Metrohm

Application Work AW US6-0248-062017

Analysis of Anions and Cations in Tomato Products

Branch

Food, stimulants, beverages, flavors

Keywords

IC; 940; Conductivity; Chloride; Sodium; Potassium; Magnesium; Calcium; Anions; Cations; 858; MagIC Net 3.1; Metrosep A Supp 5-100/4.0; Metrosep C6-150/4.0; 941; Eluent Production Module; Ultrafiltration

Summary

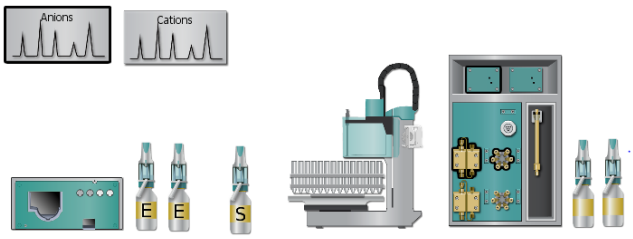
Food analysis is important to ensure that consumers are provided with safe foods, and also serves to inform them of the nutritional composition enabling knowledgeable decisions about diet. Food manufacturers are concerned with providing a product that is consistent and desirable, even though raw ingredients and processing operations vary over time. Analytical techniques such as the one described here enable rational control over the manufacturing process and also assure consumers that they can expect a safe and consistent product. This application work shows the use of Metrohm IC to analyze tomato products for chloride, sodium, potassium, magnesium, and calcium. For this work, a Metrohm Professional IC with sequential suppression and conductivity detection was used in combination with the 858 Sample Processor with Ultrafiltration. The in-line Ultrafiltration protects the column and system components from particulates and ensures trouble-free operation. The rapid analysis and simple sample preparation, combined with the ability to perform simultaneous determinations of anions and cations, enables high throughput and minimized labor. This application was performed using Metrohm's in-Vial Dilution technique which automates standard preparation and performs both known and intelligent dilutions for samples outside of the calibrated range. The Ultrafiltration is powered by Dosinos rather than peristaltic pumps, which reduces maintenance on the system. The 941 Eluent Production Module automates the preparation of the eluent leading to consistent eluent production for both anions and cations and ensures stable chromatography. Dosino regeneration and STREAM rinsing are used for the MSM.

Reagents

- Metrohm A Supp 5 20x Eluent Concentrate (64 mM Na_2CO_3 and 20 mM $NaHCO_3$); Metrohm USA ERA-IC1101
- Sulfuric acid, CAS 7664-93-9
- Nitric acid, CAS 7697-37-2
- Ultrapure water, resistivity >18 MΩ·cm (25 °C)
- Metrohm Custom Anion Mix 3, 100 ppm fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate; Metrohm USA ERA-IC1035
- Metrohm Custom Cation Mix 2, 100 ppm lithium, sodium, ammonium, potassium , magnesium, calcium; Metrohm USA ERA-IC1230
- Metrohm Individual Anion and Cation Standards, 1000 ppm
    - Chloride, Metrohm USA ERA-IC1002
    - Sodium, Metrohm USA ERA-IC1202

Instruments

940 Professional IC Vario TWO/SeS	2.940.2400
IC conductivity detector (x2)	2.850.9010
858 Professional Sample Processor	2.858.0010
Sample Rack 148 place + 3 Special Beakers	6.2041.440
Rinsing Station	6.2841.100
941 Eluent Prep Module	2.941.0010
MagIC Net 3.1	6.6059.302
Metrosep A Supp 5 – 100/4.0	6.1006.510
Metrosep A Supp 4/5 Guard	6.1006.500
Metrosep C6-150/4.0	6.1051.420
Metrosep C6 Guard/4.0	6.1051.500
800 Dosino (x5)	2.800.0010
Dosing Unit 2 mL (x2)	6.3032.120
Dosing Unit 10 mL	6.3032.210
Dosing Unit 50 mL (x2)	6.3032.250
M6 T Connector	6.1808.060
10 mL Transfer Tubing with Holder (x2)	6.1562.130
Ultrafiltration Equipment	6.5330.110
18 cm FEP Tubing	6.1805.050
M6 Needle Holder	6.2833.020
10 L Canister	6.1621.000
20 µL sample loop (x2)	6.1825.210
MSM Rotor A	6.2832.000
Nylon Filtration Membrane, 0.2 µm	SNG-IC14020



Solutions

Anion Eluent: 3.2 mM sodium carbonate + 1.0 mM sodium bicarbonate. Automatically prepared from 20 x concentrate by 941 Eluent Production Module.

Cation Eluent: 5.0 mM nitric acid. Automatically prepared from 72.5 mM nitric acid by 941 Eluent Production Module.

Regenerant for Suppressor: 500 mM sulfuric acid
28 mL of concentrated sulfuric acid is transferred to a 1 L reagent bottle containing 0.5 L of ultrapure water and is diluted to 1 L with ultrapure water.

Diluent for Dilutions: Ultrapure water

Samples

Tomato paste

Diced tomatoes in juice

Standards

100 ppm Custom Anion Mix 3 was used for system preparation of all working anion calibration standards. 100 ppm Custom Cation Mix 2 was used for system preparation of all working cation calibration standards.

