



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



Sylvia Singh, Ph.D.

Anne Shearow, Ph.D.

Prepared for:

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 – CO₂ Suppressor
- METROSEP A Supp 5 – 250/4.0
- MagIC Net 3.3



Chromatographic Conditions

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

Standards & Samples

1. Standards:

- From 1000mg/L stock of F⁻, Cl⁻, Br⁻ and SO₄²⁻)

2. Samples:

- 10X Dilution

3. Spiked Samples

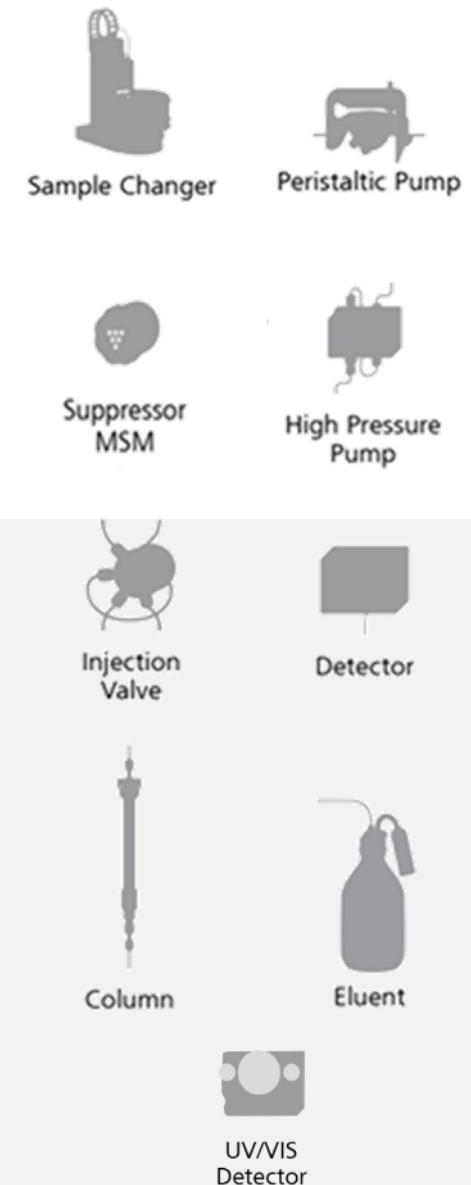
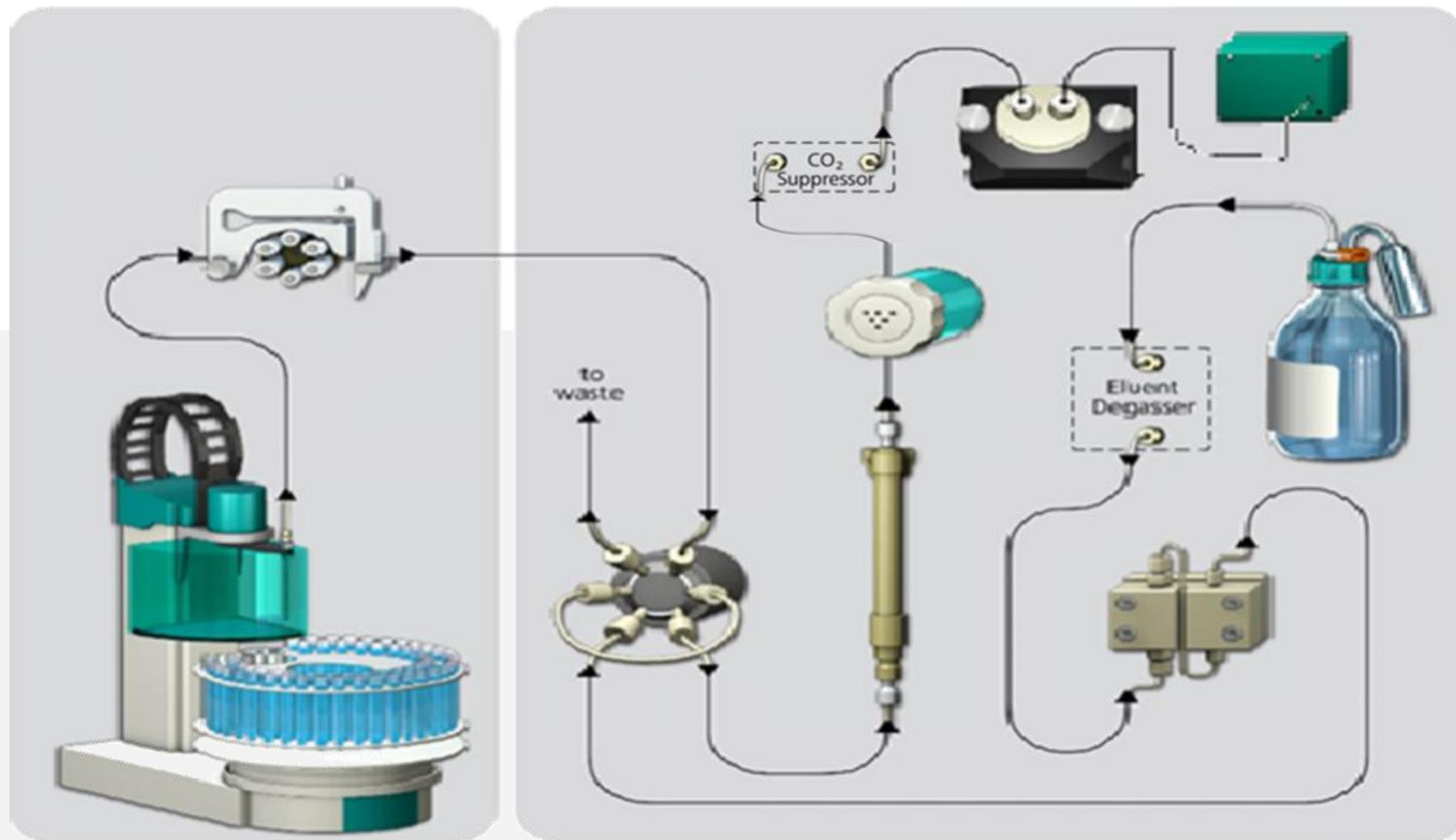
- Spiked with Br⁻

