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Modern IC Solutions for Food & Beverage

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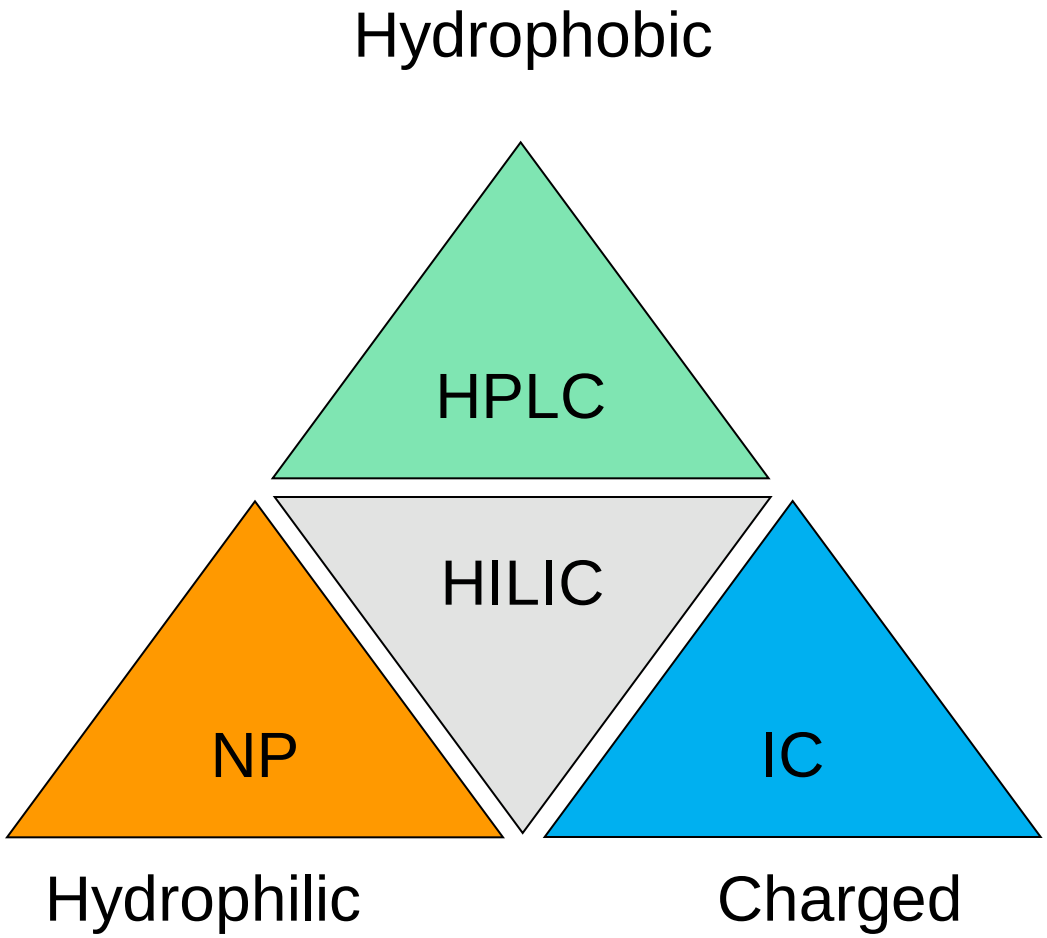
Palermo

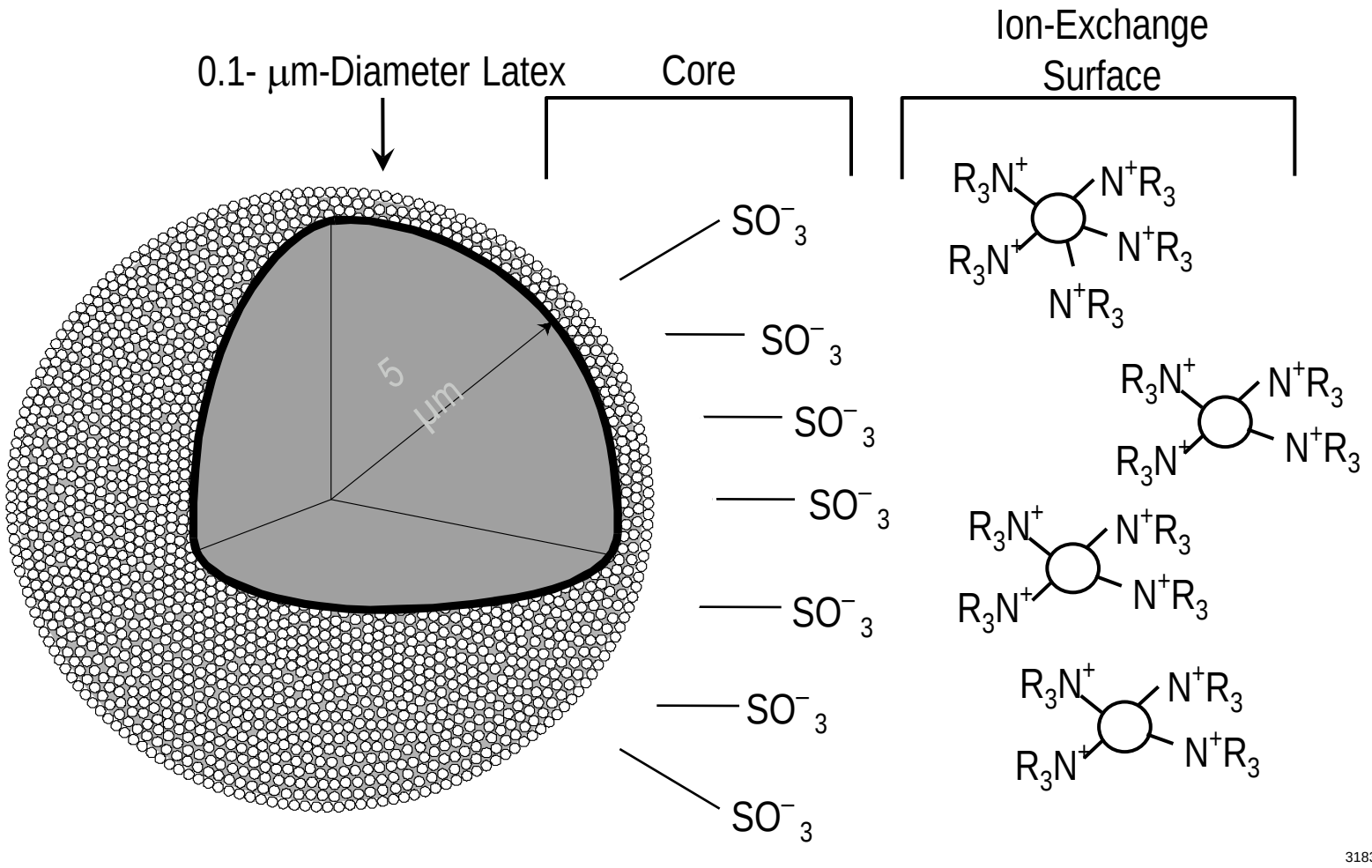
17 Maggio 2013

Positioning Modern LC-Techniques



Adapted from: H. Hayen, Nachrichten aus der Chemie, 58, April 2010

Pellicular Anion-Exchange Beads (Latex)

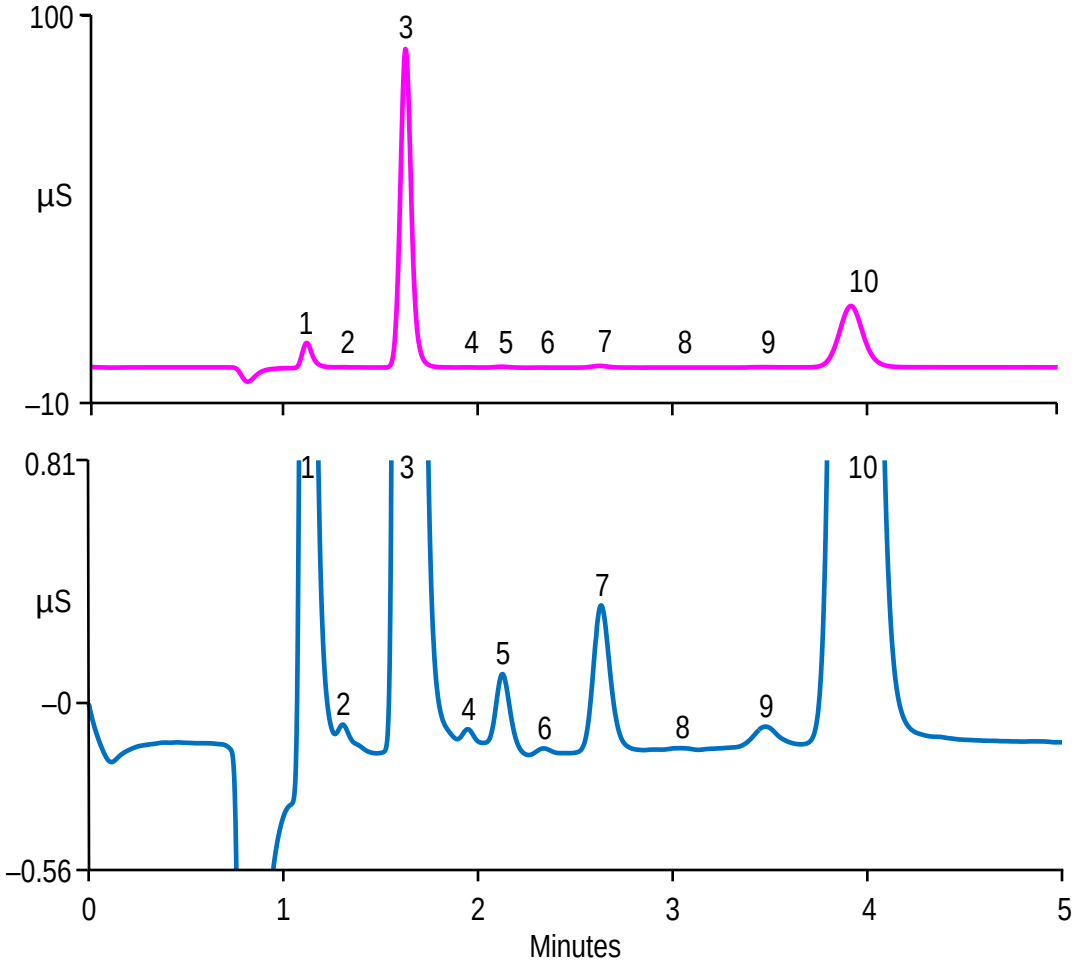


Highly efficient chromatographic separations, due to the small, chromatographically relevant Latex-beads

Agenda

- Anions
- Organic Acids : Ion Exclusion & Ion Exchange
- Gradient Elution
- IC – MS
- Cations
  - Alkali & Alkaline Earth
  - Biogenic Amines
- Amino Acids
- Carbohydrates
- *News !*

Analysis of a Municipal Drinking Water Fast Column



Column:	IonPac AS22-Fast, 4 × 150 mm
Eluent:	4.5 mM Sodium carbonate 1.4 mM Sodium bicarbonate
Flow Rate:	2.0 mL/min
Inj. Volume:	100 µL
Temperature:	30 °C
Detection:	Suppressed conductivity, ASRS 300, 4 mm, AutoSuppression recycle mode

Peaks:

1. Fluoride
2. Formate
3. Chloride
4. Nitrite
5. Chlorate
6. Bromide
7. Nitrate
8. Carbonate
9. Phosphate
10. Sulfate

26269

Faster than an AS4A but with 6x capacity

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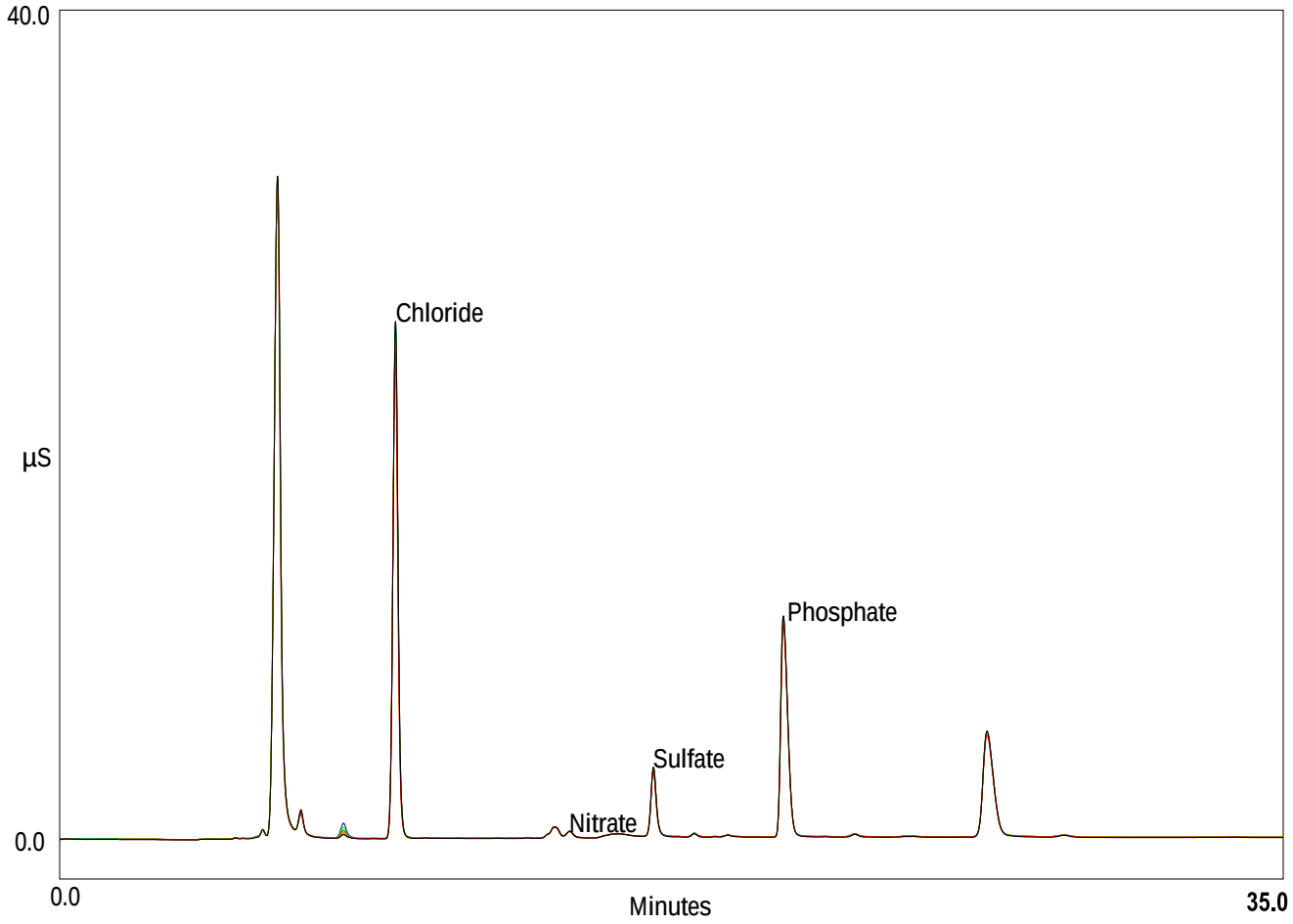
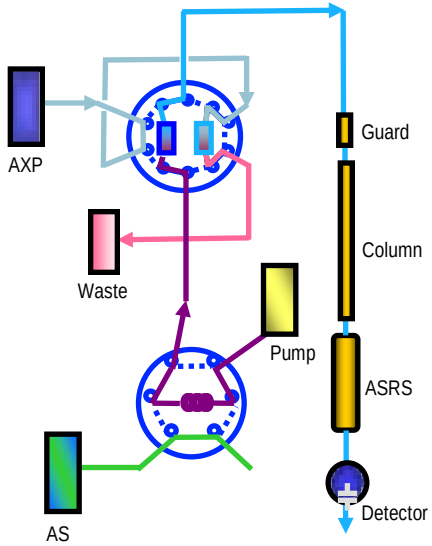
Matrix Elimination: Nitrate in Yogurt



