Determination of Fluoride, Chloride, Bromide and Sulfate by Anion Exchange Ion Chromatography Based on EPA 300.0

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Prepared for: [redacted]

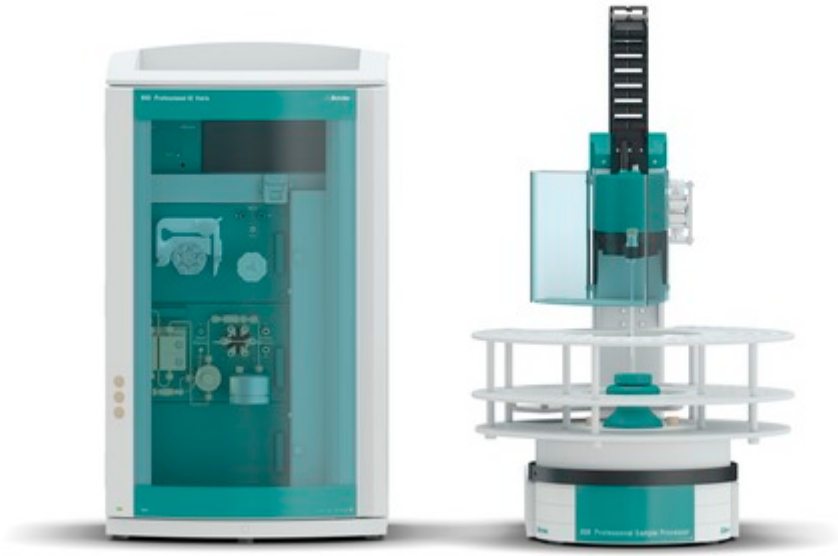
Company Confidential

Objective

- To determine fluoride, chloride, bromide and sulfate in water samples:
  - AEO1137
  - AEO1367
- To determine if UV detection is required to determine bromide in the presence of high chloride

Instrumentation

- 940 Professional IC
- 858 Autosampler
- Conductivity Detector
- UV/Vis Detector
- Dosino for Regeneration
- MSM Suppressor Rotor A
- MCS – CO_2 Suppressor
- METROSEP A Supp 5 – 250/4.0
- MagIC Net 3.3



Approach

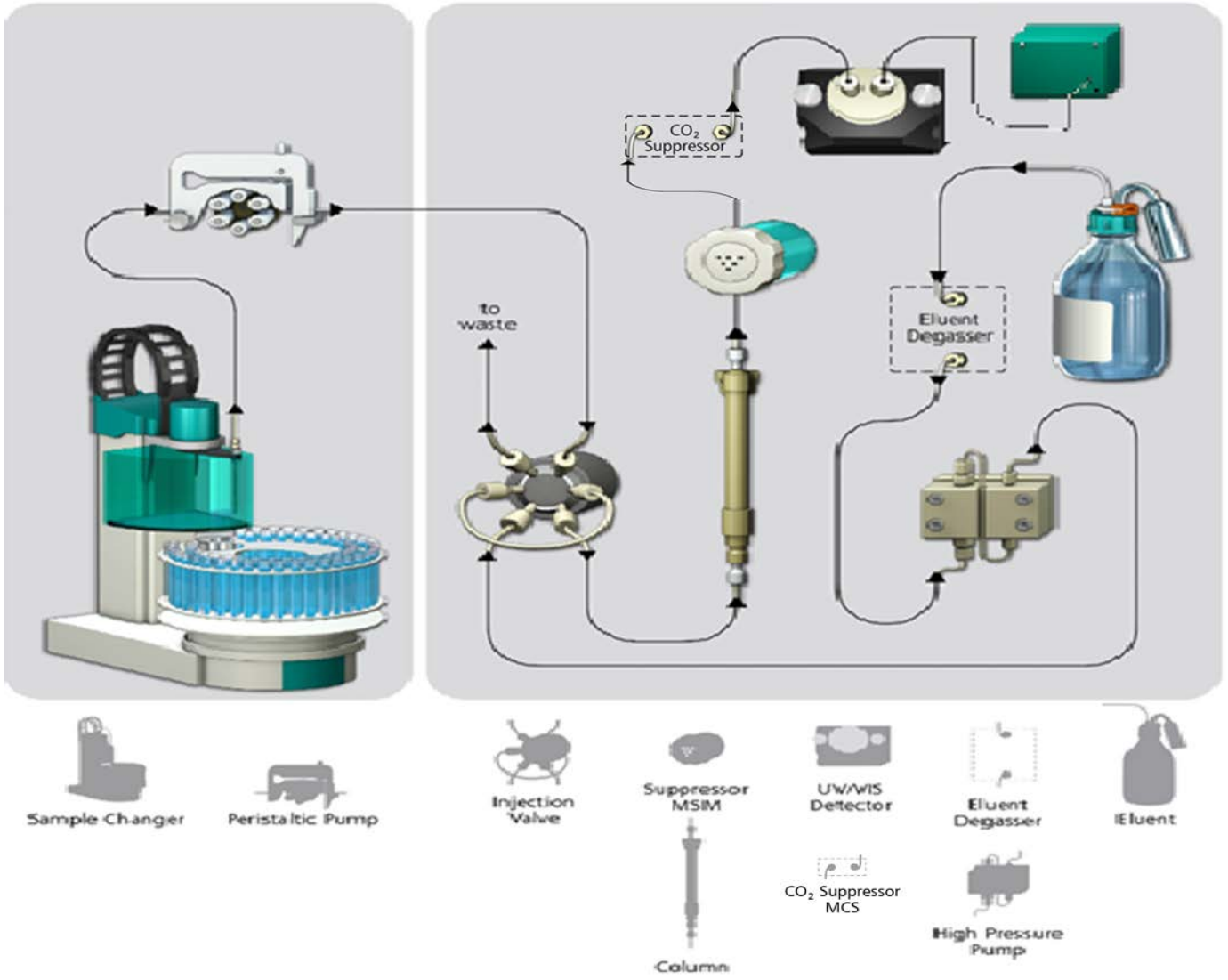
Parameter	Description
Flow	0.7 mL/min
Pressure Max	15 MPa
Loop Volume	20 µL
Column Temperature	40 °C
Eluent (in ultra pure water)	Sodium hydrogen carbonate: 1.0 mmol/L and Sodium carbonate: 3.2 mmol/L
Dosino Regenerant (in ultra pure water)	500 mM Sulfuric Acid
Blank – Ultra Pure Water	ASTM Type 1 Water - 18.2 MΩ
Run Time	40 mins

Standards, Samples and Spiked Samples

- Standards (From 1000mg/L stock of F^- ,Cl^- ,Br^- and SO_4^{2-}):
- Samples from [redacted]: 10X Dilution
- Spiked Samples
  - Spiked with Br-
- Blank – Ultra pure water (18.2 MΩ)