In ultrapure water (ppm)

	S1	S2	S3	S4	S5	S6
All Anions	1	5	10	25	50	100
All Cations	1	5	10	25	50	100
Dilution	100x	20x	10x	4x	2x	1x

Sample Preparation

Approximately 0.2 g of homogenized sample is diluted to 40 g in ultrapure water. The sample is then placed on a wrist-actin shaker for 10 minutes followed by centrifugation at 4,400 rpm for 10 minutes. The supernatant is directly injected using the Metrohm in-Vial Dilution Technique with ultrafiltration and intelligent dilution.

IC Parameters

Anion eluent flow	0.7 mL/min
Cation eluent flow	0.9 mL/min.
Column temperature	45°C
Injection volume	20 µL
Anion P_{max}	15 MPa
Cation P_{max}	20 MPa
MSM Rinsing	STREAM
MCS	On
Degasser	On
Recording Time	15 minutes

Calculation

Automatic integration with MagIC Net 3.1 software using peak area for all analytes.

Results

All results summarized in the appendix.

Comments

It was discovered that sample replicate agreement, particularly for cations, improved significantly when using the nylon Ultrafiltration membrane as opposed to the cellulose acetate. It was also discovered that the resolution of sulfate, though not requested, also improved when using the nylon membrane. Ultrafiltration is highly recommended for this application due to the nature of the sample matrix, so it is advisable to utilize the nylon membranes if possible. Please see the appendix.

All dilutions are prepared during the recording time of the current sample being analyzed. The “prepare next dilution” subprogram is nested into the current analytical run and ensures that a diluted sample is ready for injection onto the IC. This improves sample throughput and decreases waiting time for the preparation of diluted samples and standards.

The use of Dosinos for Ultrafiltration provides several advantages over peristaltic pump. Maintenance is greatly reduced in the form of not having to check and periodically replace peristaltic pump tubing as wear occurs, especially for high throughput users who operate the system on a nearly continuous basis. Additionally, system performance is very stable as there is no longer a worry about varying volumes of filtrate delivery from worn peristaltic pump tubes.

References

AW US6-210-122014: Metrohm In-Vial Dilution Technique (MiVDT) for Anions with Intelligent Dilution, Ultrafiltration, Analyte Delimiter Logic, and Eluent Production Module

Date

June 8, 2017

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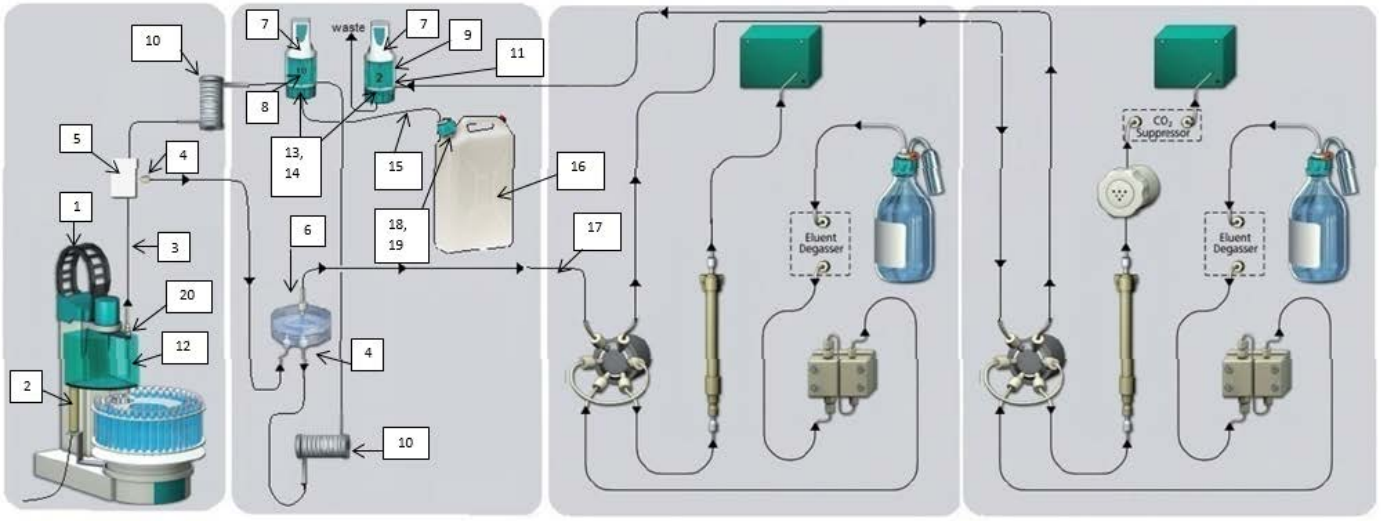
Appendix