Instrument: ICS-2100 and AS-DV
Matrix Elimination: NG1 column
Column: Ion Pac AG18/AS18
RFIC-EG: KOH Gradient
Temperature: 45° C
Flow Rate: 1.0 mL/min
Inj. Vol.: 20 µL
Detection: Suppressed conductivity
Sample: Diluted yogurt



NG1 pretreatment, 25 consecutive runs, every 5th run shown

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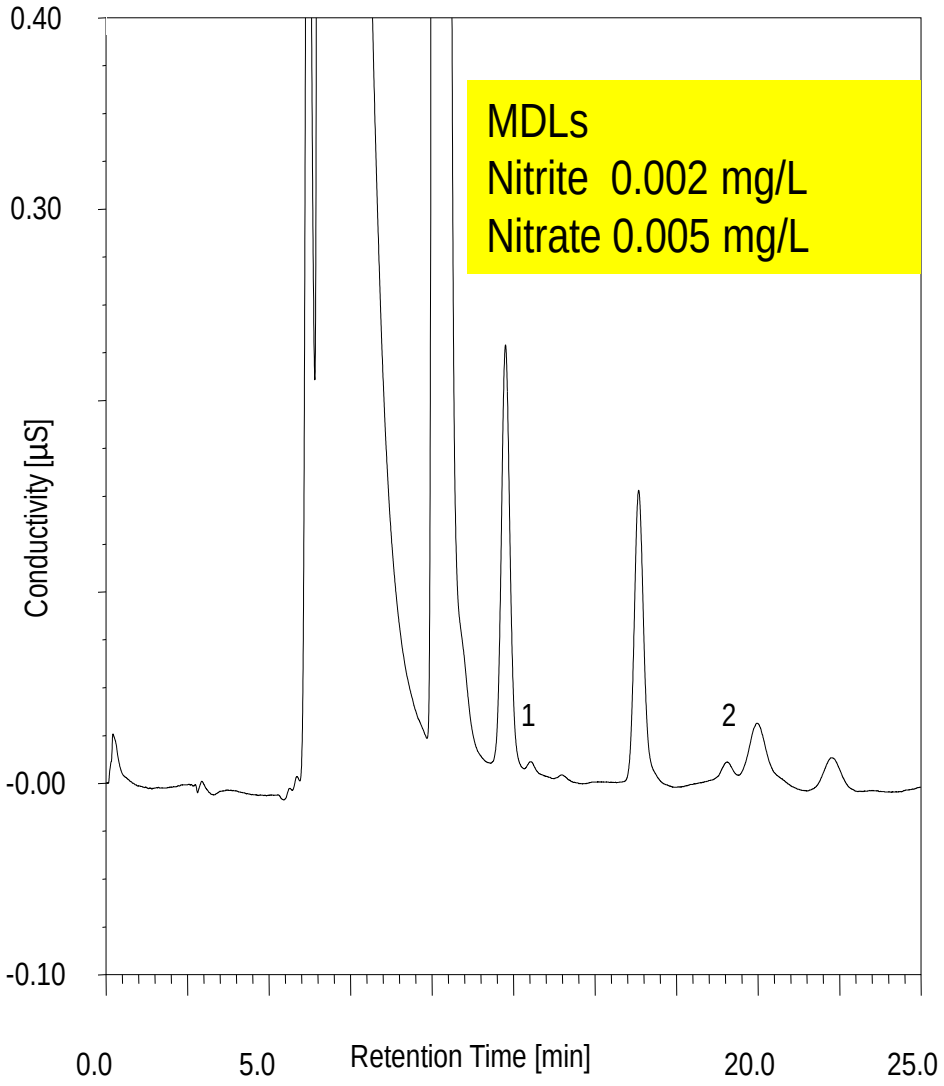
Nitrite and Nitrate in Milk – Spiked Sample for the MDL Study



Column:	IonPac AS20 Analytical, 4x250 mm
	IonPac AG20 Guard, 4x50 mm
InGuard:	HRP, 9x24 mm
Concentrator:	IonPac UTAC-LP1, 4x35 mm
Eluent Source:	EGC II KOH, gradient mode
Gradient:	KOH-Gradient
Flow Rate:	1.0 mL/min
Inj. Volume:	25 µL
Column Temperature:	30 ºC
Detection:	Suppressed conductivity, ASRS-300, with external water mode
Sample:	Spiked Sample (0.01mg/L Nitrite)

Peaks:	Conc. (mg/L)
1. Nitrite	0.007
2. Nitrate	0.019

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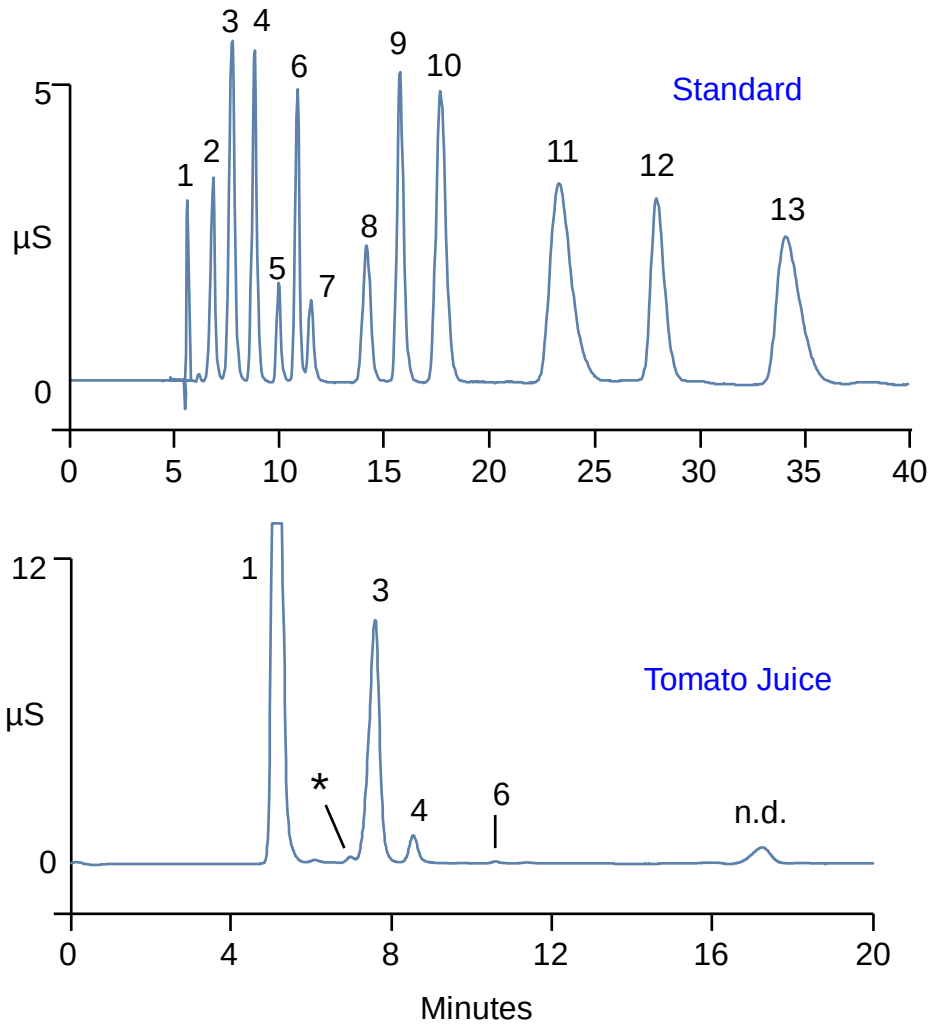
- Anions
- Organic Acids : ICE & SAX
- Gradient Elution
- IC – MS
- Cations
  - Alkali & Alkaline Earth
  - Biogenic Amines
- Amino Acids
- Carbohydrates
- Summary

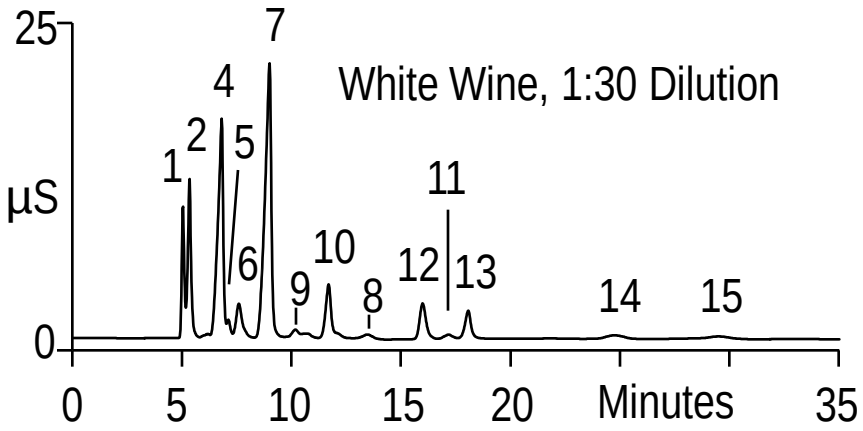
Fingerprint of organic Acids in Beverages
Ion Chromatography Exclusion (ICE)

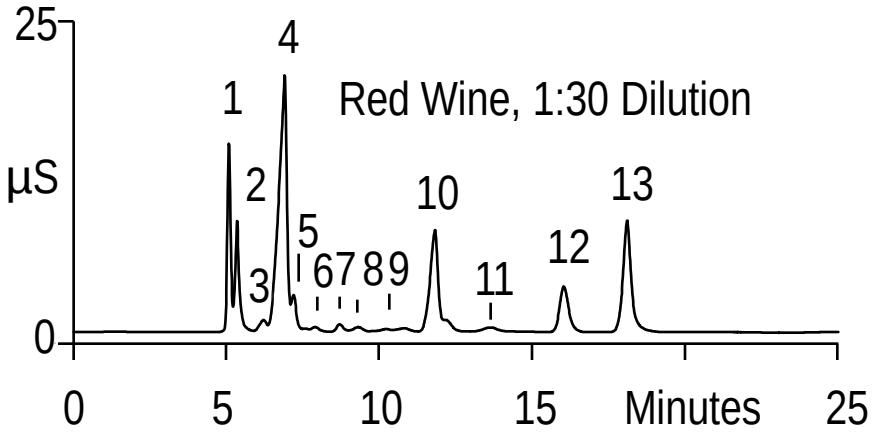


Column: IonPac ICE-AS6
Eluent: 0.4 mmol/L HFBA
Flow: 1 mL/min
Detection: Suppressed Conductivity

Peaks:		
1.	Oxalate, Anions	5.6
2.	Tartrate	6.8
*.	Malonate	7.0
3.	Citrate	7.7
4.	Malate	8.8
5.	Glycolate	9.9
6.	Formate	10.9
7.	Lactate	11.5
8.	HIBA	14.2
9.	Acetate	15.8
10.	Succinate	17.7
11.	Fumarate	23.4
12.	Propionate	28.1
13.	Glutarate	34.2

Organic Acids in Wines





Column:	IonPac® ICE-AS6
Eluent:	0.4 mM Heptafluorobutyric acid
Flow Rate:	1.0 mL/min
Inj. Volume:	50 µL
Detection:	Suppressed conductivity AMMS-ICE

Peaks:

1. Inorganics
2. Inorganics
3. Unknown
4. Tartaric
5. Galacturonic
6. Citric
7. Malic
8. Unknown
9. Glycolic
10. Lactic
11. Unknown
12. Acetic
13. Succinic
14. Fumaric
15. Propionic