Metrohm

Flow Diagram- Instrument Setup



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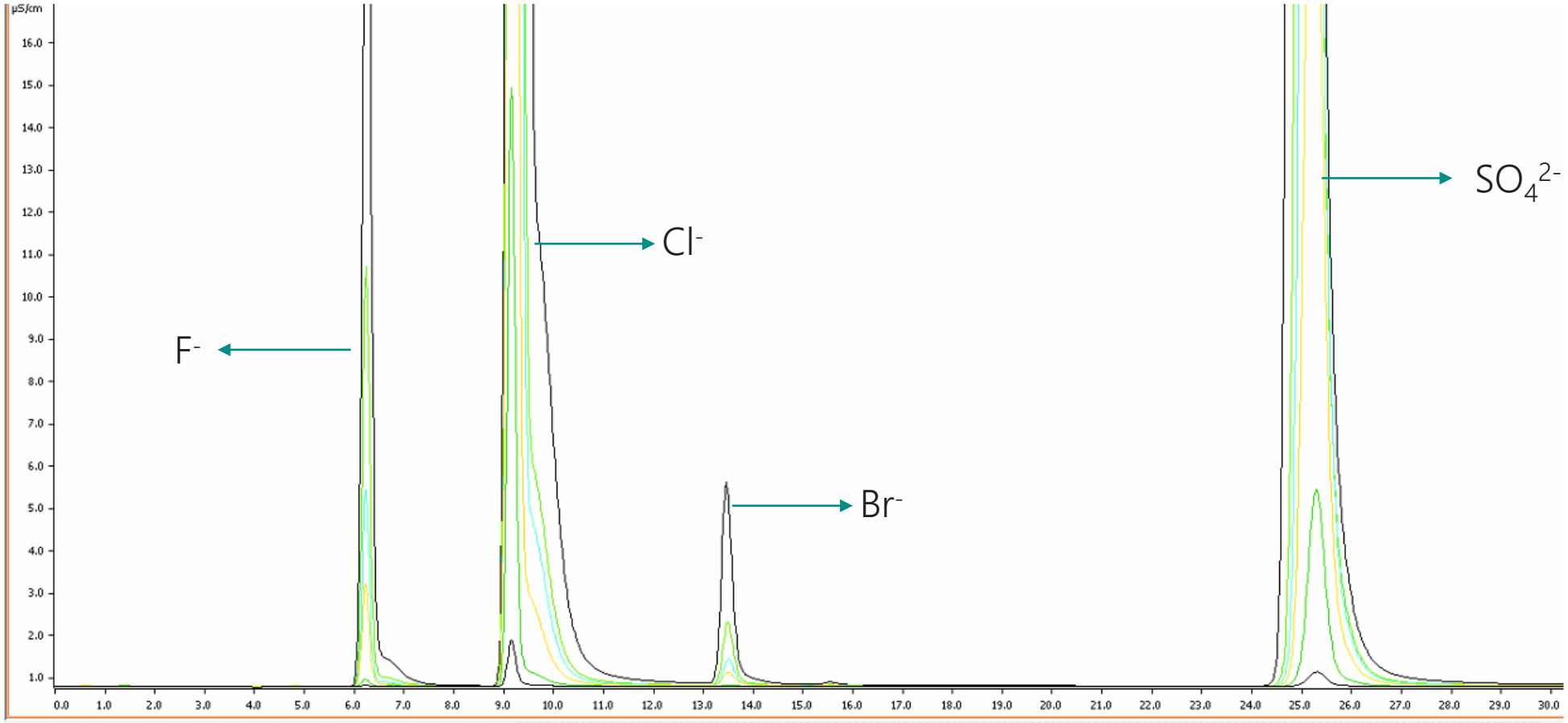
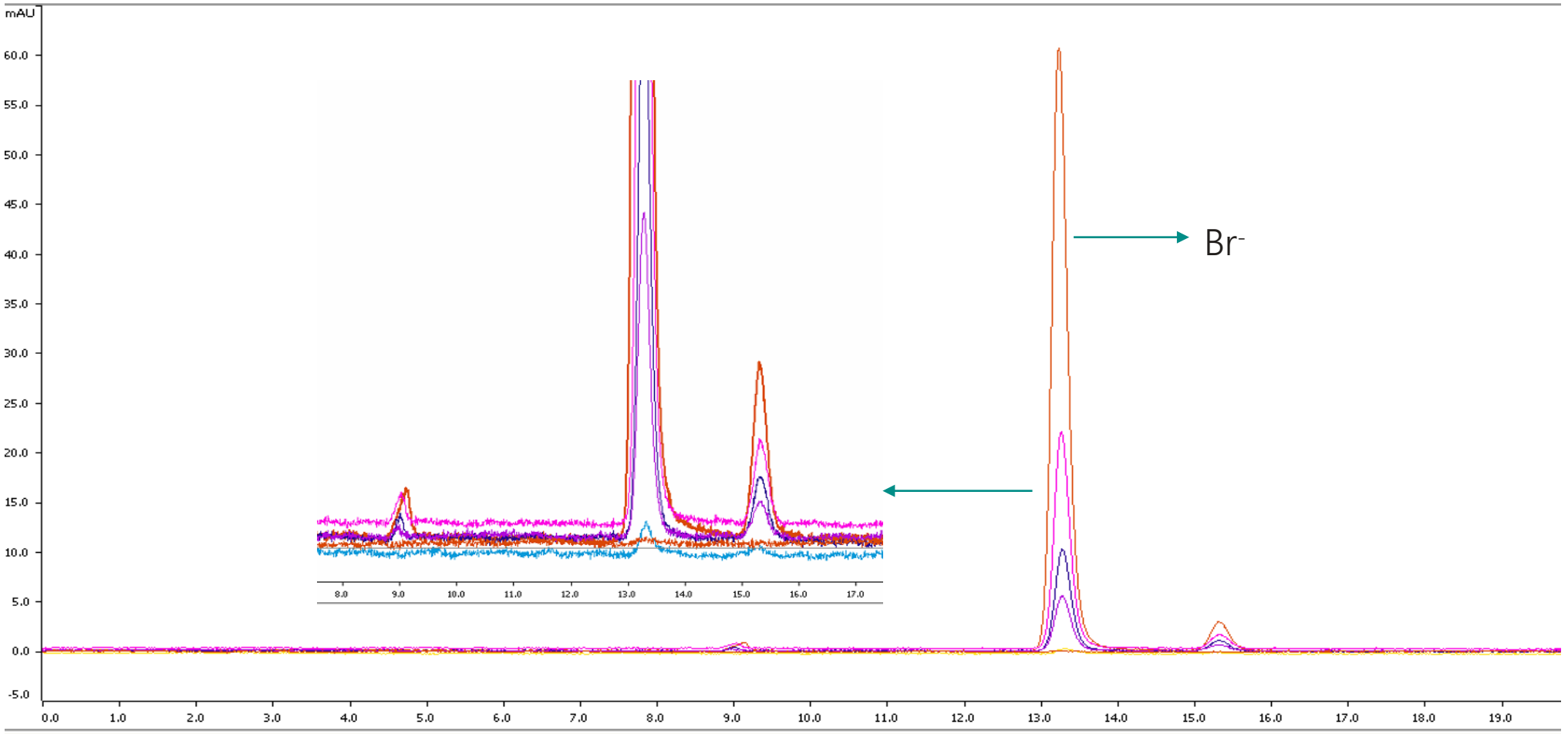
Standard Overlay Anion- Conductivity: F^-,Cl^-,Br^- and SO_4^{2-}



	Date	Number	Ident	Sample type	Volume	Dilution	Sample amount	Method	Analysis	Legend	Display
1	2020-03-09 16:55:49 UTC-4	1	Stnd 1	Standard 1	20.0	1.0	1.0		Anion		☑
2	2020-03-09 17:38:13 UTC-4	3	Stnd 2	Standard 2	20.0	1.0	1.0		Anion		☑
3	2020-03-09 18:20:37 UTC-4	5	Stnd 3	Standard 3	20.0	1.0	1.0		Anion		☑
4	2020-03-09 19:03:01 UTC-4	7	Stnd 4	Standard 4	20.0	1.0	1.0		Anion		☑
5	2020-03-09 19:45:26 UTC-4	9	Stnd 5	Standard 5	20.0	1.0	1.0		Anion		☑
6	2020-03-09 20:27:50 UTC-4	11	Stnd 6	Standard 6	20.0	1.0	1.0		Anion		☑

Standard Overlay Anion- UV/Vis: Br^-



Standard 1	20.0	1.0	1.0	[redacted]	UV Vis
Standard 2	20.0	1.0	1.0		UV Vis
Standard 3	20.0	1.0	1.0		UV Vis
Standard 4	20.0	1.0	1.0		UV Vis
Standard 5	20.0	1.0	1.0		UV Vis
Standard 6	20.0	1.0	1.0		UV Vis