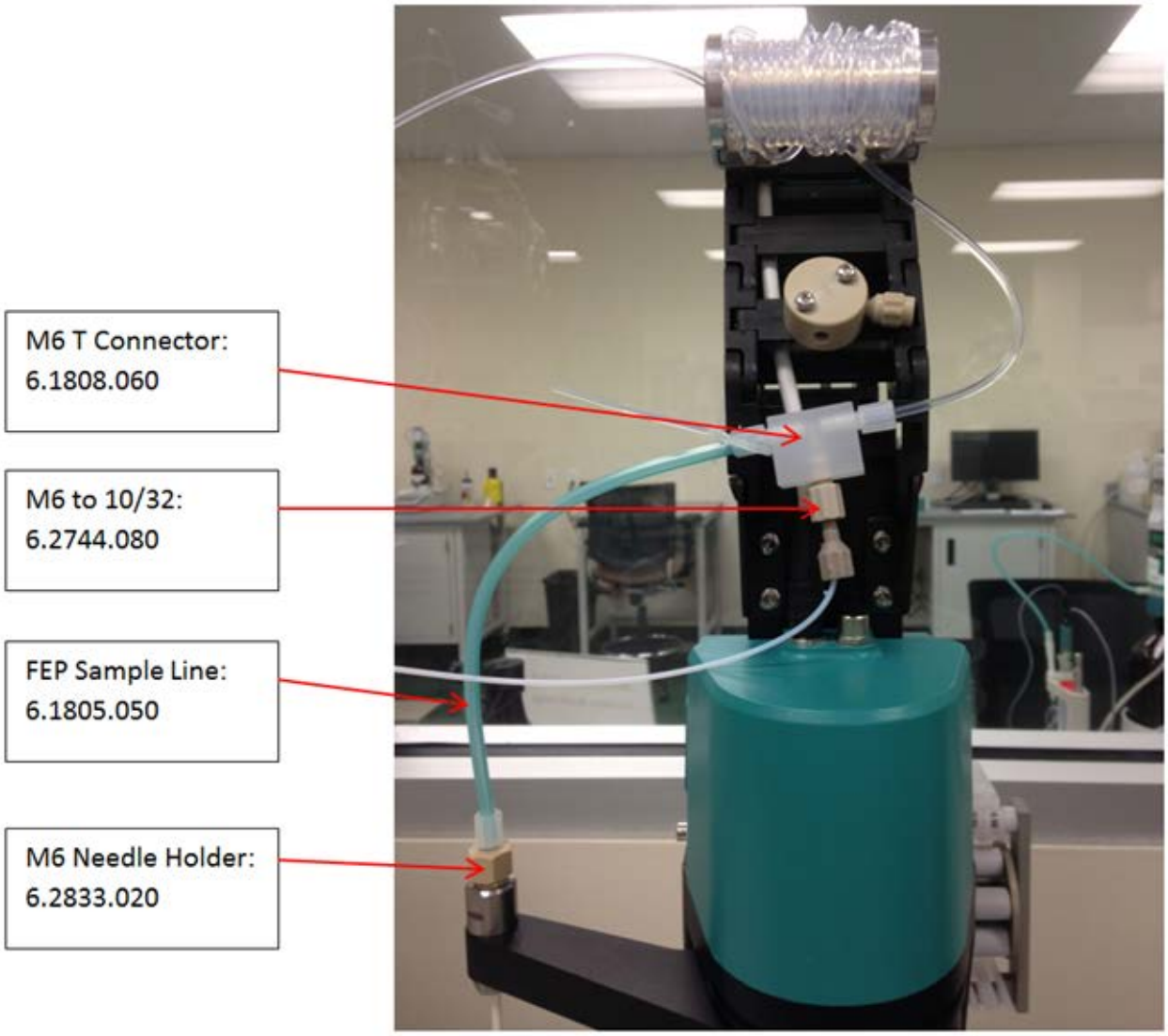
Instrumentation Set-Up



1) 2.858.0010: 858 (no valve)	11) M6 Thread/ 10/32 Coupling (6.2744.080) **x1**
2) Rinsing station (6.2841.100)	12) Sample needle made of zirconium oxide with PEEK tip (6.2846.010)
3) 18 cm FEP tubing (6.1805.050)	13) Thread adapter S 40 to GL 45 (6.1618.020) **x2**
4) Adapter UNF 10/32 outer / M6 inner (6.2744.200) **x 2**	14) Holder for Dosino to IC instruments (6.2057.210) **x1** (holds both Dosinos)
5) M6 T-Connector (6.1808.060)	15) FEP tubing, M6, 150 cm (6.1805.030) x2
6) Ultrafiltration Cell	16) 10L Canister (6.1621.000)
7) 800 Dosino (2.800.0010) **x2**	17) 0.5mm ID PTFE (6.1803.030)
8) 10mL Dosing Unit (6.3032.210)	18) Thread adapter 40mm to GL45 (6.1618.050)
9) 2mL Dosing Unit (6.3032.120)	19) Eluent bottle cap GL 45 (6.1602.160)
10) Transfer Capillary-10mL (6.1562.130) **x 2**	20) M6 Needle Holder