4. Blank:

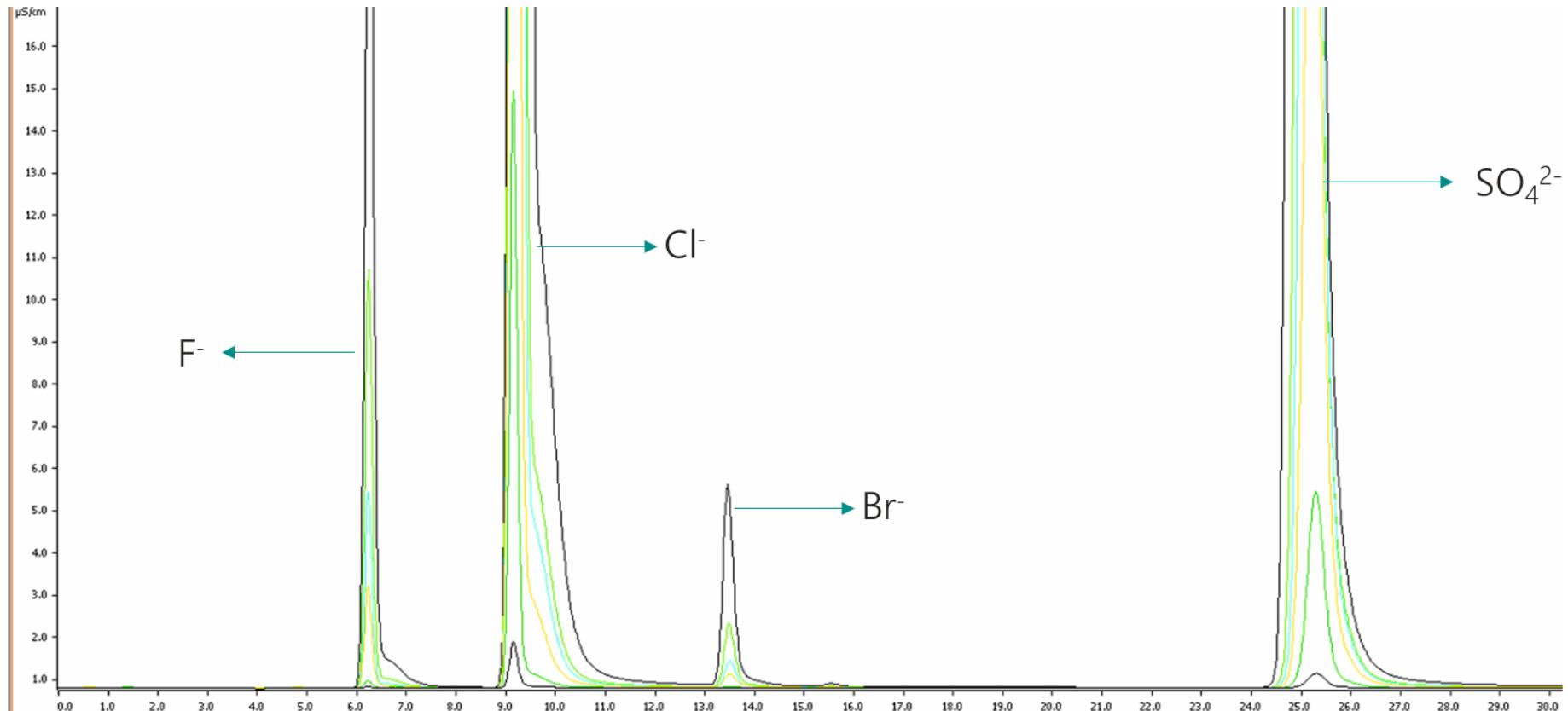
- Ultra pure water (18.2 MΩ)