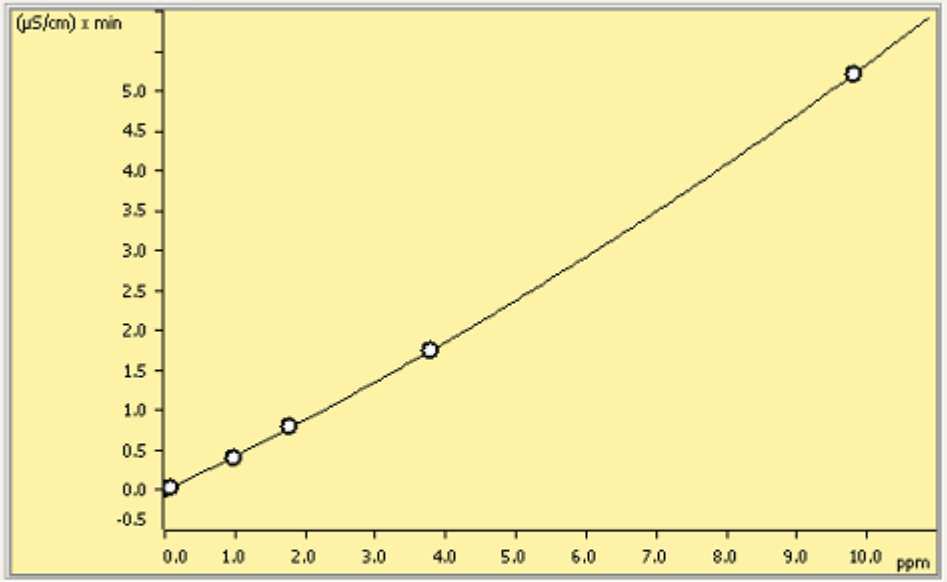
Standard: F-

Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve

Component: Fluoride



Function: A = - 4.21364E-3 + 0.0209160 × Q + 2.88916E-5 × Q²

Relative standard deviation	0.672%
Correlation coefficient	0.999994
Curve type	Quadratic
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used
1	Standard 1	1	0.0096	20.0	1.0	1.0	0.0032	Stnd 1	2020-03-09 16:55:49 UTC-4	☑
2	Standard 2	1	0.0949	20.0	1.0	1.0	0.0323	Stnd 2	2020-03-09 17:38:13 UTC-4	☑
3	Standard 3	1	0.9767	20.0	1.0	1.0	0.4072	Stnd 3	2020-03-09 18:20:37 UTC-4	☑
4	Standard 4	1	1.7809	20.0	1.0	1.0	0.7895	Stnd 4	2020-03-09 19:03:01 UTC-4	☑
5	Standard 5	1	3.7897	20.0	1.0	1.0	1.7427	Stnd 5	2020-03-09 19:45:26 UTC-4	☑
6	Standard 6	1	9.8161	20.0	1.0	1.0	5.2160	Stnd 6	2020-03-09 20:27:50 UTC-4	☑

Metrohm

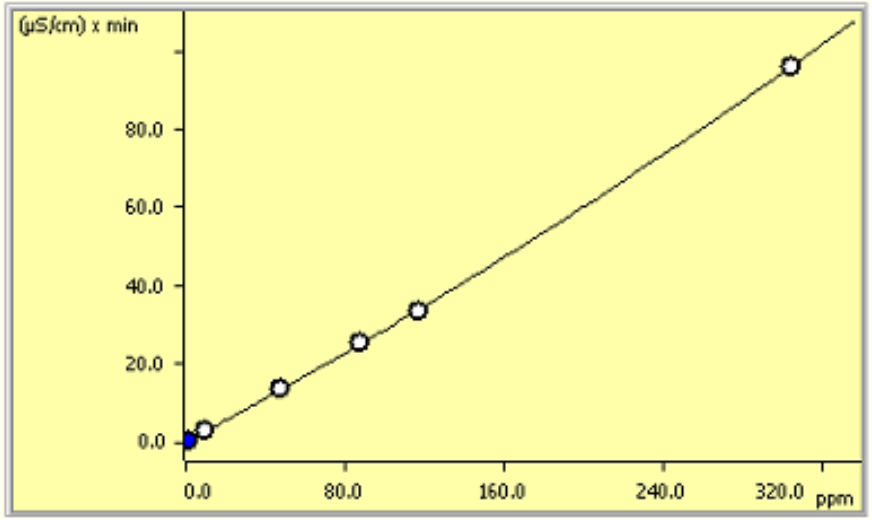
Standard: Cl-

Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve

Component: Chloride



Function: A = 0.0804965 + 0.0135832 × Q + 3.59954E-7 × Q²

Relative standard deviation	0.864%
Correlation coefficient	0.999985
Curve type	Quadratic
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used
1	Standard 1	1	0.9488	20.0	1.0	1.0	0.2330	Stnd 1	2020-03-09 16:55:49 UTC-4	☑
2	Standard 2	1	9.5667	20.0	1.0	1.0	2.6250	Stnd 2	2020-03-09 17:38:13 UTC-4	☑
3	Standard 3	1	47.8495	20.0	1.0	1.0	13.6925	Stnd 3	2020-03-09 18:20:37 UTC-4	☑
4	Standard 4	1	87.6424	20.0	1.0	1.0	25.1265	Stnd 4	2020-03-09 19:03:01 UTC-4	☑
5	Standard 5	1	116.8749	20.0	1.0	1.0	33.5360	Stnd 5	2020-03-09 19:45:26 UTC-4	☑
6	Standard 7	1	304.0237	20.0	1.0	1.0	96.0022	Stnd 7	2020-03-11 11:24:49 UTC-4	☑

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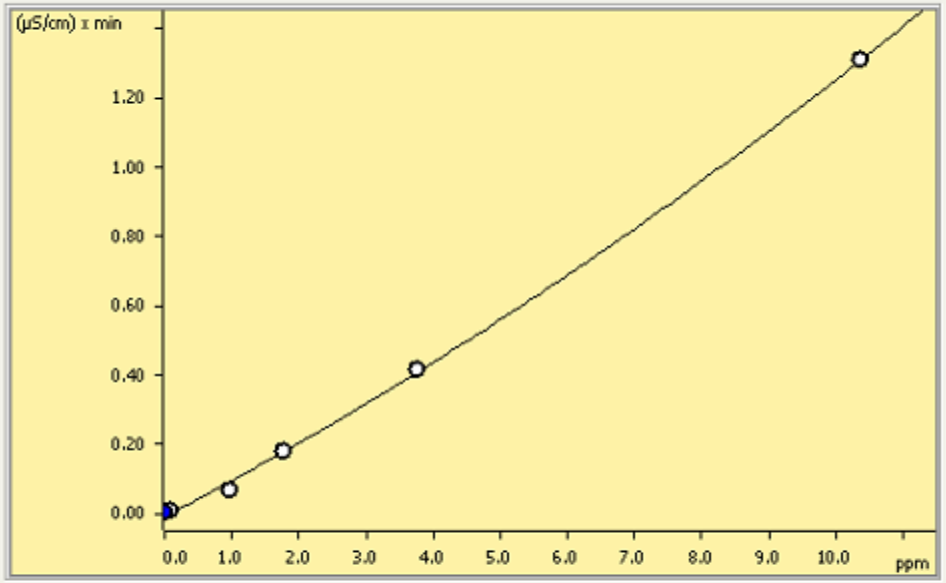
Standard: Br^- (Conductivity)

Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve

Component: Bromide



Function: A = - 9.18104E-3 + 5.06659E-3 × Q + 6.20349E-6 × Q²

Relative standard deviation	4.947%
Correlation coefficient	0.999684
Curve type	Quadratic
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used
▶ 1	Standard 1	1	0.0096	20.0	1.0	1.0	0.0009	Stnd 1	2020-03-09 16:55:49 UTC-4	☑
2	Standard 2	1	0.0946	20.0	1.0	1.0	0.0077	Stnd 2	2020-03-09 17:38:13 UTC-4	☑
3	Standard 3	1	0.9732	20.0	1.0	1.0	0.0674	Stnd 3	2020-03-09 18:20:37 UTC-4	☑
4	Standard 4	1	1.7745	20.0	1.0	1.0	0.1794	Stnd 4	2020-03-09 19:03:01 UTC-4	☑
5	Standard 5	1	3.7760	20.0	1.0	1.0	0.4169	Stnd 5	2020-03-09 19:45:26 UTC-4	☑
6	Standard 6	1	10.3645	20.0	1.0	1.0	1.3067	Stnd 6	2020-03-09 20:27:50 UTC-4	☑