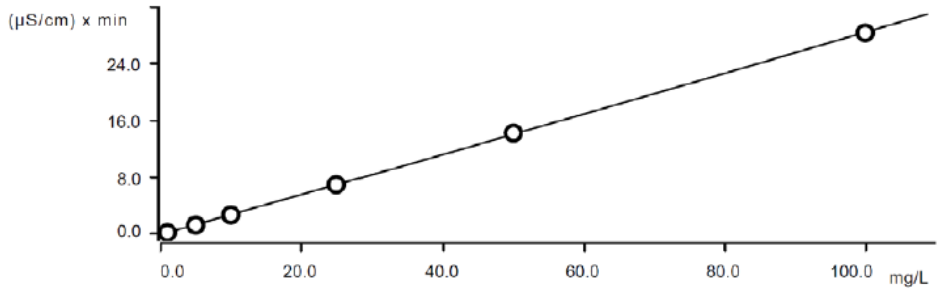
Instrumentation Set-Up

It is necessary for the 858 Professional Sample Processor to be connected as shown below in order for the dilution aliquot to travel in a straight path to the transfer coil with no change in tubing diameter.



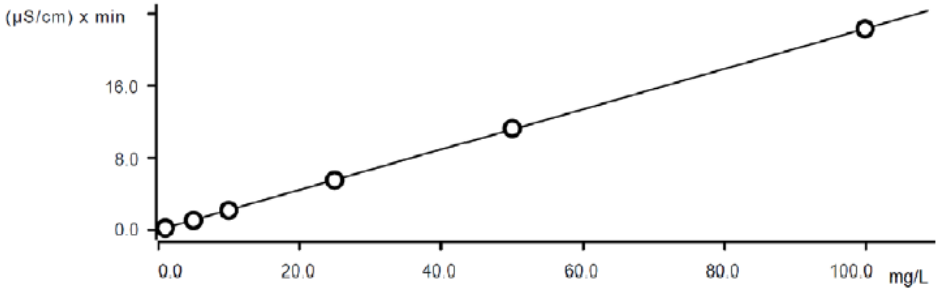
Calibration Curves

Chloride (Anions)



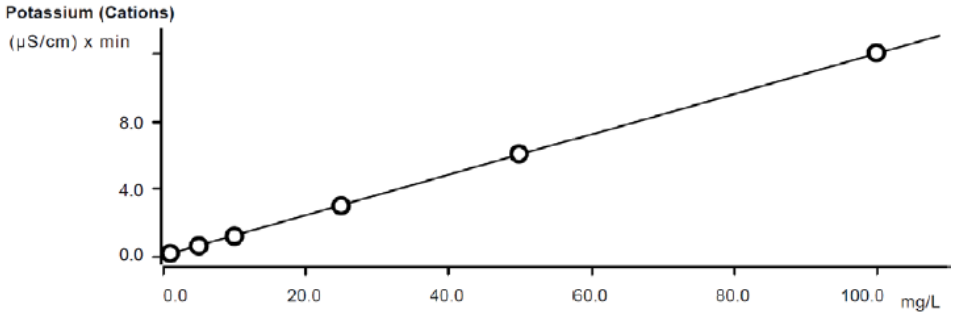
Function: . . . . . $A = -0.0645274 + 0.0139941 \times Q + 1.24867E\text{-}7 \times Q^2$
Relative standard deviation . . . . . 1.287958 %
Correlation coefficient 0.999966

Sodium (Cations)



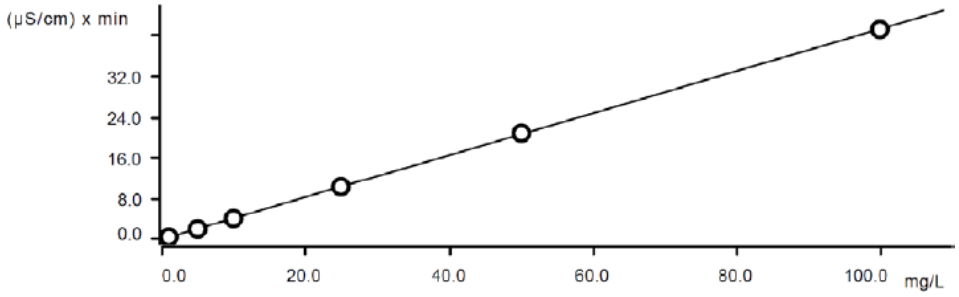
Function: . . . . . $A = 0.0462178 + 0.0111091 \times Q$
Relative standard deviation . . . . . 0.867693 %
Correlation coefficient 0.999979

Potassium (Cations)



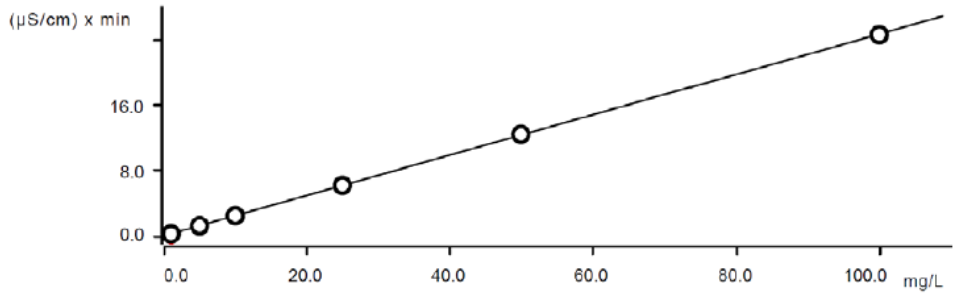
Function: . . . . . $A = 0.0439451 + 5.97477E\text{-}3 \times Q$
Relative standard deviation . . . . . 1.208187 %
Correlation coefficient 0.999958