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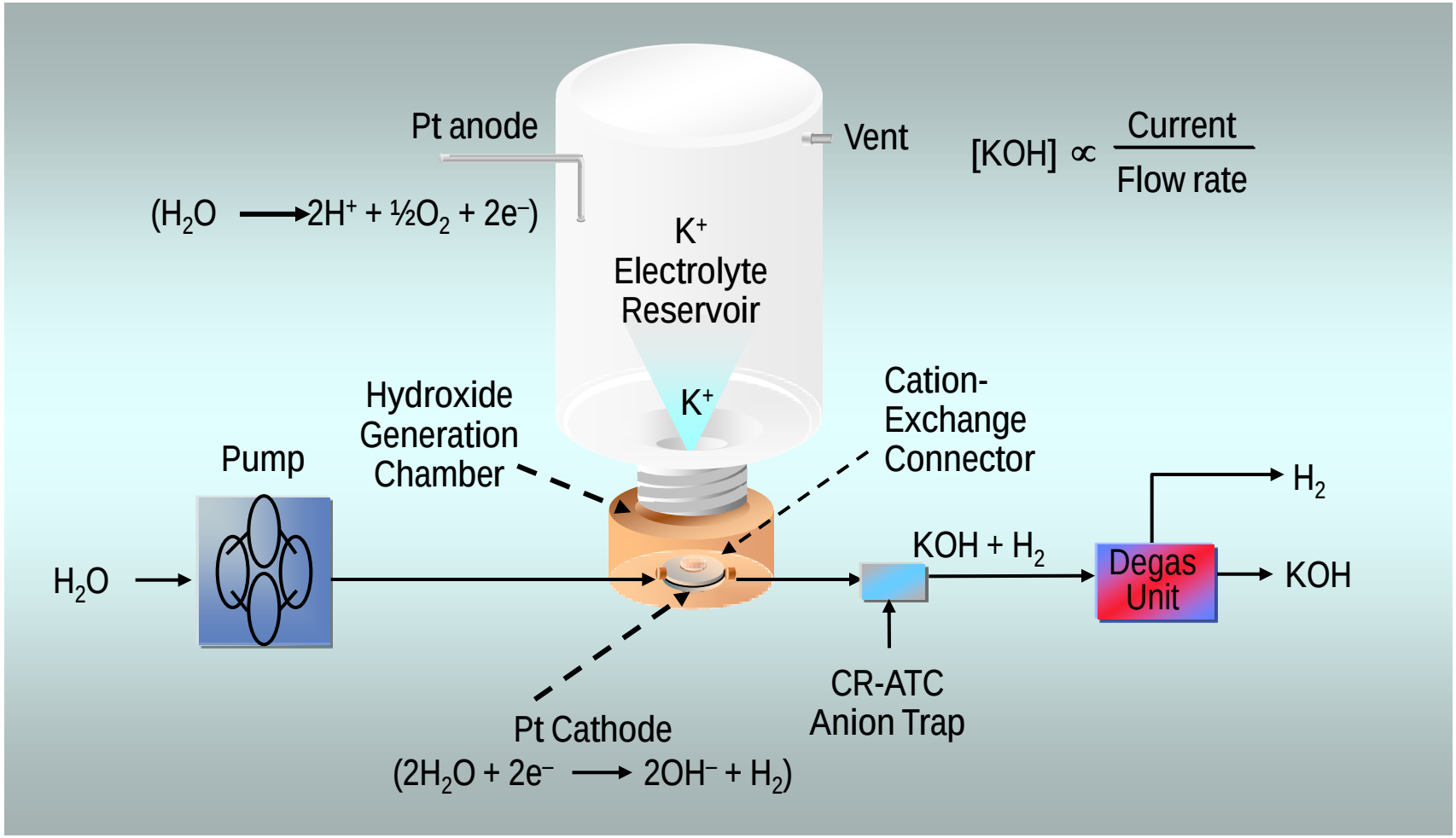
Generatore Elettrolitico di Eluente KOH



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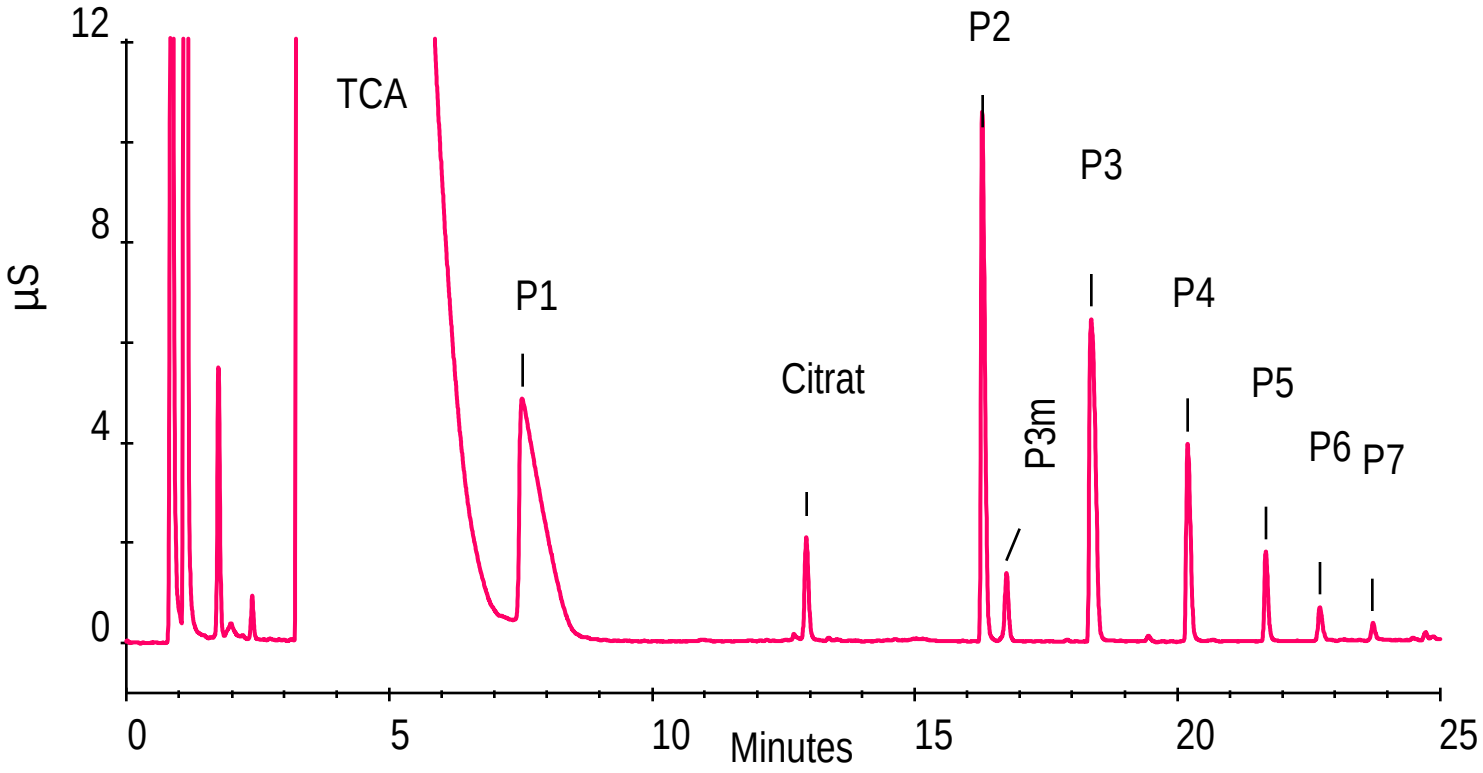
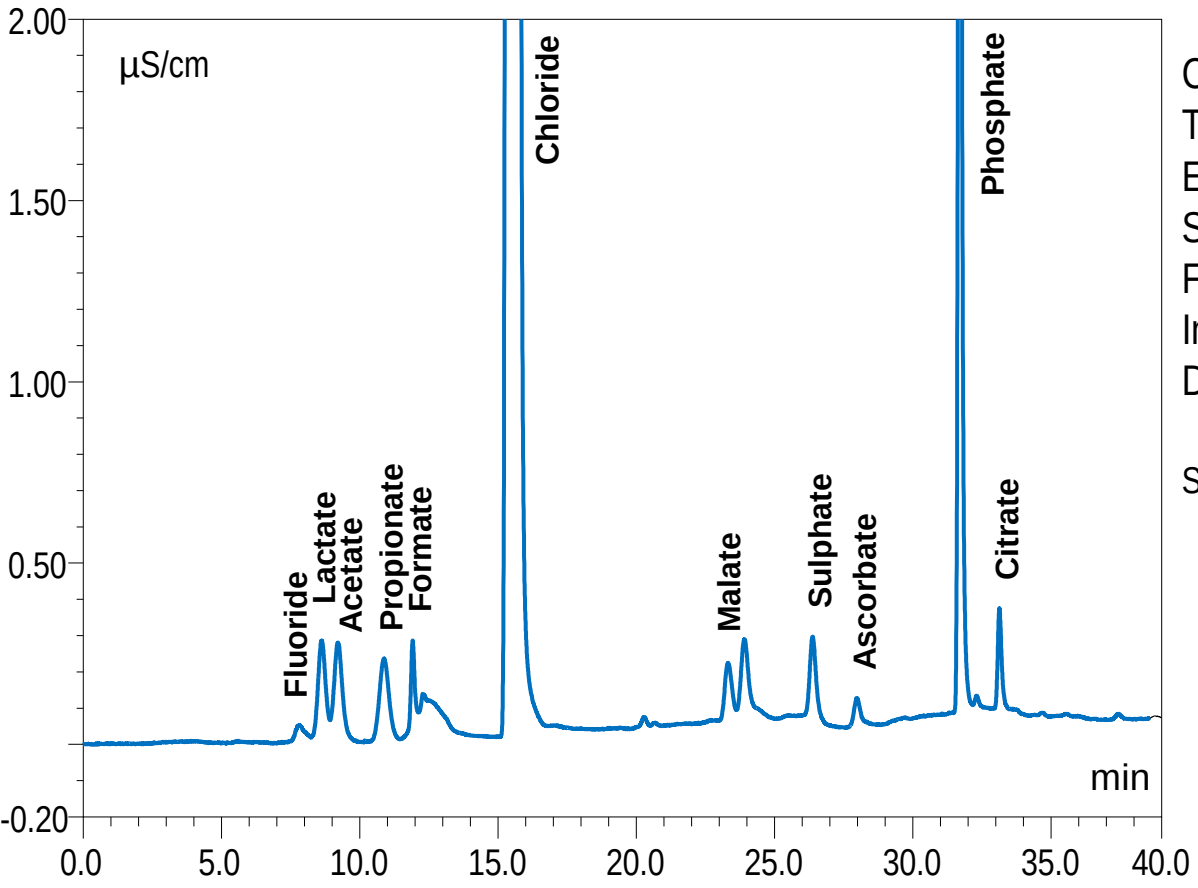
Polyphosphates in Cheese



Column:	IonPac AS16 w/ guard	Detection:	suppressed conductivity
Inj. volume:	25 µL	Flow:	0,5 mL/min
Eluent:	KOH (EG40)		

Inorganic and Organic Anions in Feed



Column:	IonPac AG11-HC and AS11-HC
Temp.:	30°C
Eluant:	KOH-Gradient
Source:	ICS-3000 (EG)
Flow rate:	0,38 mL/min
Inj. volume:	10 µL
Detection:	Suppressed Conductivity
Sample Prep:	Dilute (1 ad 100) or suspend with DI water, Centrifuge (10 min, 14500 rpm),filter through 0,2 µm membrane

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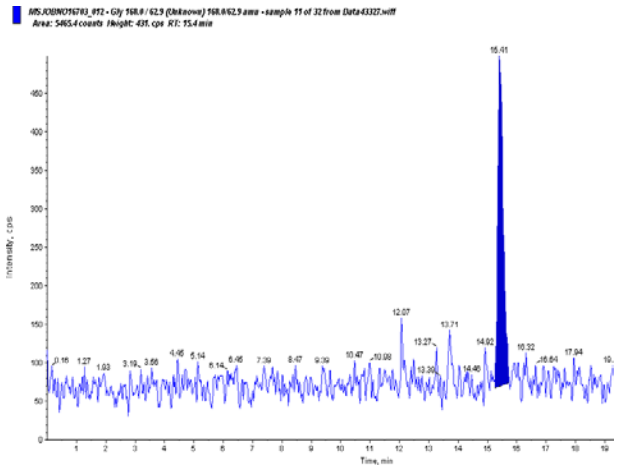
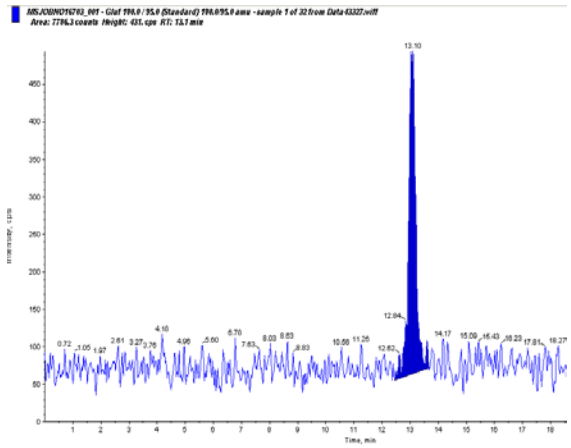
Glyphosate & Glufosinate-Cereal based Baby Food

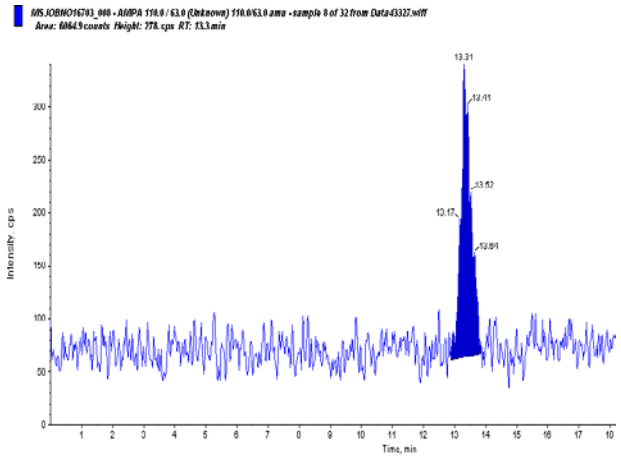
glyphosate (10 µg/kg)



glufosinate (50 µg/kg)



AMPA (100 µg/kg)



Excellent linearity, sensitivity precision for glyphosate
Accuracy?
Screening glyphosate 10 µg/kg now possible (with CAX SPE)
Confirmation of identity at 10 µg/kg is an issue
– *requires increased instrument sensitivity*