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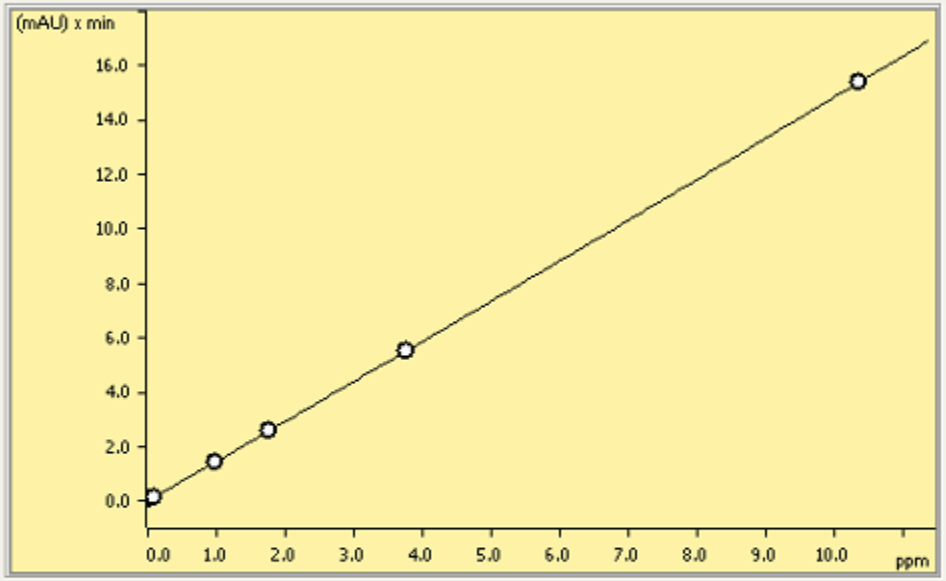
Standard: Br^- (UV/Vis)- Quadratic Fit

Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve

Component: Bromide



Function: A = 0.0204240 + 0.0722580 × Q + 8.64061E-6 × Q²

Relative standard deviation	0.473%
Correlation coefficient	0.999997
Curve type	Quadratic
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used
1	Standard 1	1	0.0096	20.0	1.0	1.0	0.0396	Stnd 1	2020-03-09 16:55:49 UTC-4	☑
2	Standard 2	1	0.0946	20.0	1.0	1.0	0.1355	Stnd 2	2020-03-09 17:38:13 UTC-4	☑
3	Standard 3	1	0.9732	20.0	1.0	1.0	1.4411	Stnd 3	2020-03-09 18:20:37 UTC-4	☑
4	Standard 4	1	1.7745	20.0	1.0	1.0	2.6142	Stnd 4	2020-03-09 19:03:01 UTC-4	☑
5	Standard 5	1	3.7760	20.0	1.0	1.0	5.5120	Stnd 5	2020-03-09 19:45:26 UTC-4	☑
6	Standard 6	1	10.3645	20.0	1.0	1.0	15.3714	Stnd 6	2020-03-09 20:27:50 UTC-4	☑

Metrohm

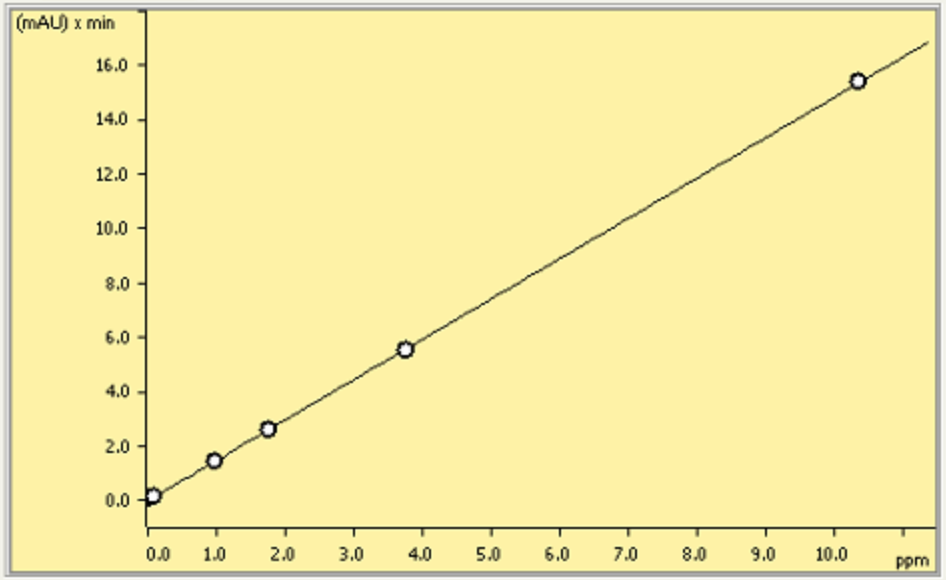
Standard: Br^- (UV/Vis)- Linear Fit

Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve

Component: Bromide



Function: A = - 0.0101520 + 0.0740771 × Q

Relative standard deviation	1.020%
Correlation coefficient	0.999979
Curve type	Linear
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used
▶ 1	Standard 1	1	0.0096	20.0	1.0	1.0	0.0396	Stnd 1	2020-03-09 16:55:49 UTC-4	☑
2	Standard 2	1	0.0946	20.0	1.0	1.0	0.1355	Stnd 2	2020-03-09 17:38:13 UTC-4	☑
3	Standard 3	1	0.9732	20.0	1.0	1.0	1.4411	Stnd 3	2020-03-09 18:20:37 UTC-4	☑
4	Standard 4	1	1.7745	20.0	1.0	1.0	2.6142	Stnd 4	2020-03-09 19:03:01 UTC-4	☑
5	Standard 5	1	3.7760	20.0	1.0	1.0	5.5120	Stnd 5	2020-03-09 19:45:26 UTC-4	☑
6	Standard 6	1	10.3645	20.0	1.0	1.0	15.3714	Stnd 6	2020-03-09 20:27:50 UTC-4	☑

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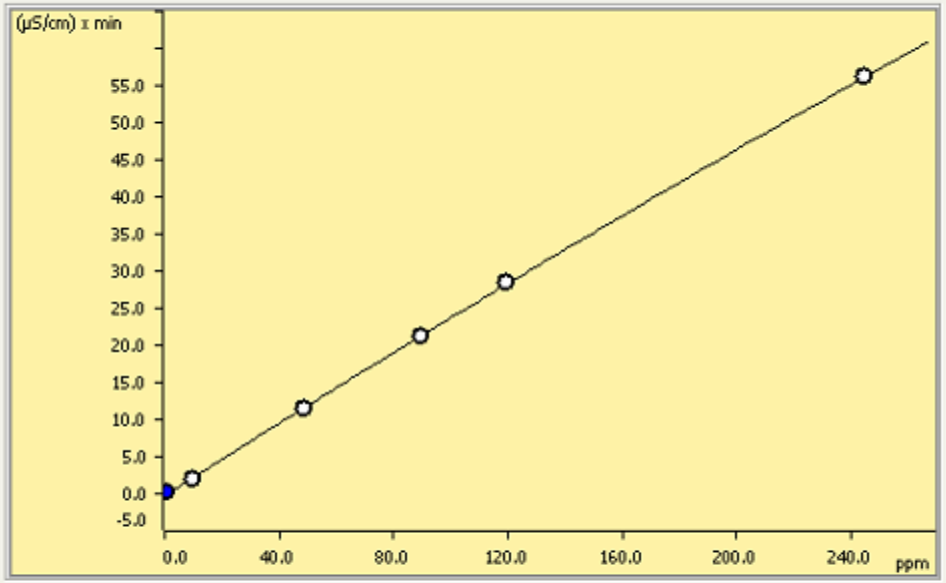
Standard: SO_4^{2-}

Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve

Component: Sulfate



Function: A = - 0.257749 + 0.0122702× Q - 1.54893E-7× Q²

Relative standard deviation	0.977%
Correlation coefficient	0.999974
Curve type	Quadratic
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date	Used
▶ 1	Standard 1	1	0.9702	20.0	1.0	1.0	0.1598	Stnd 1	2020-03-09 16:55:49 UTC-4	☑
2	Standard 2	1	9.7823	20.0	1.0	1.0	2.0512	Stnd 2	2020-03-09 17:38:13 UTC-4	☑
3	Standard 3	1	48.9280	20.0	1.0	1.0	11.3973	Stnd 3	2020-03-09 18:20:37 UTC-4	☑
4	Standard 4	1	89.6177	20.0	1.0	1.0	21.2024	Stnd 4	2020-03-09 19:03:01 UTC-4	☑
5	Standard 5	1	119.5091	20.0	1.0	1.0	28.3584	Stnd 5	2020-03-09 19:45:26 UTC-4	☑
6	Standard 6	1	244.9382	20.0	1.0	1.0	56.1057	Stnd 6	2020-03-09 20:27:50 UTC-4	☑

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Sample - Summary F-,Cl-,Br- and SO_4^{2-}

Sample	Anions	Average Concentration (ppm)	% RSD (X3)
AEO1137	F-	0.0758	0.3044
	Cl-	45.1158	0.0539
	Br-	0.3929	0.2333
	SO_4-	65.8285	0.0148
	UV Br-	0.3334	2.1762
AEO1367	F-	0.3159	0.4275
	Cl-	293.0159	0.1709
	Br-	1.9921	0.0100
	SO_4-	7.5737	0.0374
	UV Br-	1.9884	0.2481

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Sample AEO1137: F-,Cl-,Br- and SO_4^{2-}

Results

Anion

Component name	Retention time [min]	Height [µS/cm]	Area [(µS/cm) x min]	Concentration [ppm]	Resolution
Fluoride	6.22	0.143	0.0276	0.0760	0.912
Chloride	9.17	65.931	12.8530	45.0737	11.643
Bromide	13.50	0.104	0.0310	0.3931	4.291
Sulfate	25.19	33.363	15.6303	65.8366	invalid

UV Vis

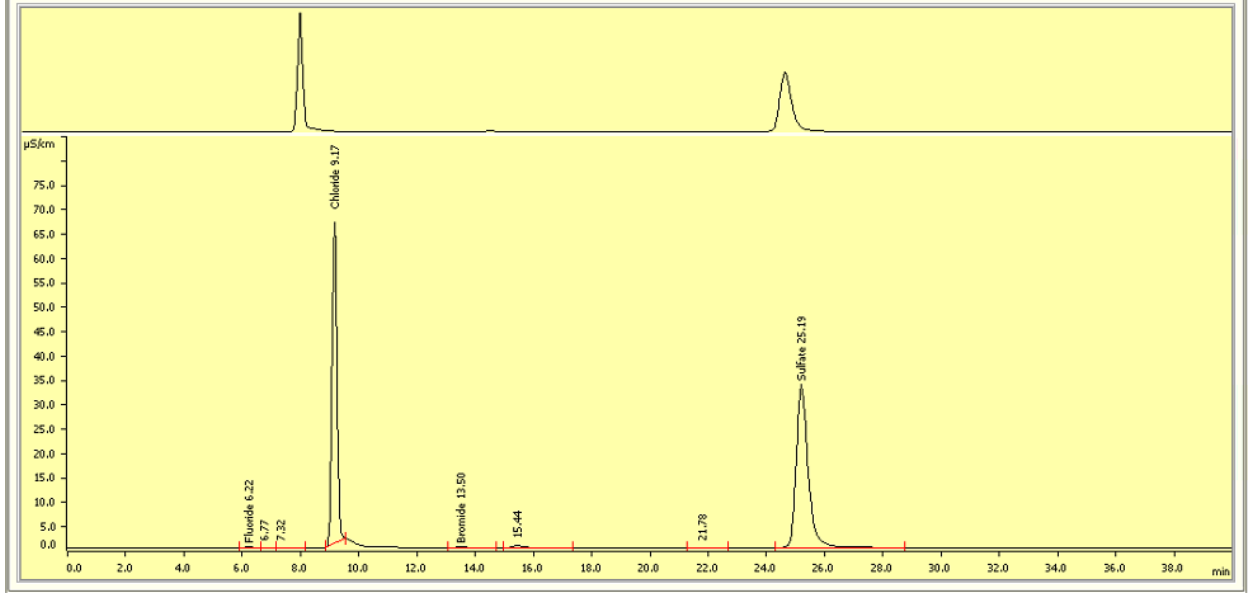
Component name	Retention time [min]	Height [mAU]	Area [(mAU) x min]	Concentration [ppm]	Resolution
Bromide	13.28	1.918	0.4881	0.3234	4.669