Magnesium (Cations)



Function: . . . . . *A = 0.0424034 + 0.0206574× Q*
Relative standard deviation . . . . . *0.773500 %*
Correlation coefficient *0.999983*

Calcium (Cations)



Function: . . . . . *A = 0.0565955 + 0.0122980× Q*
Relative standard deviation . . . . . *0.747164 %*
Correlation coefficient *0.999984*

Results

Tomato Paste #1 All Concentrations in ppm	Chloride	Sodium	Potassium	Magnesium	Calcium	Dilution
Replicate 1	5210	2010	12,220	420	130*	166.32
Replicate 2	5270	200	12,320	430	130*	166.32
Replicate 3	5270	2070	12,340	430	140*	166.32
Average	5250	2050	12,290	430	130*	
RSD (%)	0.68	1.6	0.55	1.4	2.3	
*Below reporting limit of 166 ppm						

Tomato Paste #1 SPK All Concentrations in ppm	Chloride	Chloride Recovery (%)	Sodium	Sodium Recovery (%)	Dilution
Sample	5155		2021		187.58 Chloride
Matrix Spike	8824	101.2	5890	98	196.68 Sodium
Spike: 3625 ppm chloride; 3946 ppm sodium (raw: 19.32 ppm chloride; 20.06 ppm sodium					

Tomato Paste #2 All Concentrations in ppm	Chloride	Sodium	Potassium	Magnesium	Calcium	Dilution
Replicate 1	3650	1450	10,270	340	120*	184.53
Replicate 2	3680	1480	10,330	350	110*	184.53
Replicate 3	3670	1480	10,350	340	120*	184.53
Average	3670	1470	10,320	340	110*	
RSD (%)	0.35	1.3	0.40	1.2	2.0	
*Below reporting limit of 185 ppm						

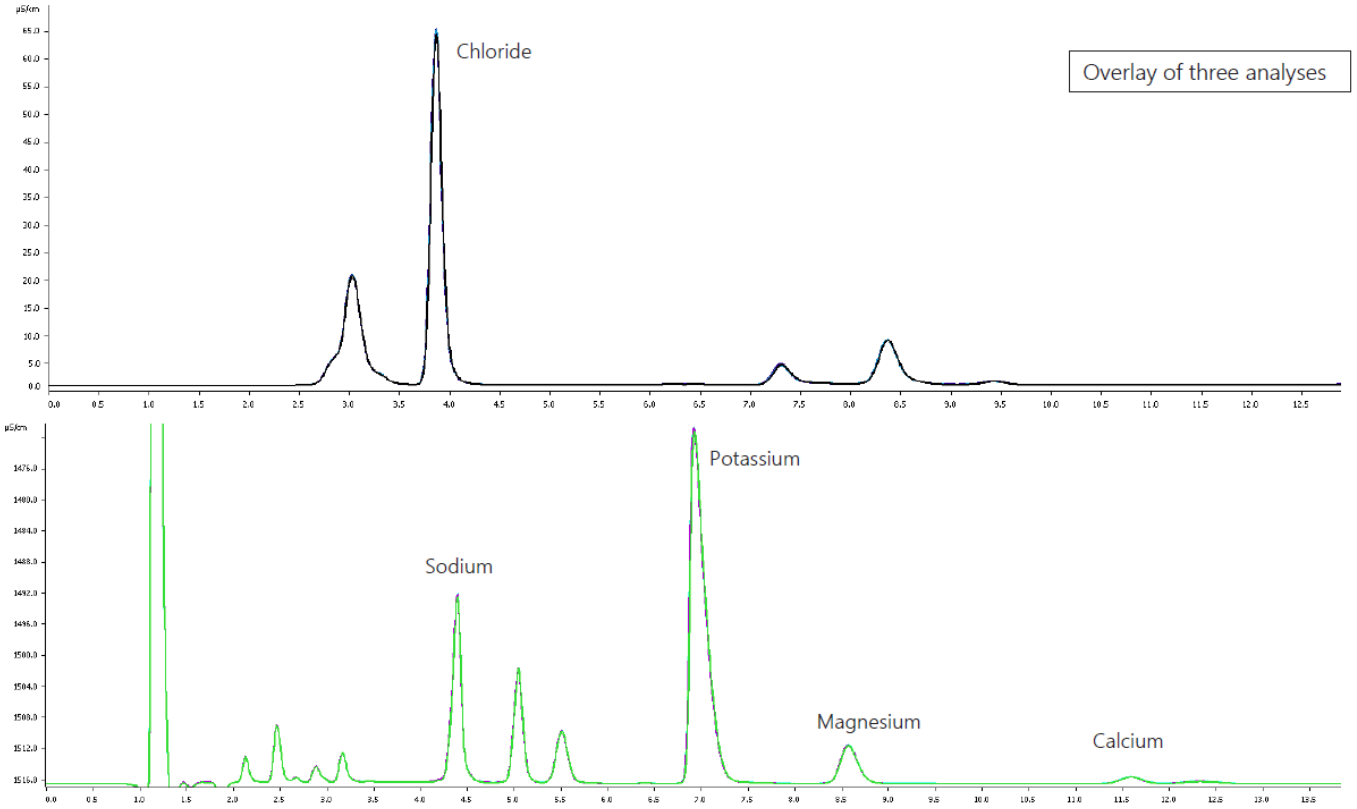
Tomato Paste #2 SPK All Concentrations in ppm	Chloride	Chloride Recovery (%)	Sodium	Sodium Recovery (%)	Dilution
Sample	3591		1464		179.67 Chloride
Matrix Spike	7254	102.1	4908	98.3	175.55 Sodium
Spike: 3589 ppm chloride; 3504 ppm sodium (raw: 19.98 ppm chloride; 19.96 ppm sodium					