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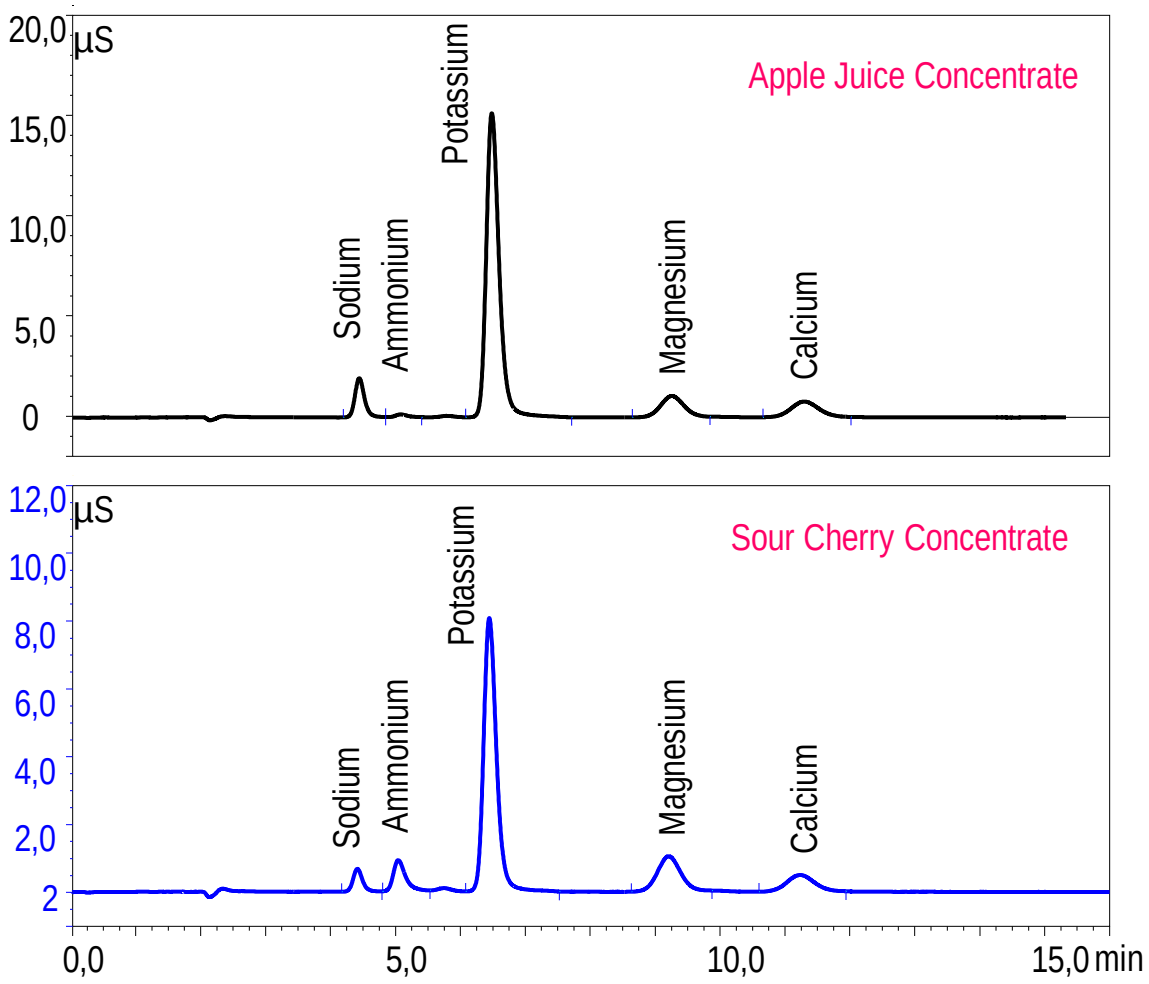
Cations in Authentic Fruit Juices



Column:	IonPac CS12A mit CG12A
Eluent:	18 mmol/L MSA
Flow:	1 mL/min
Inj. volume:	25 µL
Detection:	suppressed conductivity
Sample Prep.:	Dilution

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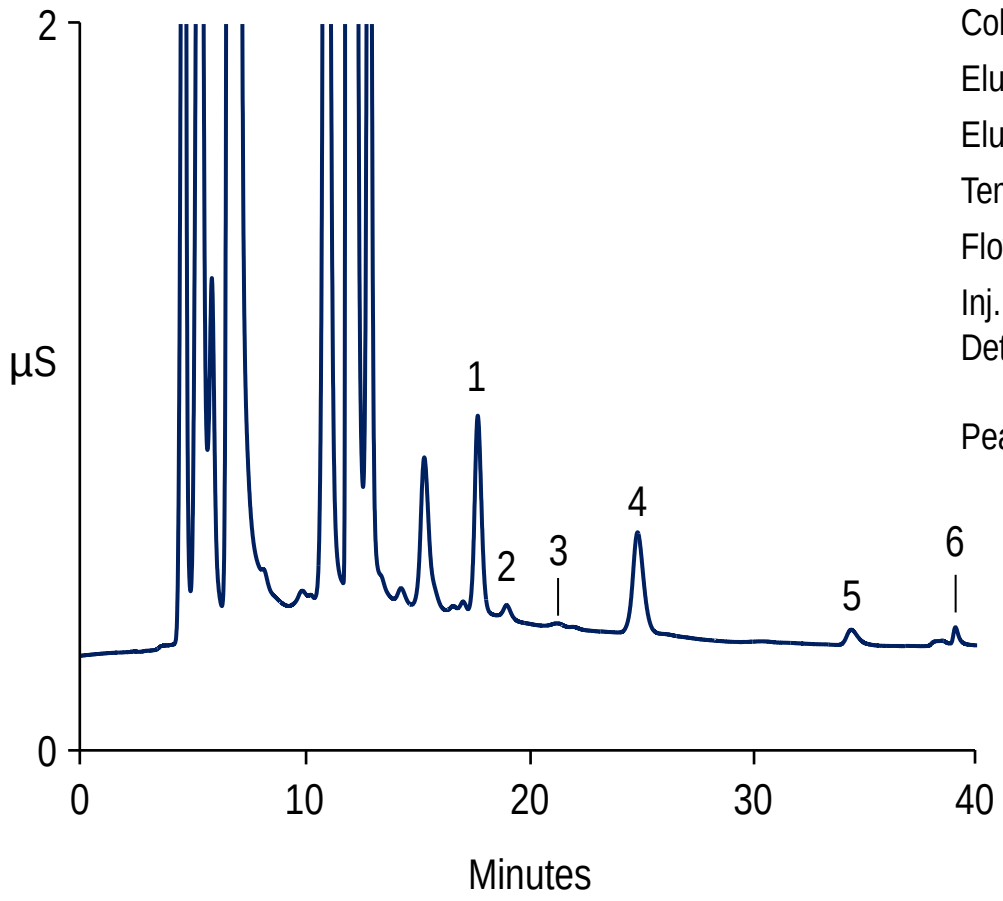
Determination of Biogenic Amines in Wheat Beer by Suppressed Conductivity Detection



Column:	IonPac® CG18, CS18, 2 mm
Eluent:	Methanesulfonic acid gradient
Eluent Source:	EGC-II MSA
Temperature:	40 °C
Flow Rate:	0.30 mL/min
Inj. Volume:	5 µL
Detection:	Suppressed conductivity, external water mode

Peaks:		
	1.Putrescine	6.6 mg/L (ppm)
	2.Cadaverine	0.67
	3.Histamine	0.60
	4.Agmatine	7.70
	5.Spermidine	1.2
	6.Spermine	0.73

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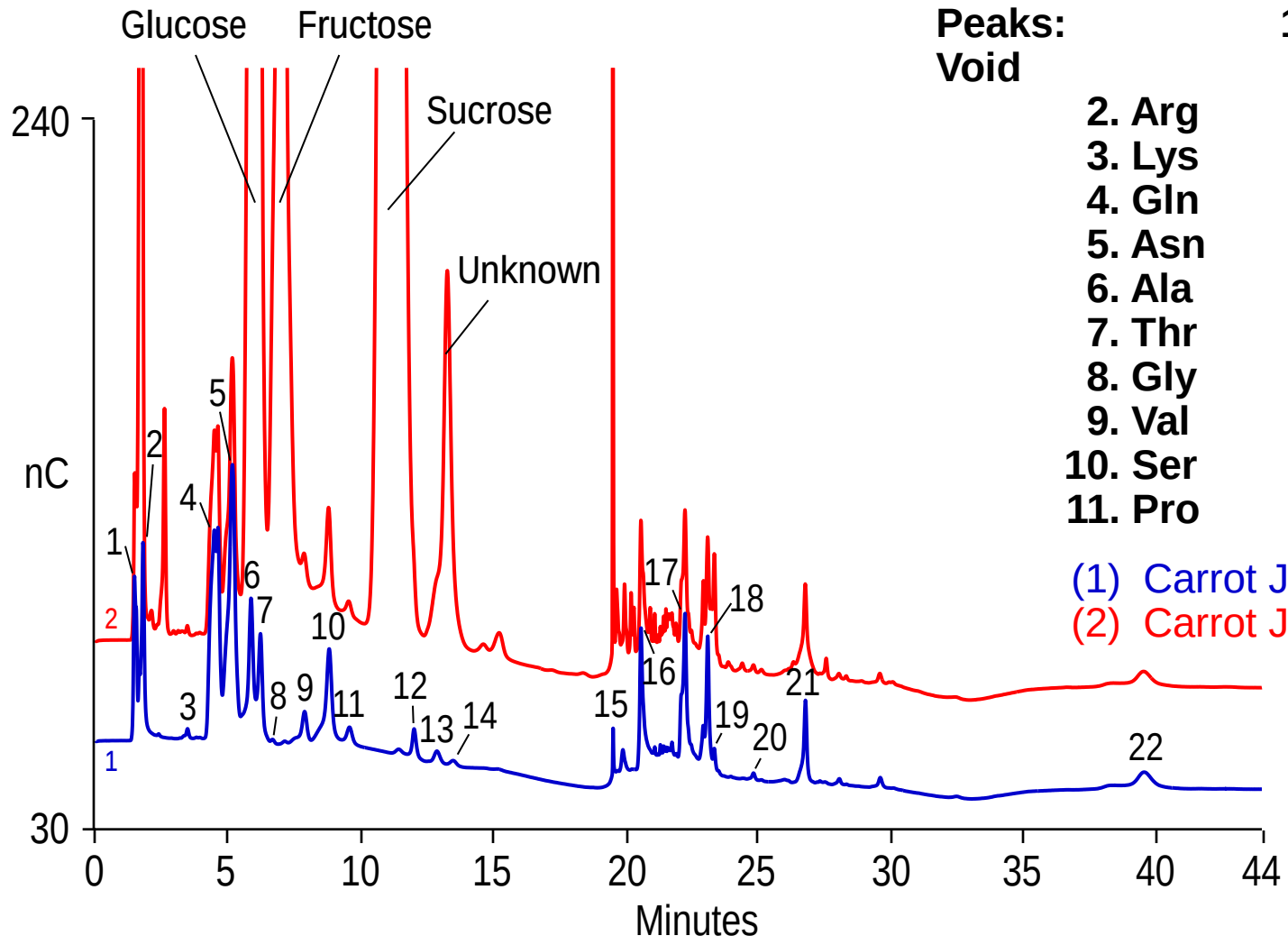
Removal of Carbohydrates from 100-Fold Diluted Carrot Juice



Peaks:

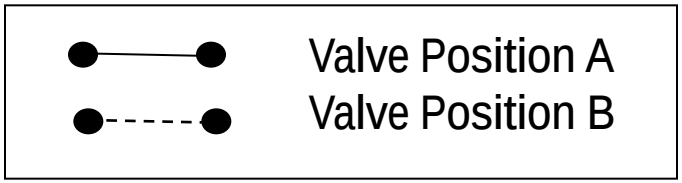
Void

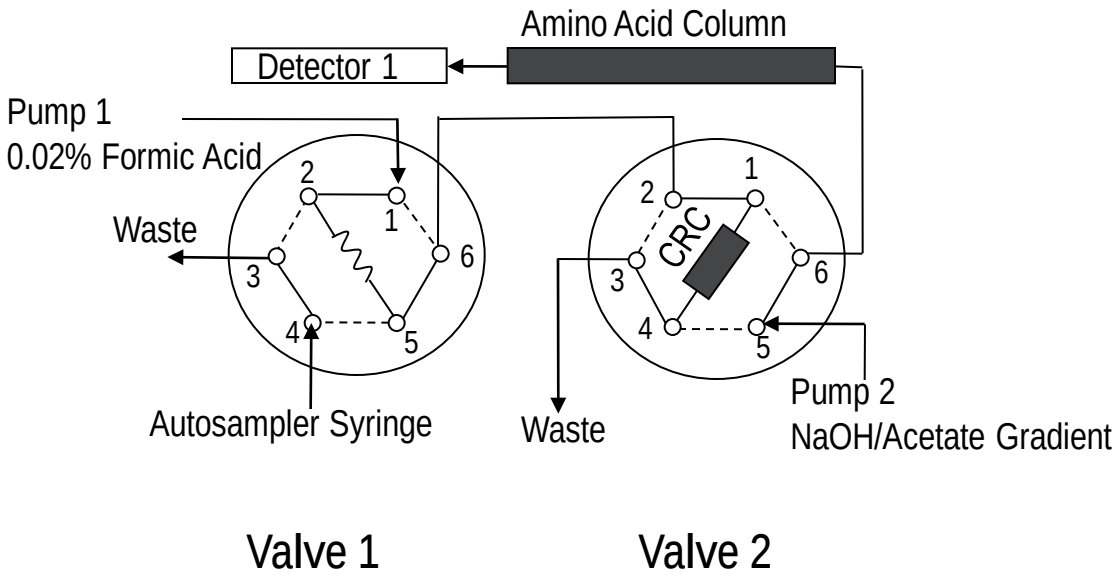
2. Arg
3. Lys
4. Gln
5. Asn
6. Ala
7. Thr
8. Gly
9. Val
10. Ser
11. Pro

1.
12. Ile
13. Leu
14. Met
15. System
16. His
17. Phe
18. Glu
19. Asp
20. Cystine
21. Tyr
22. Trp

