factory related problems and provides new options in making the industry both a cost effective and quality producer.

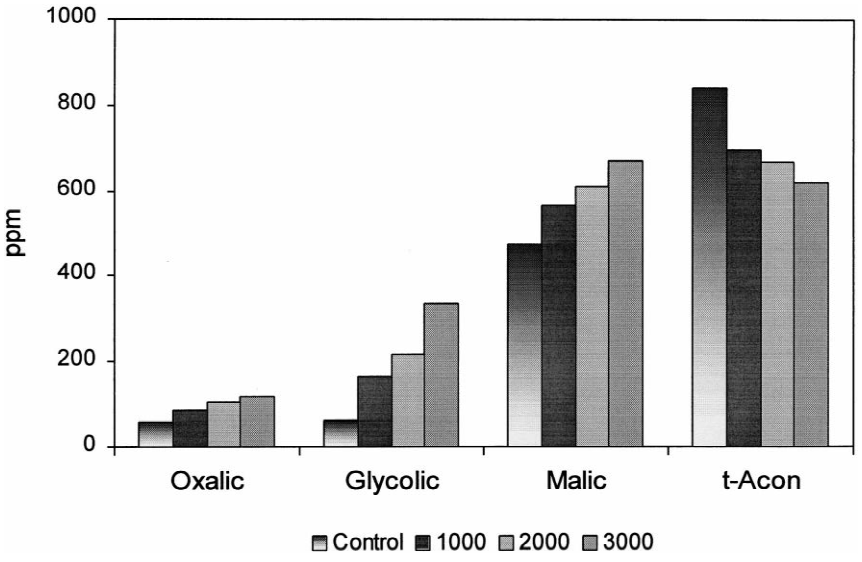

Fig. 5. Increasing organic acid content and corresponding decrease in *trans*-aconitic acid concentration in syrup with increasing ozone concentration compared to a control.

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