Diced Tomatoes in Juice All Concentrations in ppm	Chloride	Sodium	Potassium	Magnesium	Calcium	Dilution
Replicate 1	2520	930	1740	76*	470	165.16
Replicate 2	2530	930	1750	74*	470	165.16
Replicate 3	2540	940	1740	73*	470	165.16
Average	2530	930	1740	74*	470	
RSD (%)	0.47	0.60	0.13	1.8	0.82	
*Below reporting limit of 165 ppm						

Diced Tomatoes in Juice SPK All Concentrations in ppm	Chloride	Chloride Recovery (%)	Sodium	Sodium Recovery (%)	Dilution
Sample	2577		959		222.79 Chloride
Matrix Spike	7059	101.6	4737	98.9	191.39 Sodium
Spike: 4412 ppm chloride; 3819 ppm sodium (raw: 19.80 ppm chloride; 19.95 ppm sodium					

Chromatography

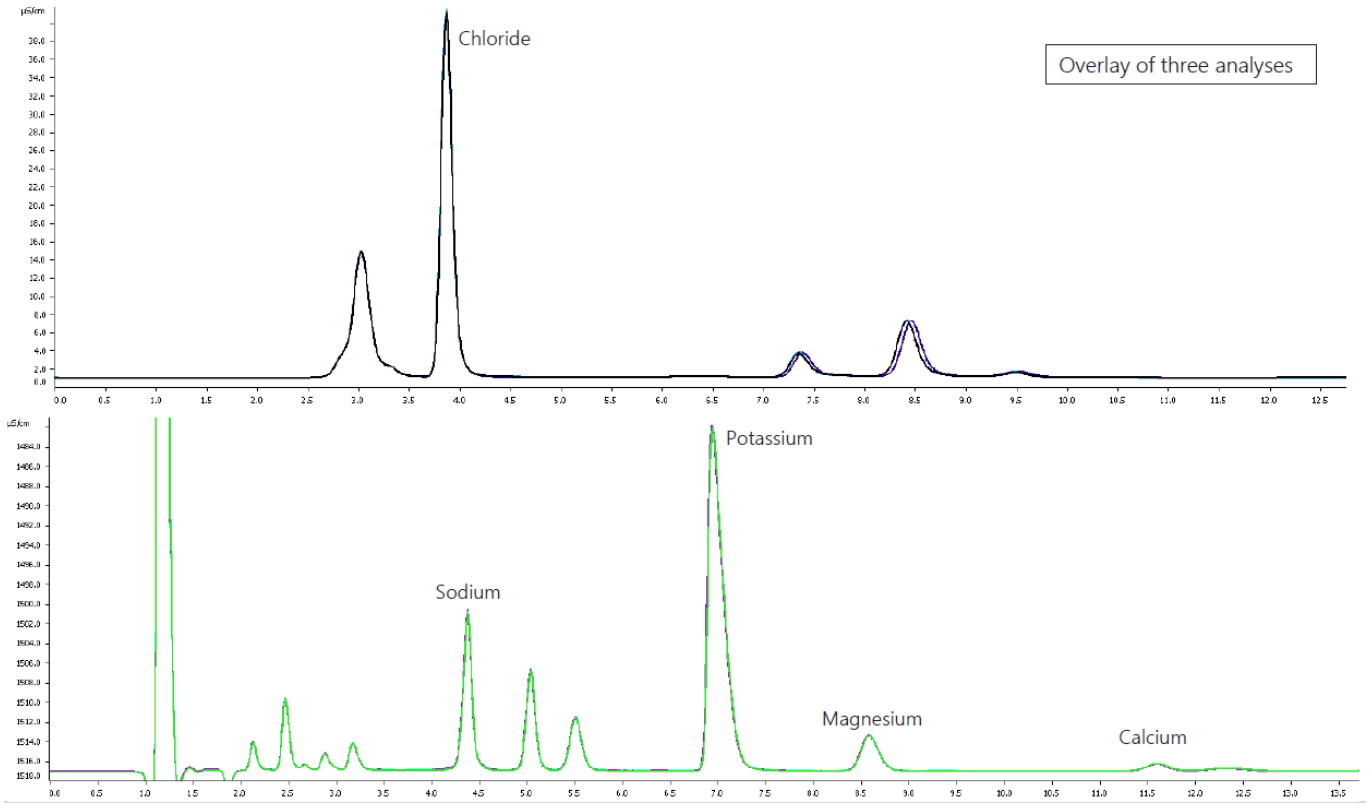
Tomato Paste #1, 0.241 g sample to 40.083 g in ultrapure water (166.32x dilution)