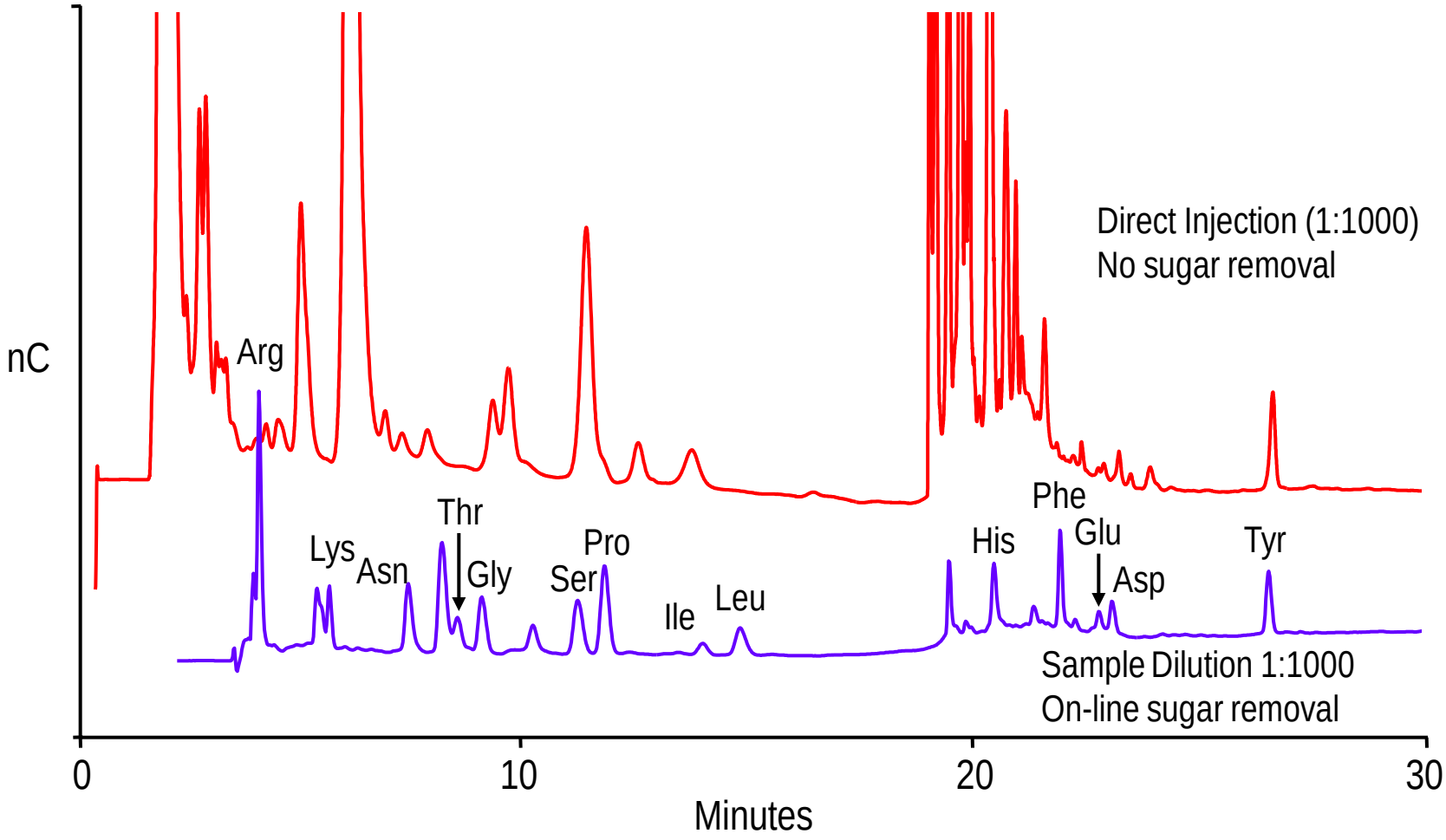
(1) Carrot Juice with the CRA
(2) Carrot Juice without the CRA

In-Line Carbohydrate Removal





Amino Acids in Rice Wine



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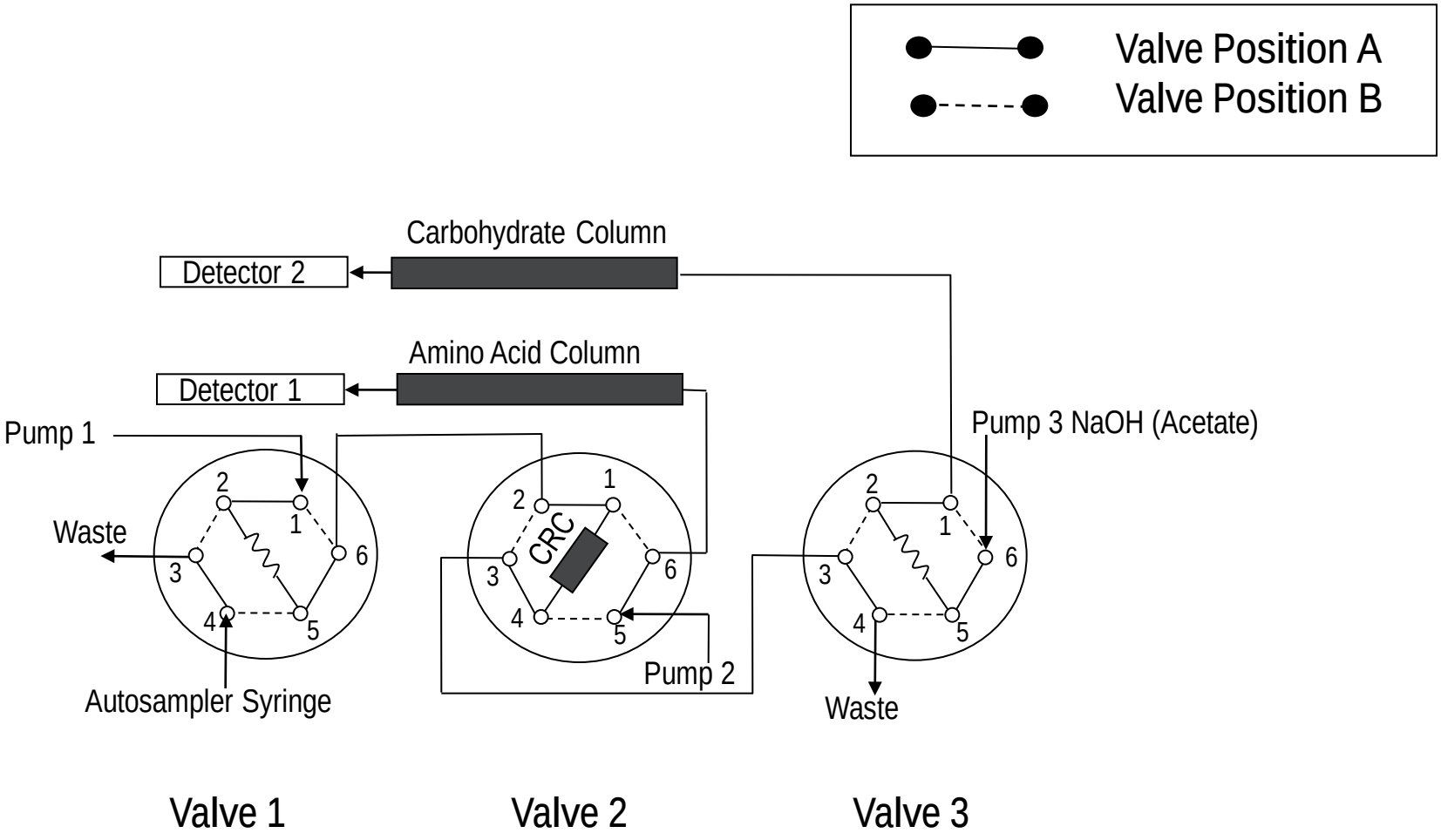
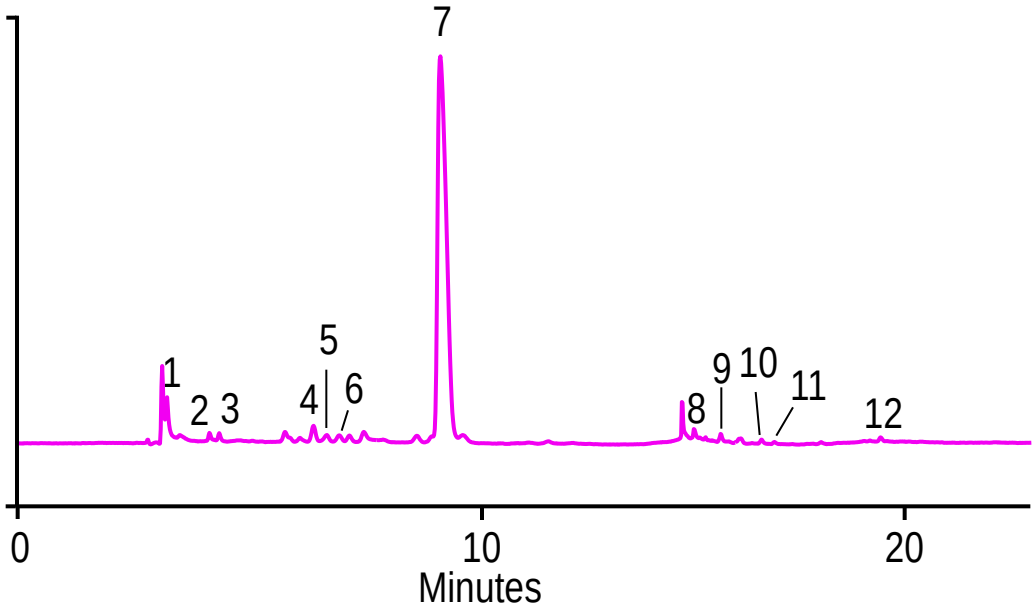
2D IC of Amino Acids and Carbohydrates



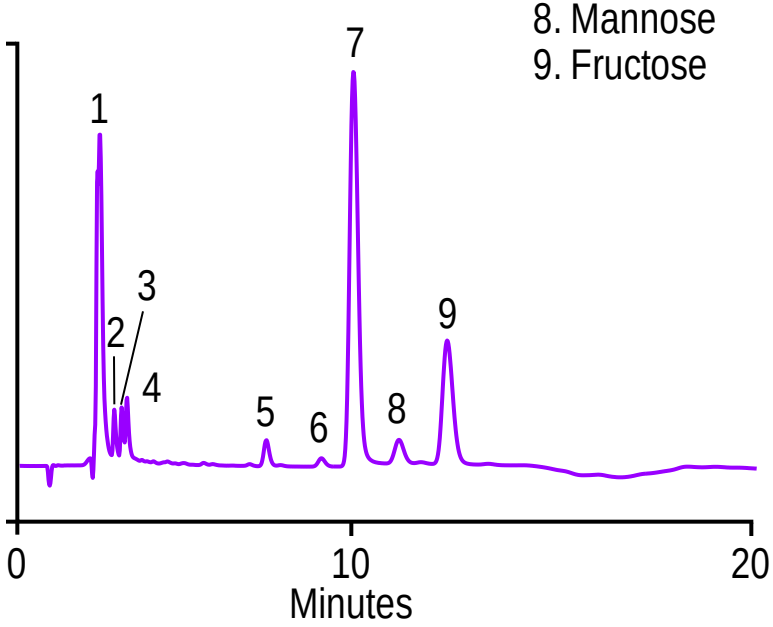
2D Separation

Red Wine 1:500; 2nd Dimension: CarboPac PA20

Peaks: 1. Arginine
2. Unknown
3. Lysine
4. Alanine
5. Threonine
6. Glycine
7. Proline
8. Histidine
9. Phenylalanine
10. Glutamate
11. Aspartate
12. Tyrosine



Peaks: 1. Unknown
2. Xylitol
3. Sorbitol
4. Mannitol
5. Unknown
6. Galactose
7. Glucose
8. Mannose
9. Fructose



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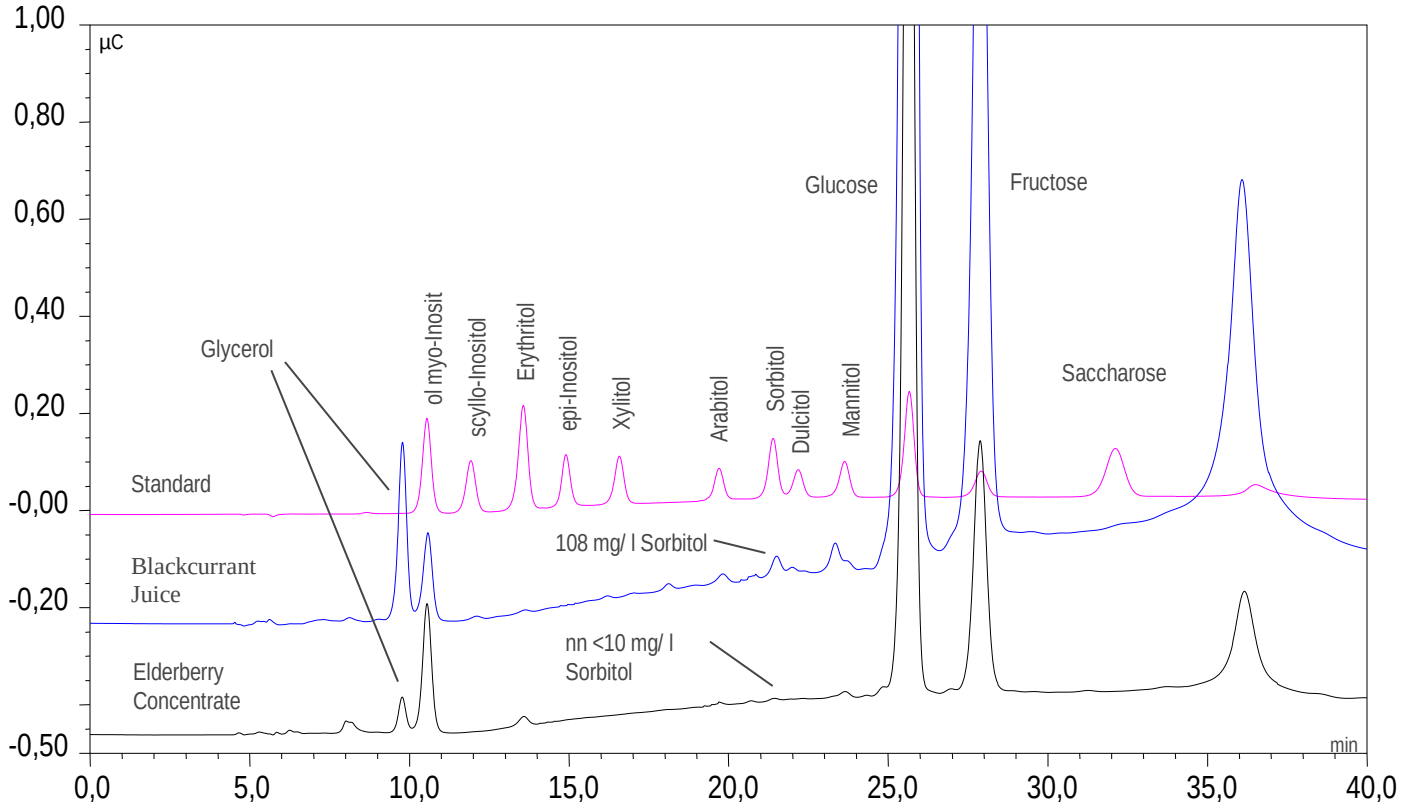
Sugar Alcohols in Fruit Juices – Trace Determination of Sorbitol