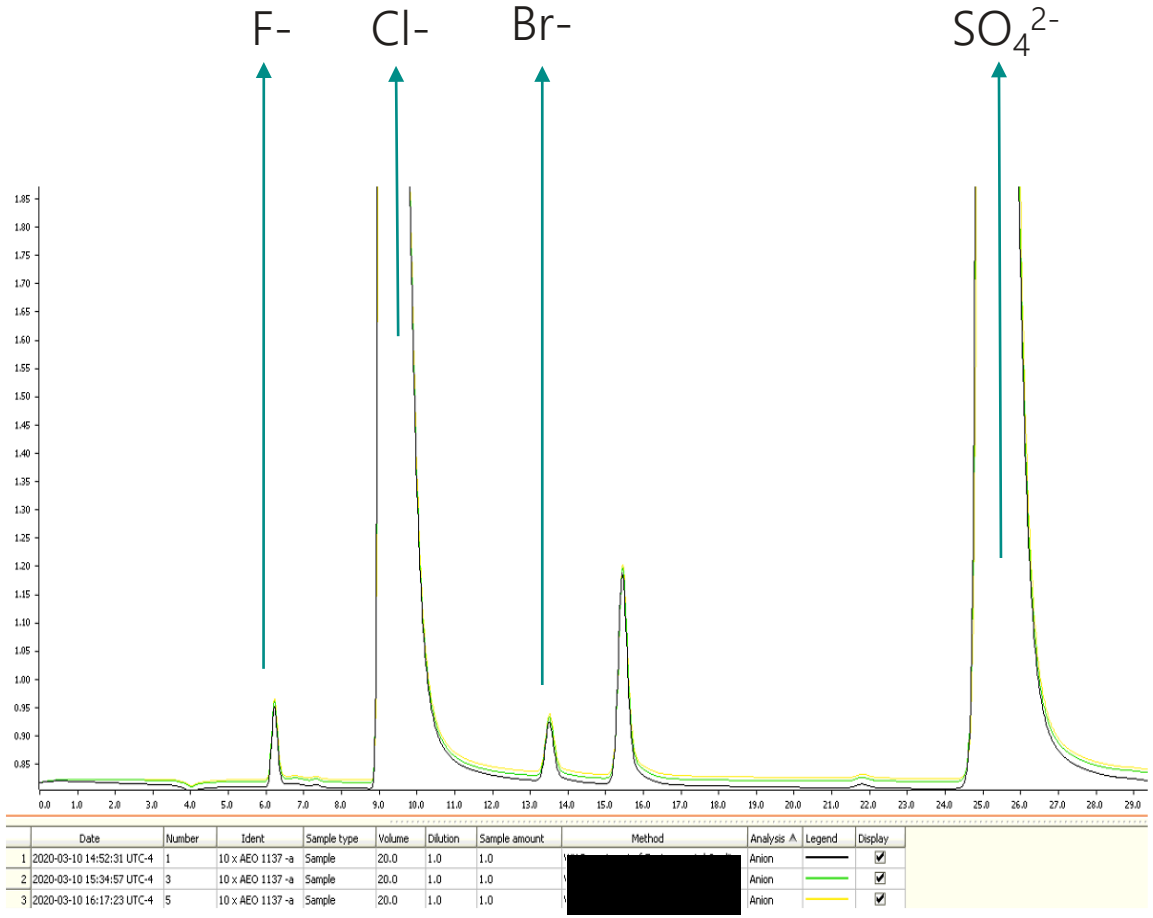
Chromatograms

Anion | UV Vis

Chromatogram / Calibration curve — Chromatogram

5.78 min
3.85 µS/cm





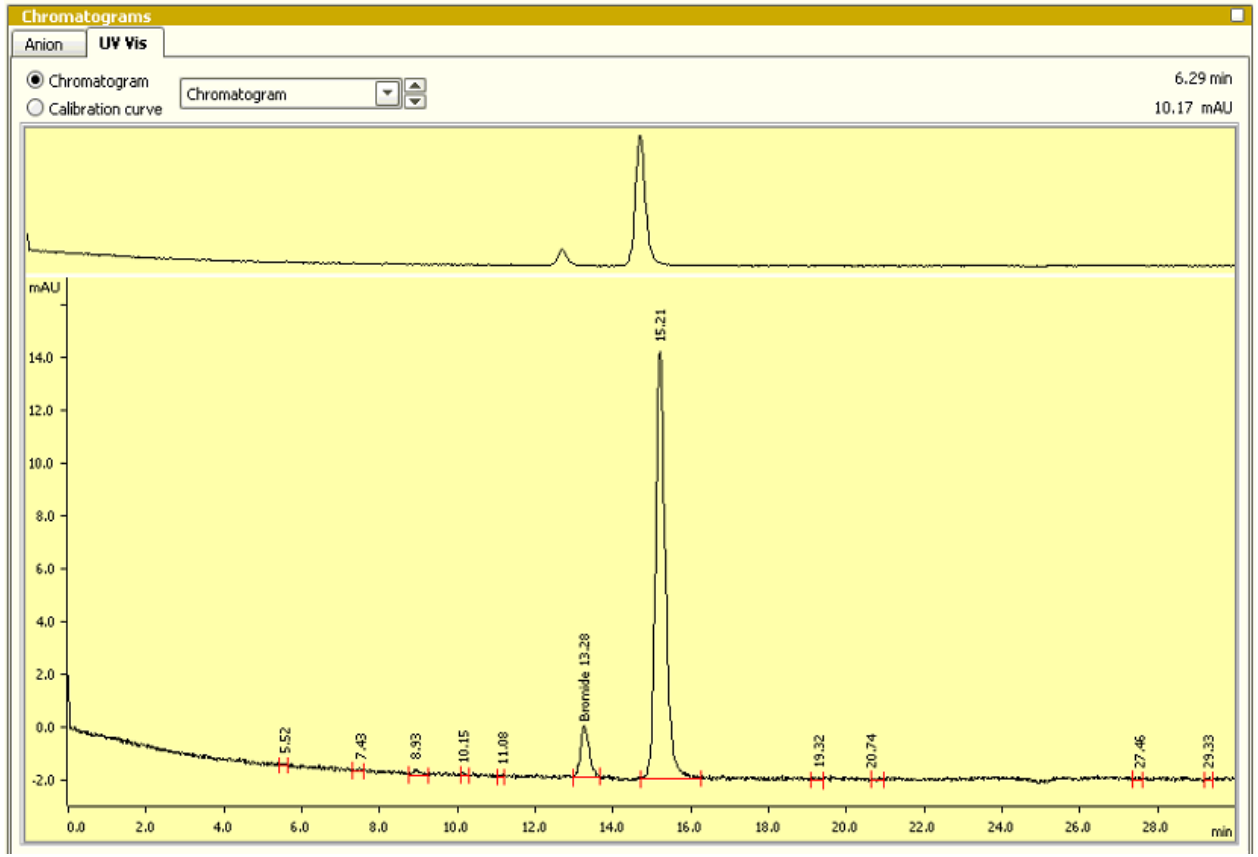
	Date	Number	Ident	Sample type	Volume	Dilution	Sample amount	Method	Analysis	Legend	Display
1	2020-03-10 14:52:31 UTC-4	1	10 x AEO 1137 -a	Sample	20.0	1.0	1.0	[redacted]	Anion		☑
2	2020-03-10 15:34:57 UTC-4	3	10 x AEO 1137 -a	Sample	20.0	1.0	1.0		Anion		☑
3	2020-03-10 16:17:23 UTC-4	5	10 x AEO 1137 -a	Sample	20.0	1.0	1.0		Anion		☑

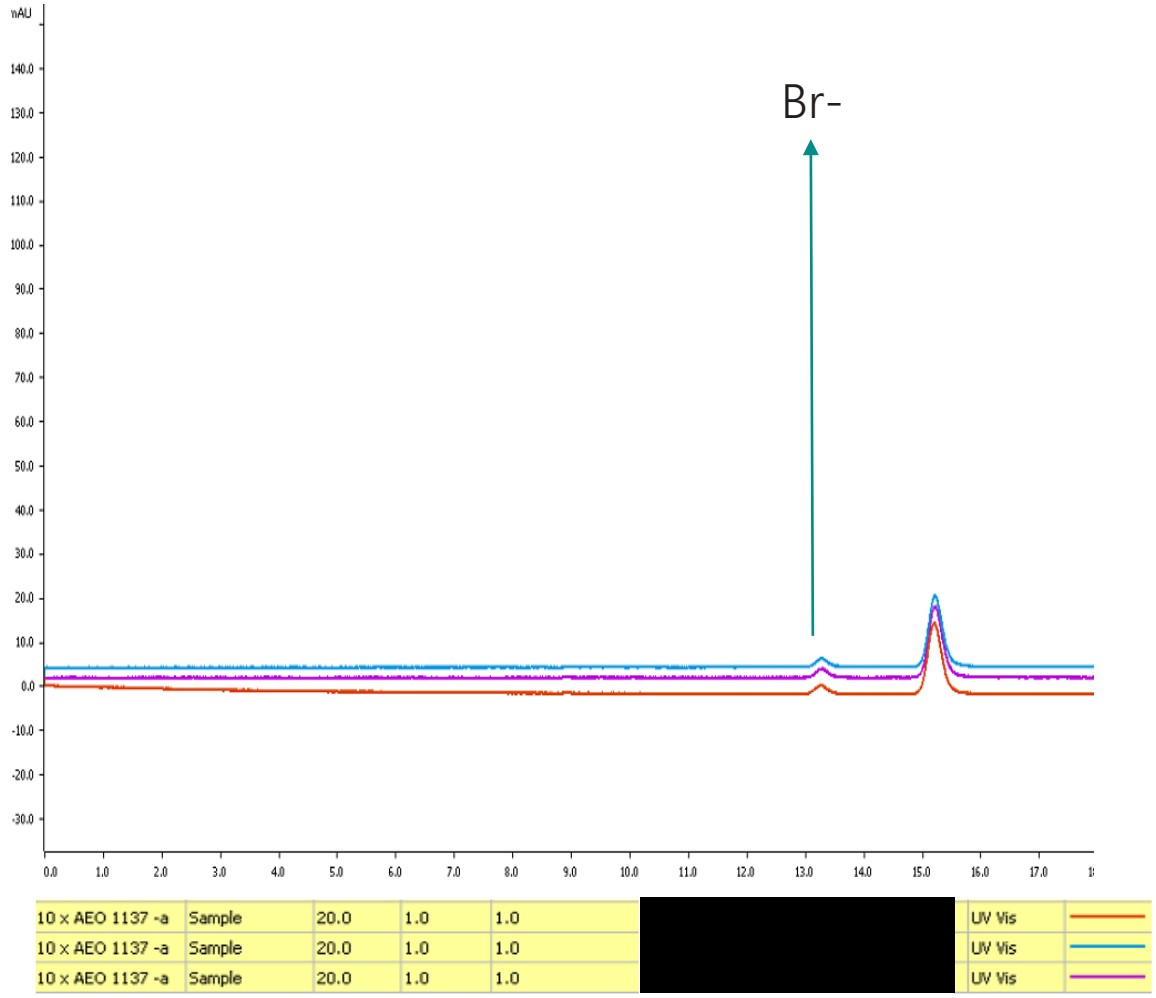
Metrohm

Sample AEO1137: Br- (UV/Vis)