Tomato Paste #1 All Concentrations in ppm	Chloride	Sodium	Potassium	Magnesium	Calcium
Average	5250	2050	12,290	430	130*
RSD (%)	0.68	1.6	0.55	1.4	2.3

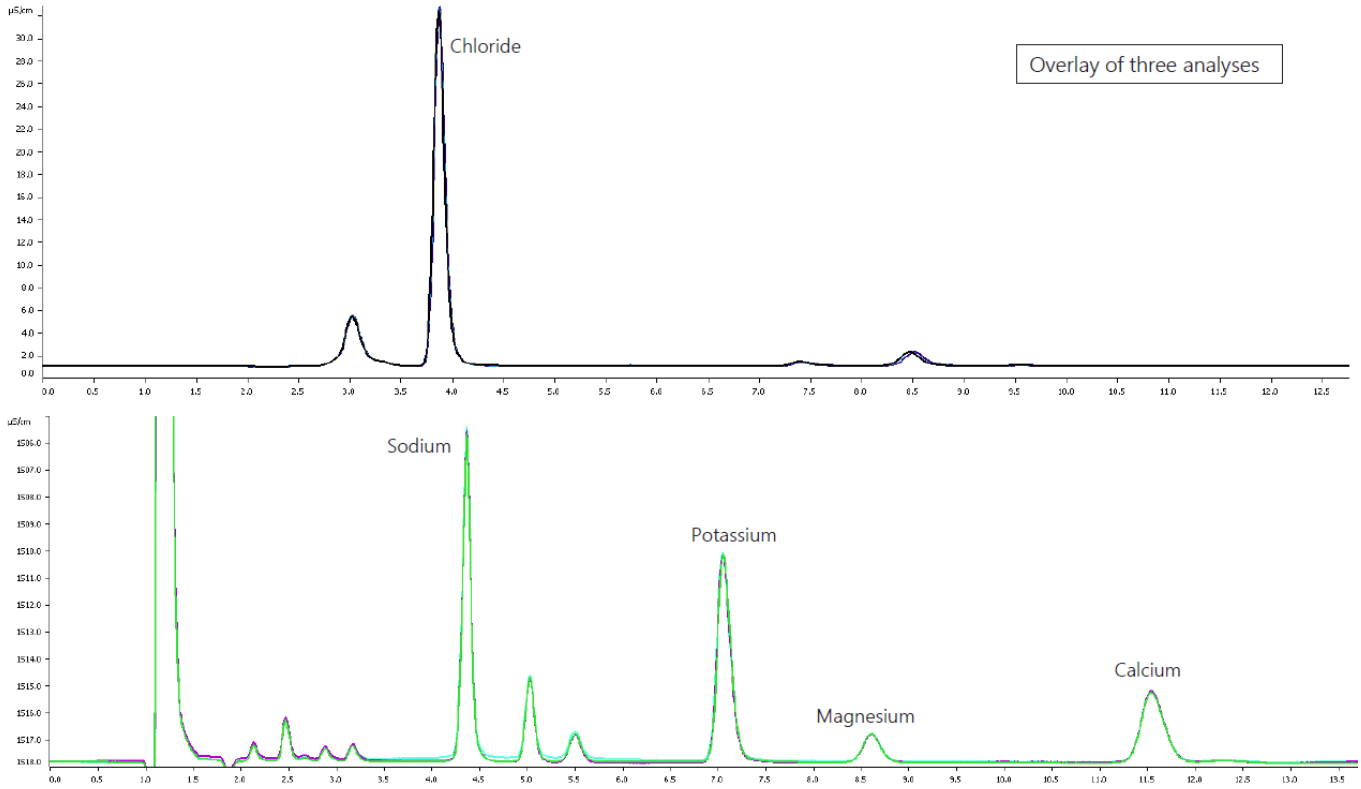
*Below reporting limit of 166 ppm

Tomato Paste #2, 0.219 g sample to 40.411 g in ultrapure water (184.53 dilution)



Tomato Paste #2 All Concentrations in ppm	Chloride	Sodium	Potassium	Magnesium	Calcium
Average	3670	1470	10,320	340	110*
RSD (%)	0.35	1.3	0.40	1.2	2.0
*Below reporting limit of 185 ppm					