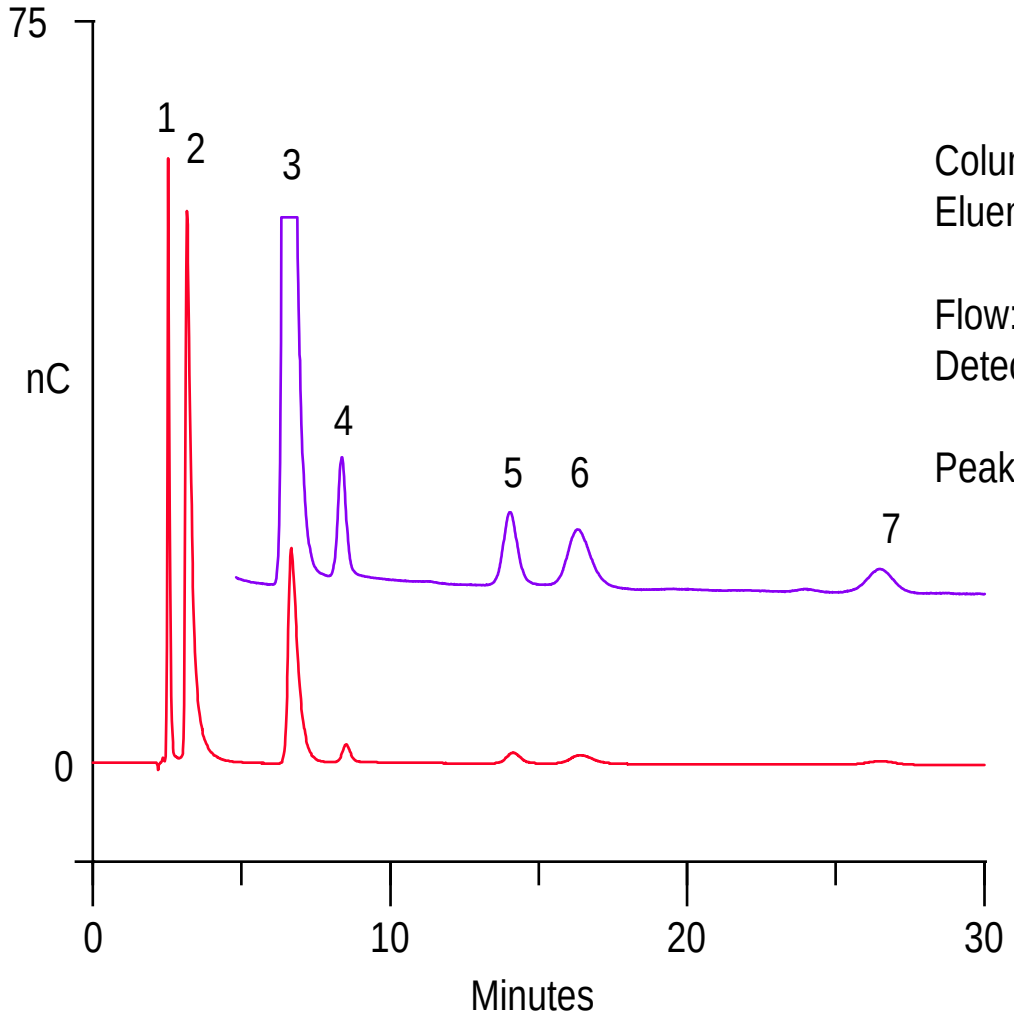


Column: CarboPac MA 1 + Guard + Borat-Trap

Eluents: A: DI Water, B: 1 mol/L NaOH,
0-4 min 4% B, 4 -15 min to 100% B

Detection: IPAD (Au-Electrode)

Carbohydrates in Milk



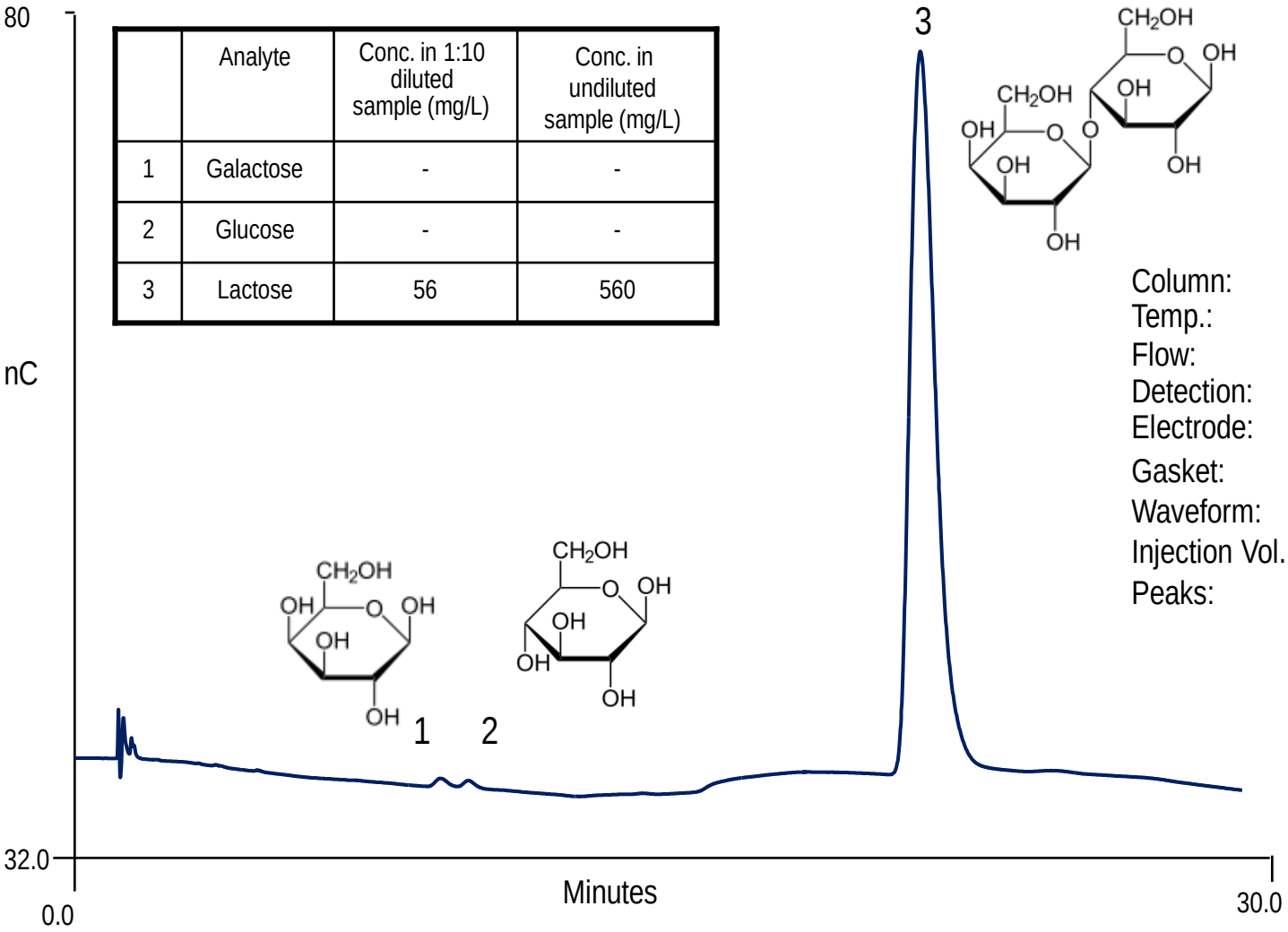
Column:	CarboPac PA 1
Eluent:	12 mmol/L NaOH, 2.5 mmol/L NaOAc
Flow:	1.0 mL/min
Detection:	PAD (Gold)

Peaks:

1. *meso* -Erythritol	40 µmol/L
2. Mannitol	40 µmol/L
3. Rhamnose	40 µmol/L
4. Saccharose	1 µmol/L
5. Lactose	1 µmol/L
6. Lactulose	1 µmol/L
7. Turanose	1 µmol/L

Separation of Carbohydrates in Whole Milk

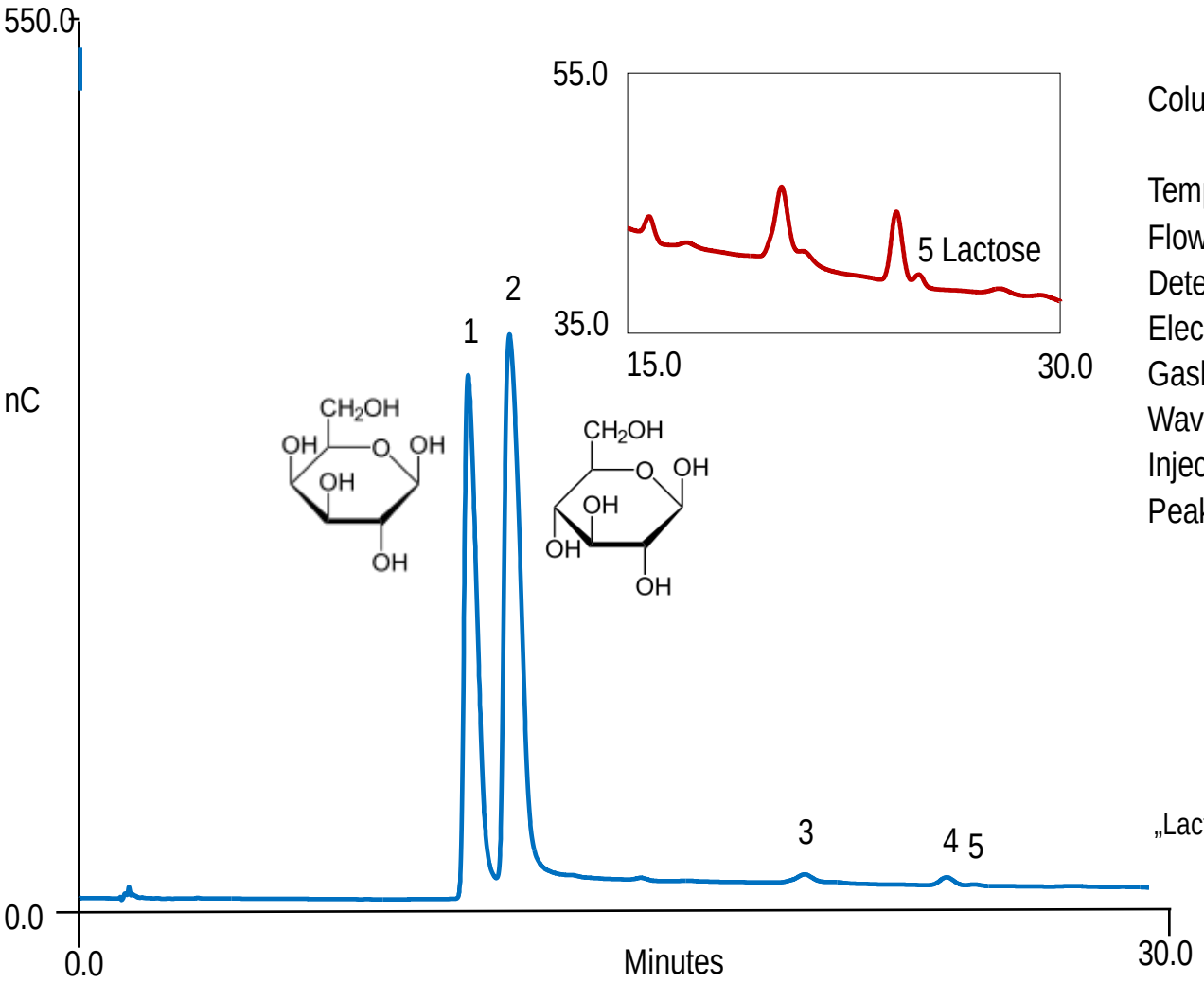
	Analyte	Conc. in 1:10 diluted sample (mg/L)	Conc. in undiluted sample (mg/L)
1	Galactose	-	-
2	Glucose	-	-
3	Lactose	56	560



Column: CarboPac PA 20 w/ guard
Temp.: 30 °C
Flow: 0.4 mL/min
Detection: PAD
Electrode: Disposable Gold on PTFE
Gasket: 2 mil
Waveform: Carbohydrate (standard quad)
Injection Vol.: 10 µL
Peaks: 1. Galactose
2. Glucose
3. Lactose

Sample Prep.: Carrez-Precipitation followed by Dilution (1 ad 10)