UV Vis

Component name	Retention time [min]	Height [mAU]	Area [(mAU) x min]	Concentration [ppm]	Resolution
Bromide	13.28	1.918	0.4881	0.3234	4.669





Sample AEO1367: F-,Cl-,Br- and SO_4^{2-}

Results

Results

Anion

Component name	Retention time [min]	Height [µS/cm]	Area [(µS/cm) x min]	Concentration [ppm]	Resolution
Fluoride	6.22	0.709	0.1285	0.3145	1.524
Chloride	9.36	263.064	85.3069	293.5901	9.108
Bromide	13.51	0.745	0.2025	1.9923	15.285
Sulfate	25.33	3.561	1.5979	7.5759	4.922

UV Vis

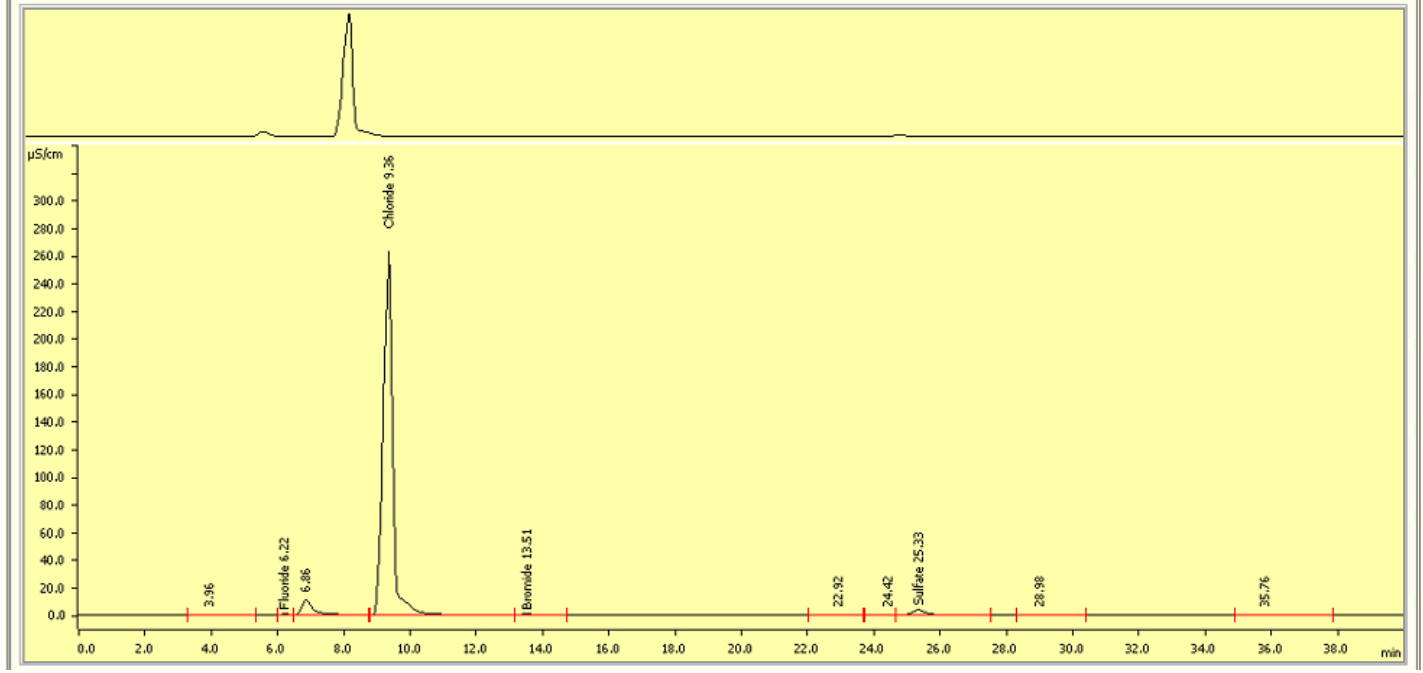
Component name	Retention time [min]	Height [mAU]	Area [(mAU) x min]	Concentration [ppm]	Resolution
Bromide	13.29	11.595	2.9043	1.9861	5.752