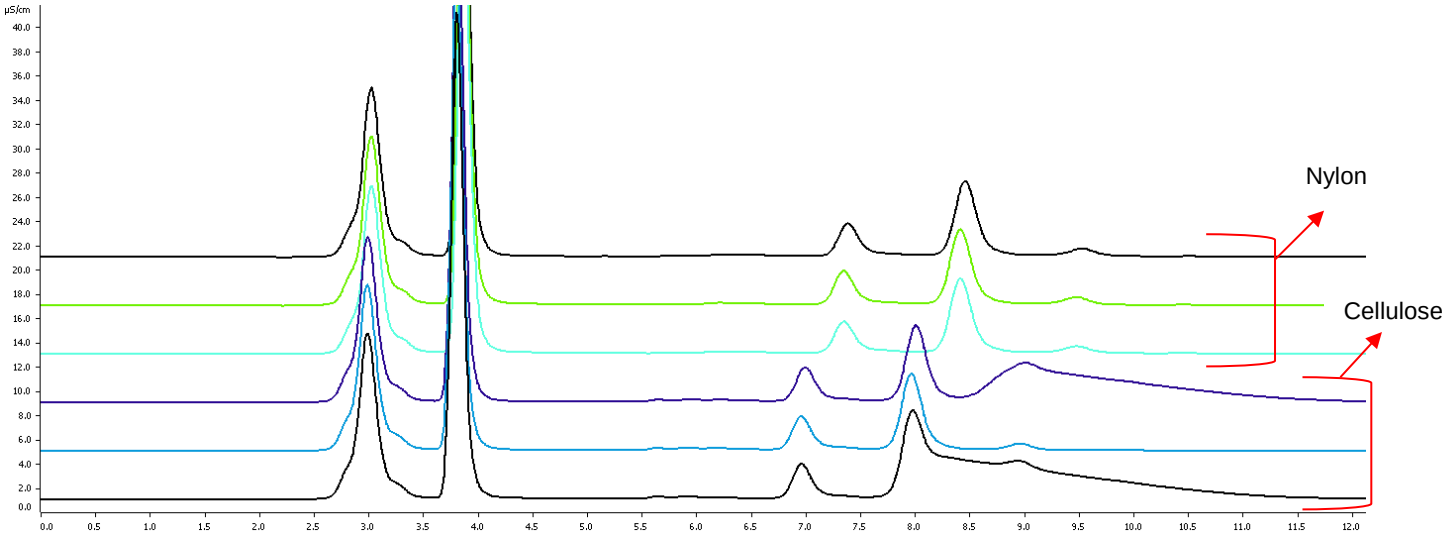
Diced Tomatoes in Juice, 0.244 g sample to 40.2990 g in ultrapure water (165.16x dilution)



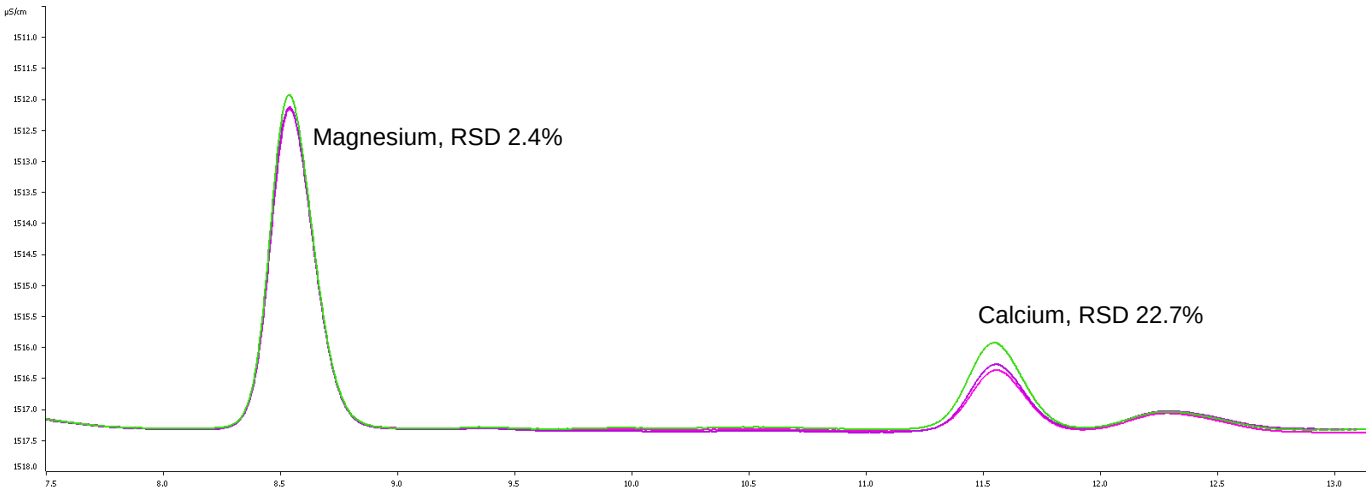
Diced Tomatoes in Juice All Concentrations in ppm	Chloride	Sodium	Potassium	Magnesium	Calcium
Average	2530	930	1740	74*	470
RSD (%)	0.47	0.60	0.13	1.8	0.82
*Below reporting limit of 165 ppm					

Ultrafiltration membrane, nylon vs. celluose acetate

Anions, Tomato Paste #2



Cations, cellulose acetate membrane, Tomato Paste #1, overlay of three injections, magnesium and calcium zoom



Cations, nylon membrane, Tomato Paste #1, overlay of three injections, magnesium and calcium zoom