Separation of Carbohydrates in Lactose-free Low Fat Milk

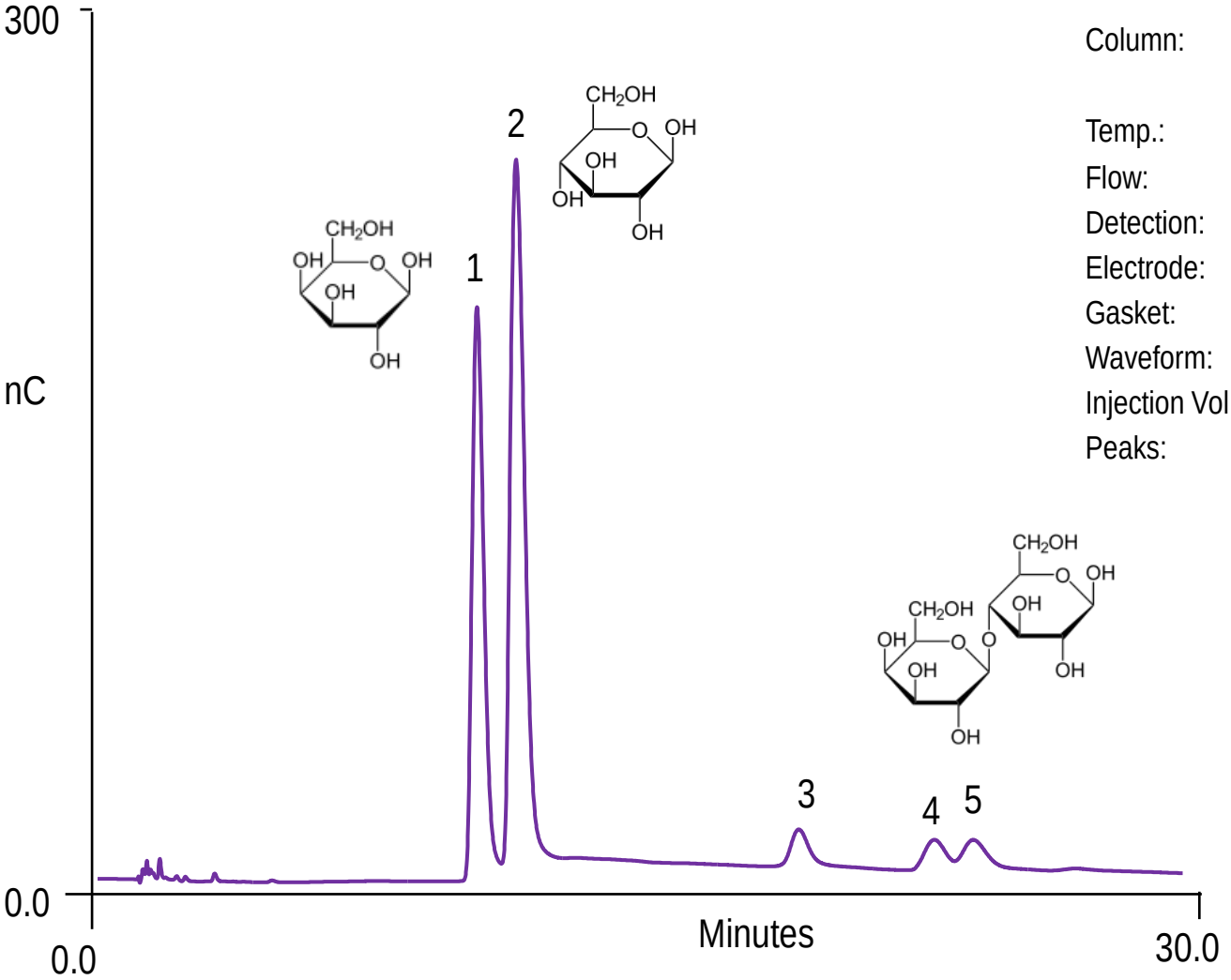


Column:	CarboPac PA20 (3 x 250 mm)
	Guard (3 x 50 mm)
Temp.:	30 °C
Flow:	0.4 mL/min
Detection:	PAD
Electrode:	Disposable Gold on PTFE
Gasket:	2 mil
Waveform:	Carbohydrate (standard quad)
Injection Vol.:	10 µL
Peaks:	1. Galactose - mg/L
	2. Glucose - mg/L
	3. Unknown - mg/L
	4. Unknown - mg/L
	5. Lactose 0.6 mg/L = 0.00006%

„Lactose-free“: 0.1% = 0.1 g Lactose /100g = 1000 ppm

Sample Prep.: Carrez-Precipitation followed by Dilution (1 ad 10)

Separation of Carbohydrates in Lactose-free Low Fat Cottage Cheese



Column:	CarboPac PA20 (3 x 250 mm)
	Guard (3 x 50 mm)
Temp.:	30 °C
Flow:	0.4 mL/min
Detection:	PAD
Electrode:	Disposable Gold on PTFE
Gasket:	2 mil
Waveform:	Carbohydrate (standard quad)
Injection Vol.:	10 µL
Peaks:	1. Galactose - mg/L
	2. Glucose - mg/L
	3. Unknown - mg/L
	4. Unknown - mg/L
	5. Lactose 2.17 mg/L = 0.00217%

Sample Prep.: Carrez-Precipitation followed by Dilution (1 ad 10)

High Pressure / High Resolution _ 4µm/5000psi

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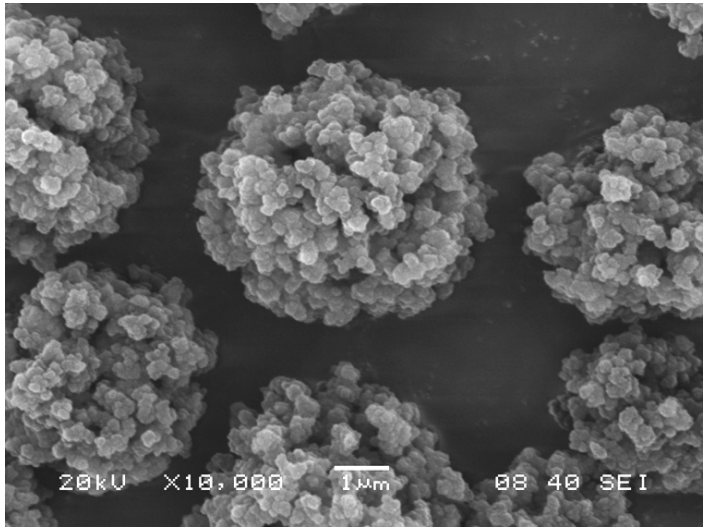
New High Efficiency Thermo Scientific Dionex IonPac 4 µm Capillary IC Columns

Improved Resolution Provides Faster Runs and Better Results

Ion-exchange columns with 4 µm particle-size

Benefits

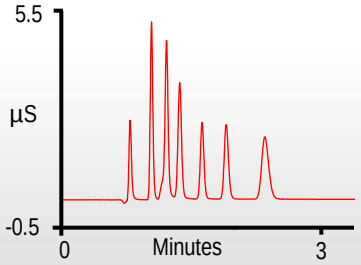
- Smaller particles provide better performance
- Fast run times with higher flow rates using 150 mm columns
- High resolution with standard flow rates using 250 mm columns



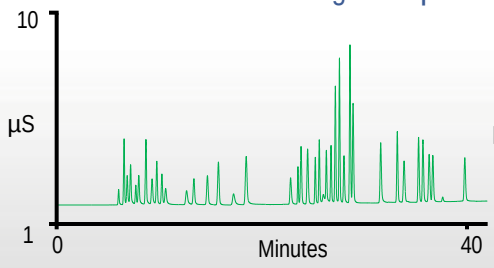
SEM Image of 4 µm Supermacroporous Bead

Applications

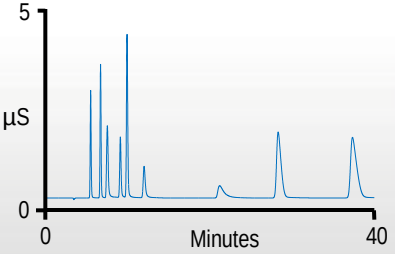
- Anions in waters
- Organic acids in foods and beverages
- Amines



Fast Run using the Dionex IonPac™ AS18-4µm



High Resolution using the Dionex IonPac AS11-HC-4µm



High Resolution using the Dionex IonPac CS19-4µm

Ion Chromatography Reagent-Free IC Capillary IC Chromeleon Data System

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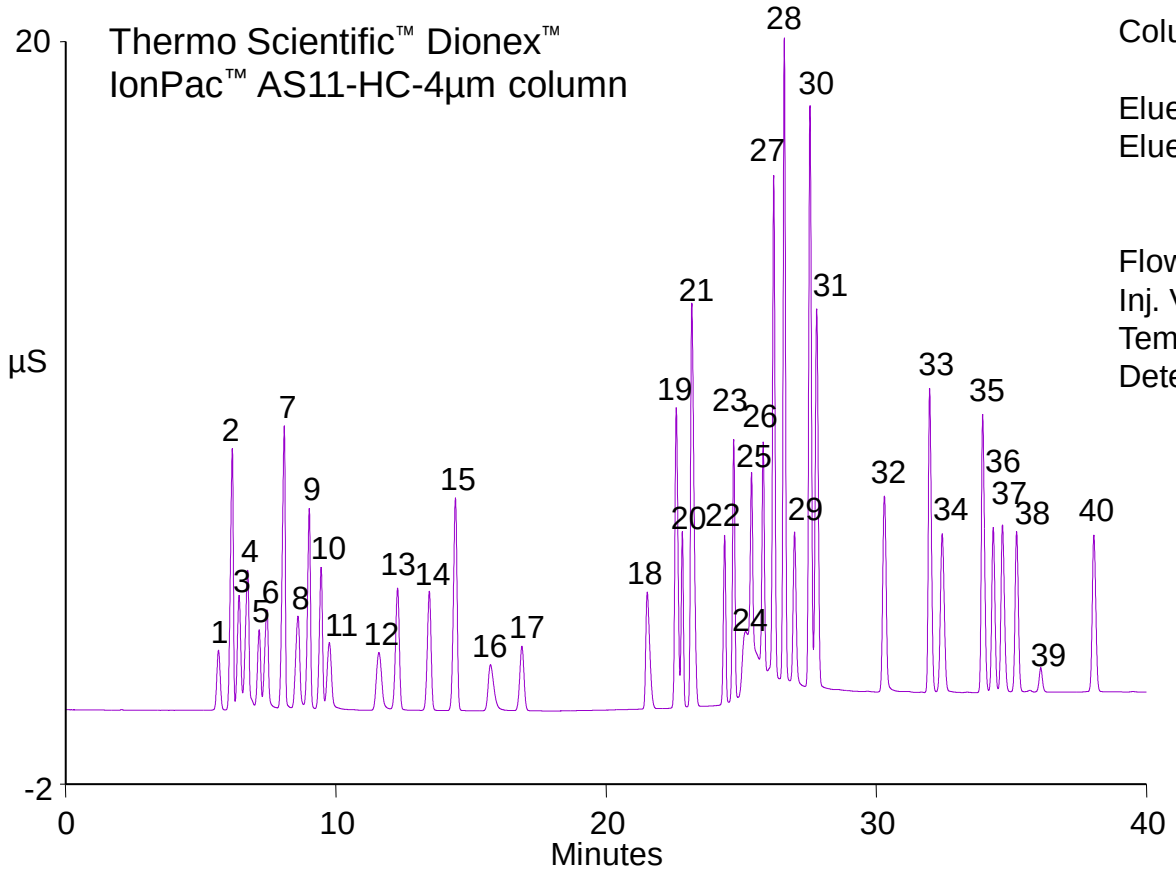
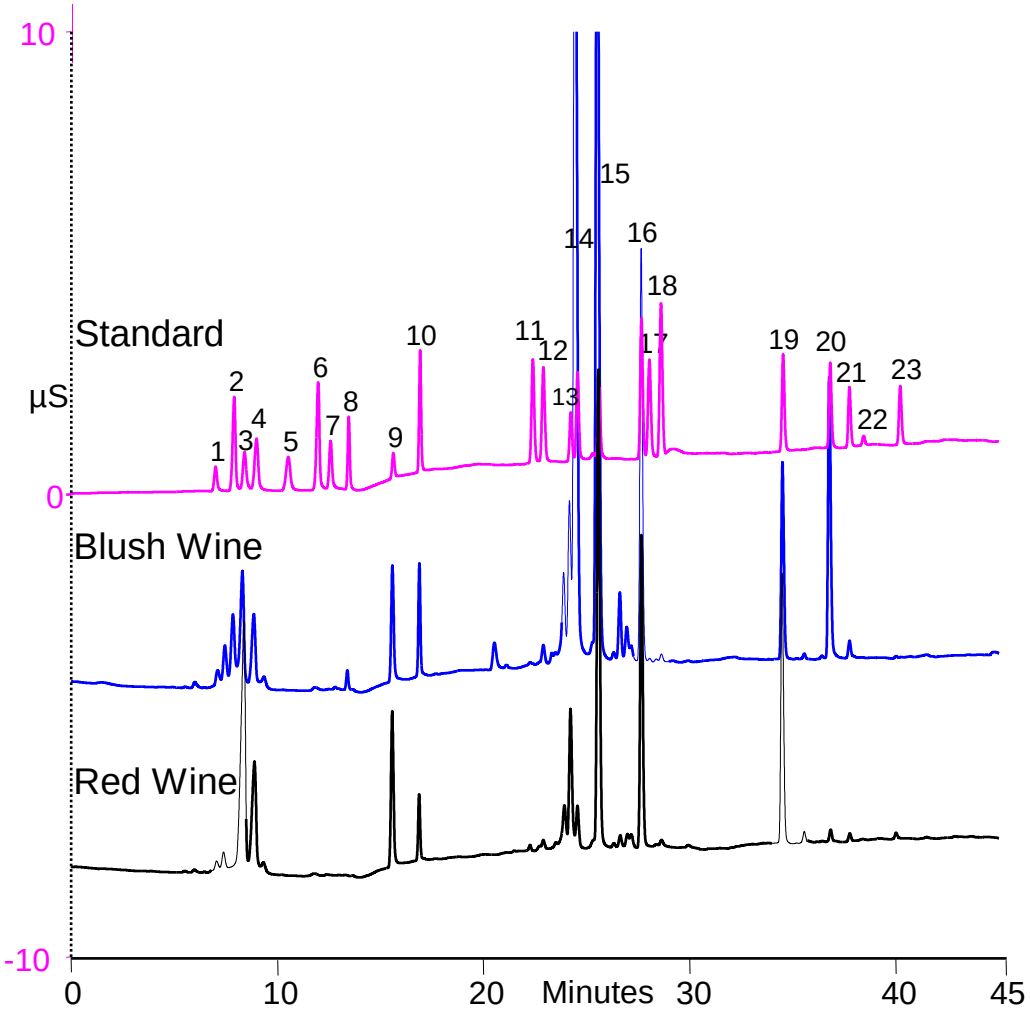
AS 11HC a 4 µm high-resolution small-particle columns