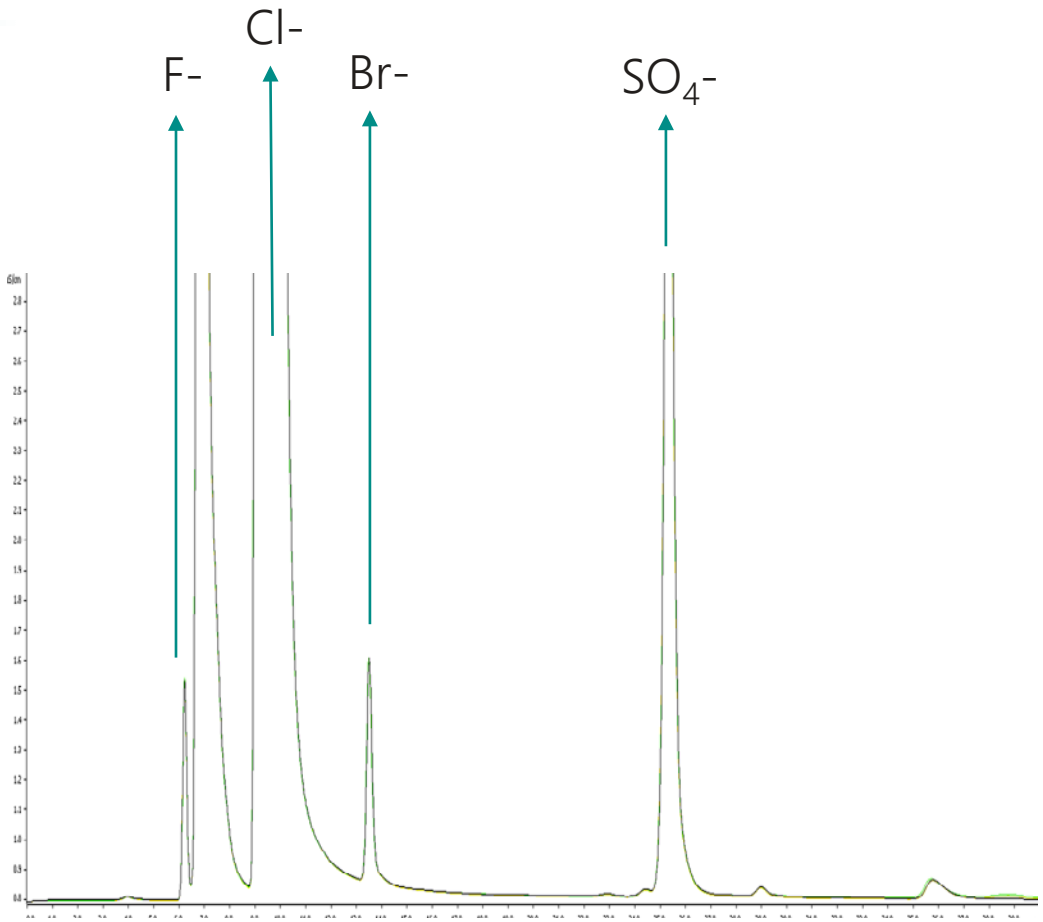
Chromatograms

Anion | UV Vis

Chromatogram
Calibration curve
Chromatogram

21.09 min
-3.21 µS/cm



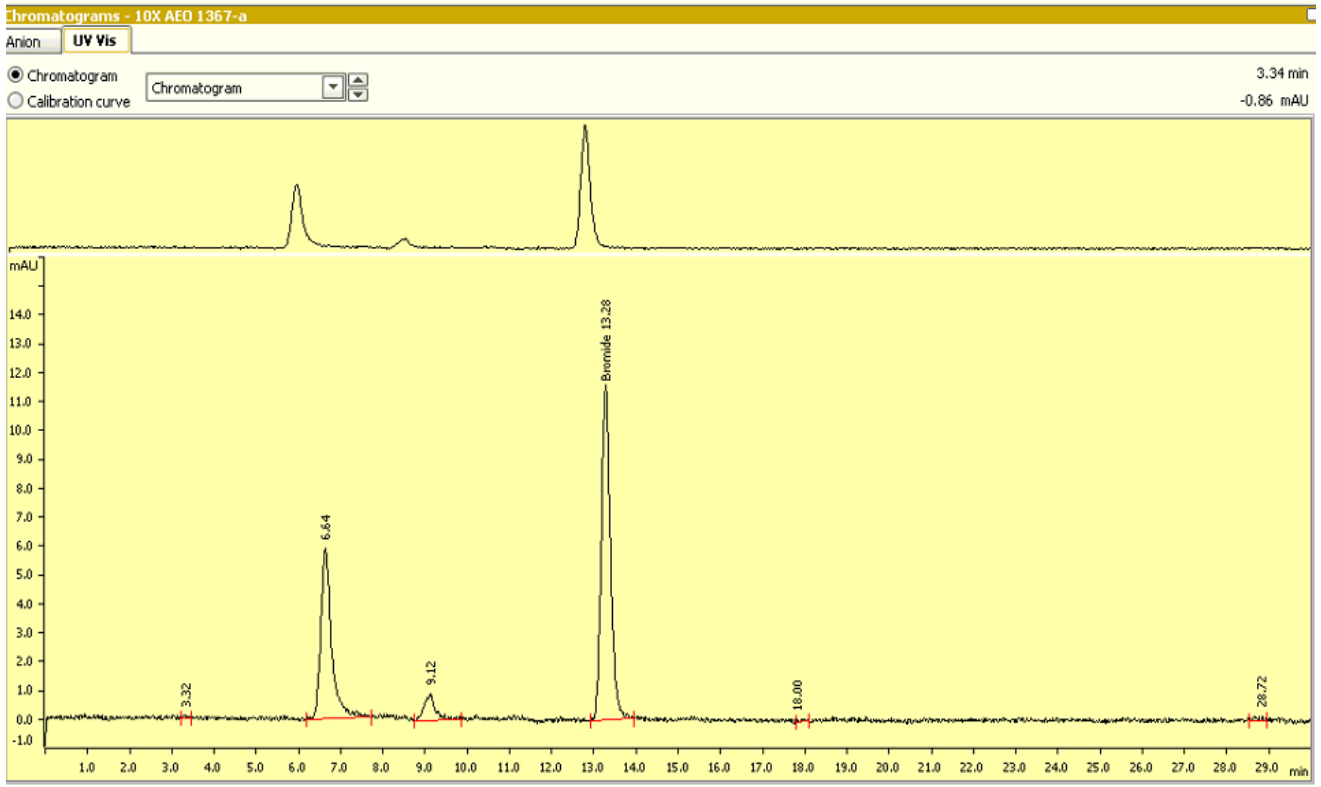


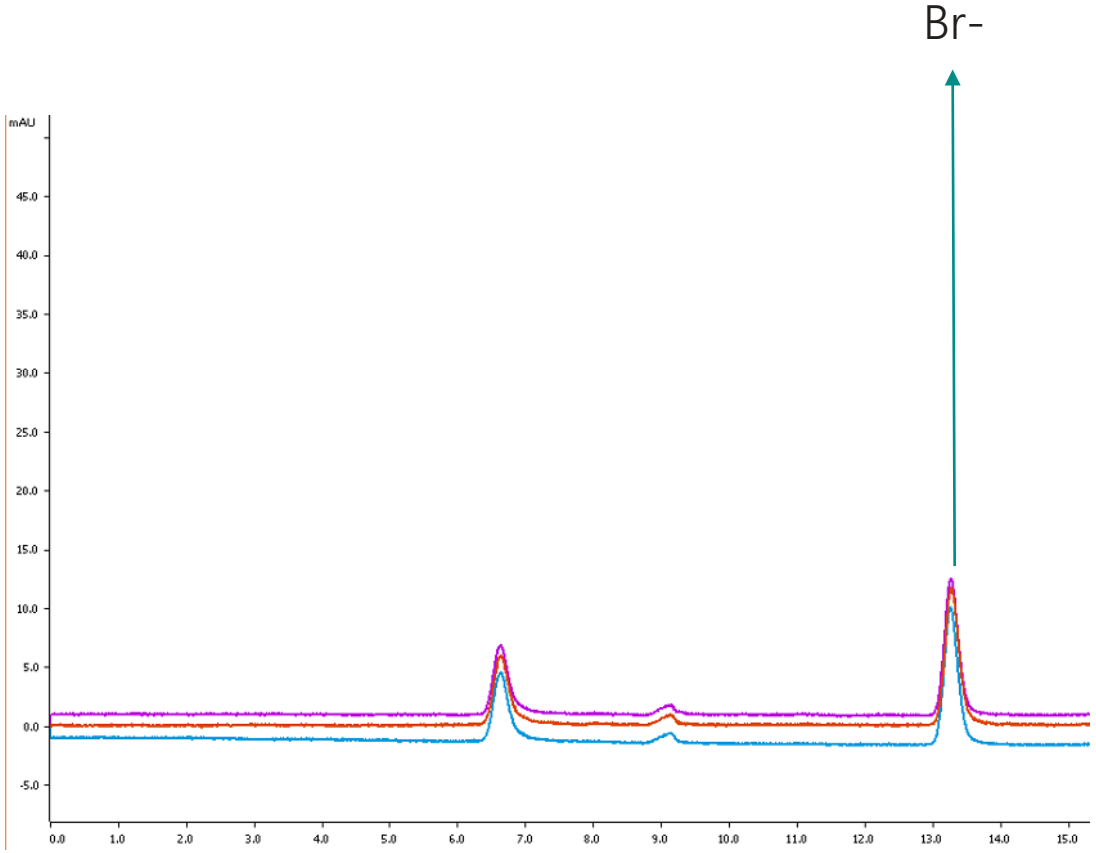
Metrohm

Sample AEO1137: Br- (UV/Vis)

UV Vis

Component name	Retention time [min]	Height [mAU]	Area [(mAU) x min]	Concentration [ppm]	Resolution
Bromide	13.28	11.594	2.9028	1.9851	15.111





Sample Spike - Summary

$$\left(\frac{(Concentration\ of\ Spiked\ Sample - Concentration\ of\ Sample)}{Concentration\ added}\right) \times 100\%$$

Sample (Conductivity)	Anions	Conc. of Spike (Ave in ppm)	Conc. of Sample (Ave in ppm)	Conc. of Added (Ave in ppm)	% Recovery
AEO1137	Br-	5.1378	0.3929	4.7620	99.6412
AEO1367	Br-	6.7939	1.9921	4.7820	100.4141

Sample (UV/Vis)	Anions	Conc. of Spike (Ave in ppm)	Conc. of Sample (Ave in ppm)	Conc. of Added (Ave in ppm)	% Recovery
AEO1137	Br-	5.0561	0.3438	4.7620	98.9574
AEO1367	Br-	6.6815	1.9884	4.7820	98.1403

All samples were spiked with 5 ppm of Br-

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Conclusion

- Ability to detect F-,Cl-,Br- and SO_4^{2-} in samples
  - Shows repeatability through RSD values

- % Recovery for spiked samples at 5 ppm were excellent
  - Br- within 90-100% for both conductivity and UV detection