Column:	Dionex IonPac AG11-HC-4µm/ AS11-HC-4µm (0.4 × 250 mm)
Eluent Source:	Dionex EGC-KOH (Capillary)
Eluent:	1 mM KOH (0.1 min), 1–5 mM KOH (0.1–15 min); 5–55 mM KOH (15–40 min)
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 µL
Temperature:	30 °C
Detection:	Suppressed conductivity, Thermo Scientific™ Dionex™ ACES™ 300, recycle mode

1. Quinate
2. Fluoride
3. Lactate
4. Acetate
5. 2-Hydroxybutyrate
6. Propionate
7. Formate
8. Butyrate
9. Methylsulfonate
10. Pyruvate
11. Isovalerate
12. Valerate
13. Monochloroacetate
14. Bromate
15. Chloride
16. 2-Oxovalerate
17. Nitrite
18. Ethylphosphate
19. Trifluoroacetate
20. Bromide
21. Nitrate
22. Citramalate
23. Malate
24. Carbonate
25. Malonate
26. Citraconitate
27. Maleate
28. Sulfate
29. α-Ketoglutarate
30. Oxalate
31. Fumarate
32. Tungstate
33. Phosphate
34. Phthalate
35. Arsenate
36. Citrate
37. Chromate
38. Isocitrate
39. *cis*-Aconitate
40. *trans*-Aconitate

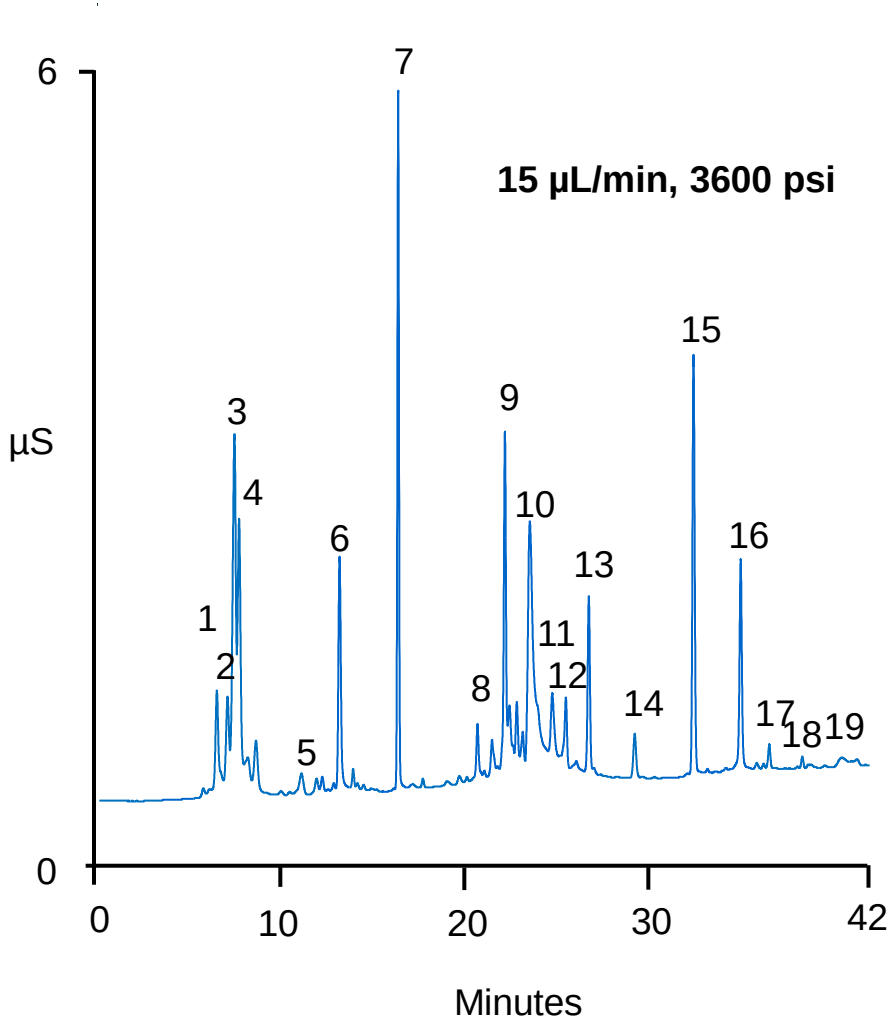
Blush and Red Wine Samples



Column:	Dionex IonPac AG11-HC-4µm, AS11-HC-4µm (2 × 250 mm)
Gradient:	1 mM KOH, 2% methanol (8 min), 10% Methanol (at 8.1 min), 1–15 mM KOH, 10% methanol (10 min) 15–30 mM KOH,10% methanol (10 min), 30–60 mM KOH,10% methanol (10 min)
Eluent Source:	Dionex EGC 500 KOH cartridge
Flow Rate:	0.38 mL/min
Inj. Volume:	2.5 µL
Temperature:	30 ˚C
Detection:	Suppressed conductivity, Dionex ASRS 300, 2 mm, external water mode
Sample Prep.:	20-fold dilution

Peaks (Standard):	mg/L		mg/L
1. Quinate	5	14. Malate	10
2. Fluoride	3	15. Tartrate	10
3. Lactate	5	16. Sulfate	10
4. Acetate	5	17. Fumarate	10
5. Propionate	5	18. Oxalate	10
6. Formate	5	19. Phosphate	15
7. Butyrate	5	20. Citrate	15
8. Pyruvate	10	21. Isocitrate	15
9. Galacturonate	10	22. *cis*-Aconitate	--
10. Chloride	5	23. *trans*-Aconitate	15
11. Bromide	5		
12. Nitrate	5		
13. Succinate	10		

Spoiled Orange Juice



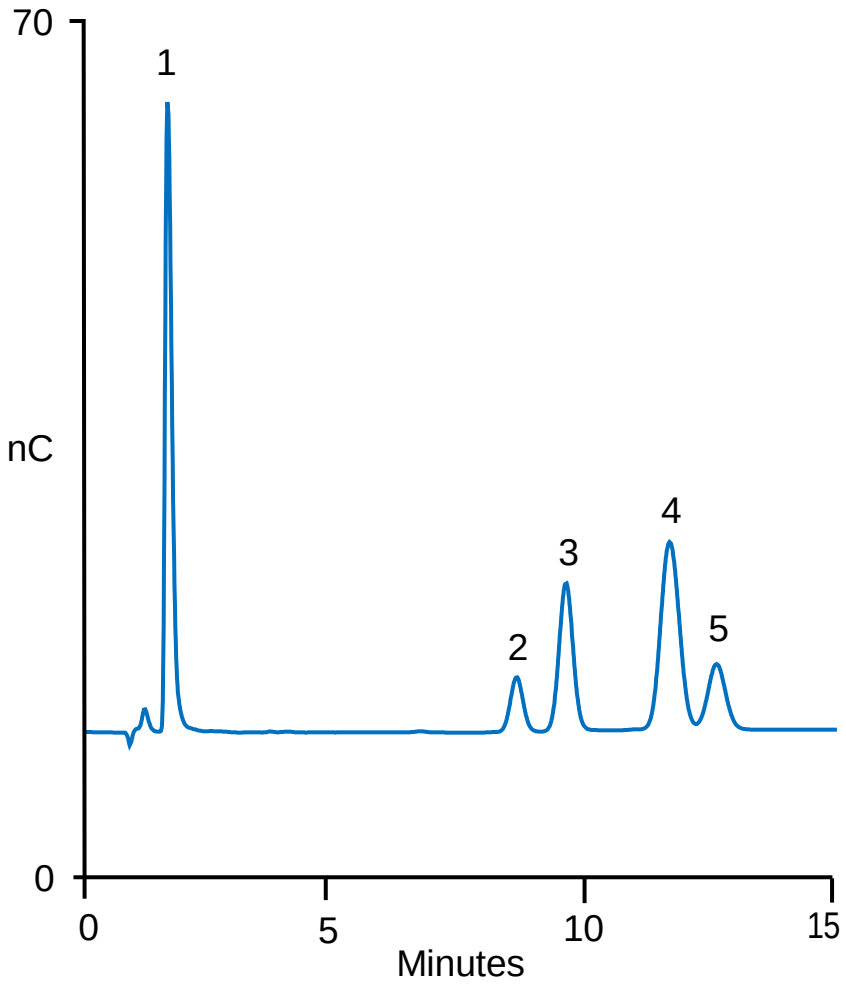
Columns:	Dionex IonPac AS11-HC-4µm set Capillary (0.4 × 250 mm)
Eluent Source:	Dionex, EGC-KOH (Capillary)
Gradient:	Potassium hydroxide, 1 mM (0–8 min), 1–30 mM (8–28 min), 30–60 mM (28–38 min), 60 mM (38–42 min)
Flow Rate:	0.015 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	Suppressed conductivity, Dionex ACES 300, recycle mode
Sample Prep.:	40-fold dilution with deionized water

Peaks:

1. Quinate
2. Fluoride
3. Lactate ↑
4. Acetate ↑
5. Formate
6. Pyruvate
7. Chloride
8. Unknown
9. Malate-Succinate
10. Carbonate
11. Maleate
12. Sulfate
13. Oxalate
14. Unknown* ↑
15. Phosphate
16. Citrate
17. *cis*-Aconitate
18. *trans*-Aconitate
19. Unknown

* Possibly oxaloacetate

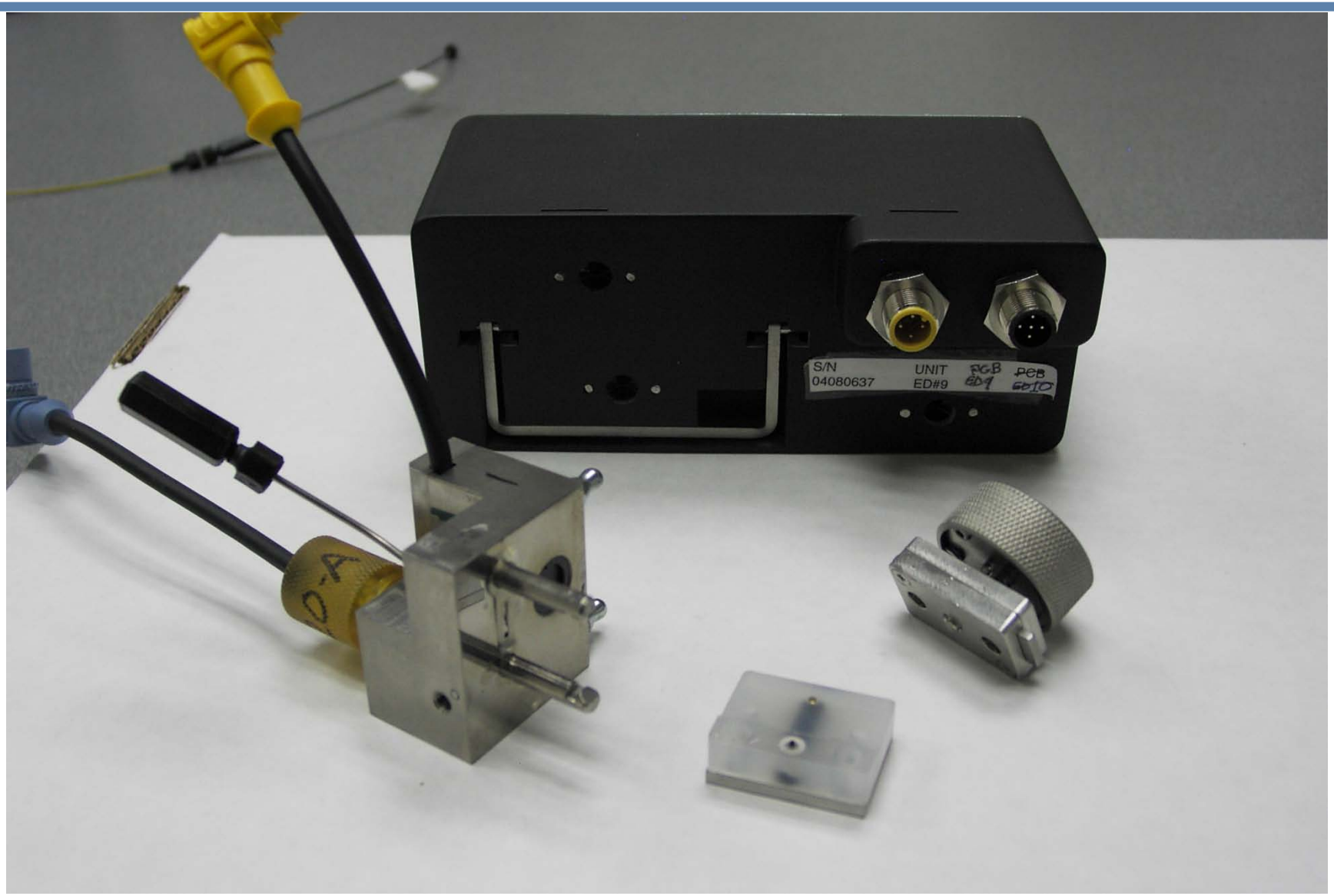
Coconut Water with diluted Sugar Cane



Column:	Dionex CarboPac PA20, 0.4 mm
Eluent Source:	Dionex EGC-KOH capillary with capillary Dionex CR-ATC
Eluent:	10 mM KOH (15 min)
Flow Rate:	0.008 mL/min
Inj. Volume:	0.4 µL
Column Temp.:	30 °C
Detection:	PAD, Au on PTFE disposable, Four-Potential Carbohydrate waveform
Gasket:	0.001” PTFE
Ref. Electrode:	Ag/AgCl
Sample Prep.:	5000-fold dilution

Peaks:		mg/L	% Ratio
1.	Void Volume	--	--
2.	Galactose	0.9	37
3.	Glucose	4	16
4.	Sucrose	2	21
5.	Fructose	2	18

Amperometric Cell



Thank you!

RFIC

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Starter Line IC System Smallest Footprint Drinking Water Analysis	Basic Integrated RFIC™ System Routine IC Drinking & Waste Water Analysis	Standard Integrated RFIC™ System Routine Drinking & Waste Water Analysis	Superior Integrated RFIC™ System Award Winning Great Performance High Purity Water and Beverage Analysis	Integrated Dedicated Capillary IC System Capillary HPIC RFIC-EG Technology Carbohydrate Analysis Drinking & Waste Water Analysis	Premier High-End HPIC & RFIC™ System Award Winning Flexible Dual Channel Ion Analysis Carbohydrate & Amino Acid Analysis

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