Flow Diagram- Instrument Setup

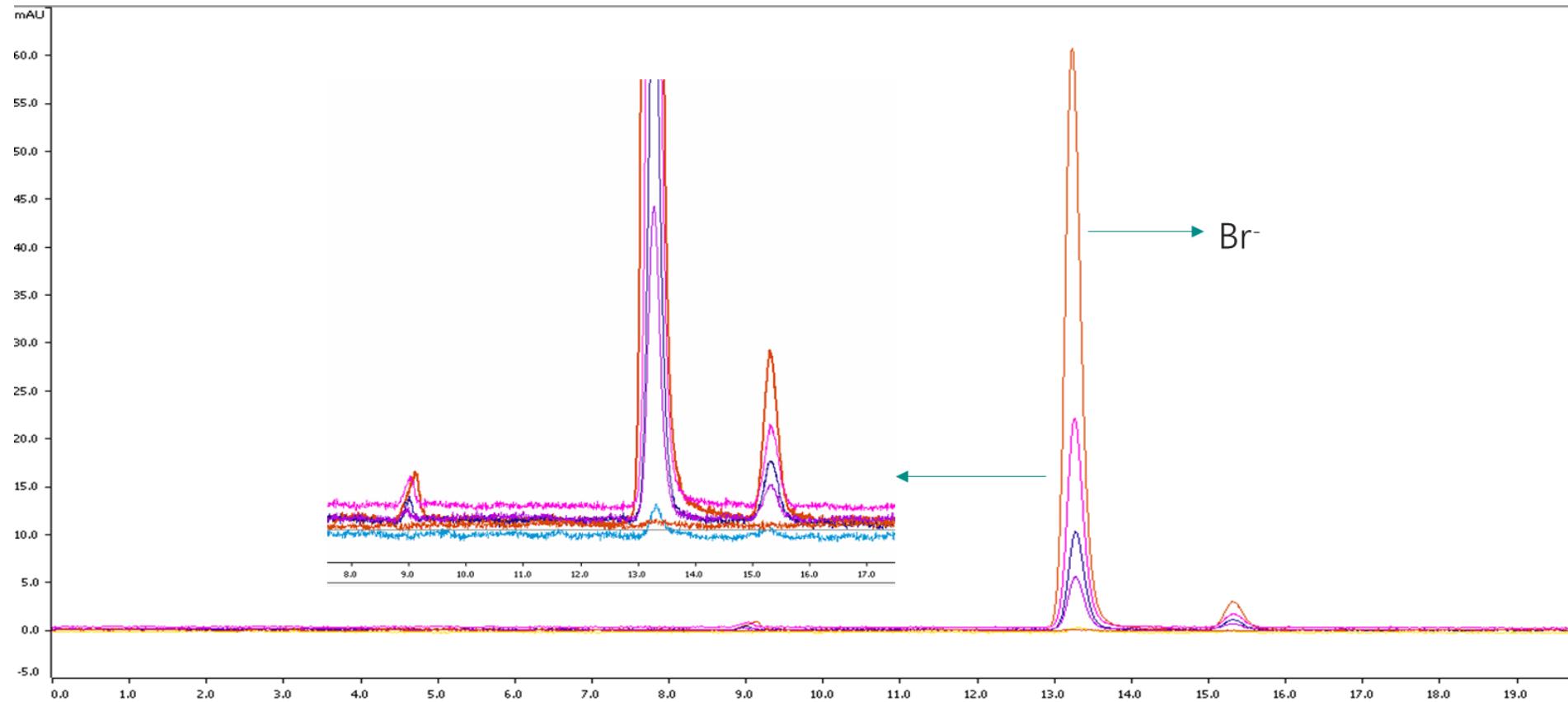


Standard Overlay Anion- UV/Vis: Br-



	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	—	<input checked="" type="checkbox"/>
2	2020-03-09 17:38:13 UTC-4	3	Stnd 2	Standard 2	20.0	1.0	1.0		Anion	—	<input checked="" type="checkbox"/>
3	2020-03-09 18:20:37 UTC-4	5	Stnd 3	Standard 3	20.0	1.0	1.0		Anion	—	<input checked="" type="checkbox"/>
4	2020-03-09 19:03:01 UTC-4	7	Stnd 4	Standard 4	20.0	1.0	1.0		Anion	—	<input checked="" type="checkbox"/>
5	2020-03-09 19:45:26 UTC-4	9	Stnd 5	Standard 5	20.0	1.0	1.0		Anion	—	<input checked="" type="checkbox"/>
6	2020-03-09 20:27:50 UTC-4	11	Stnd 6	Standard 6	20.0	1.0	1.0		Anion	—	<input checked="" type="checkbox"/>

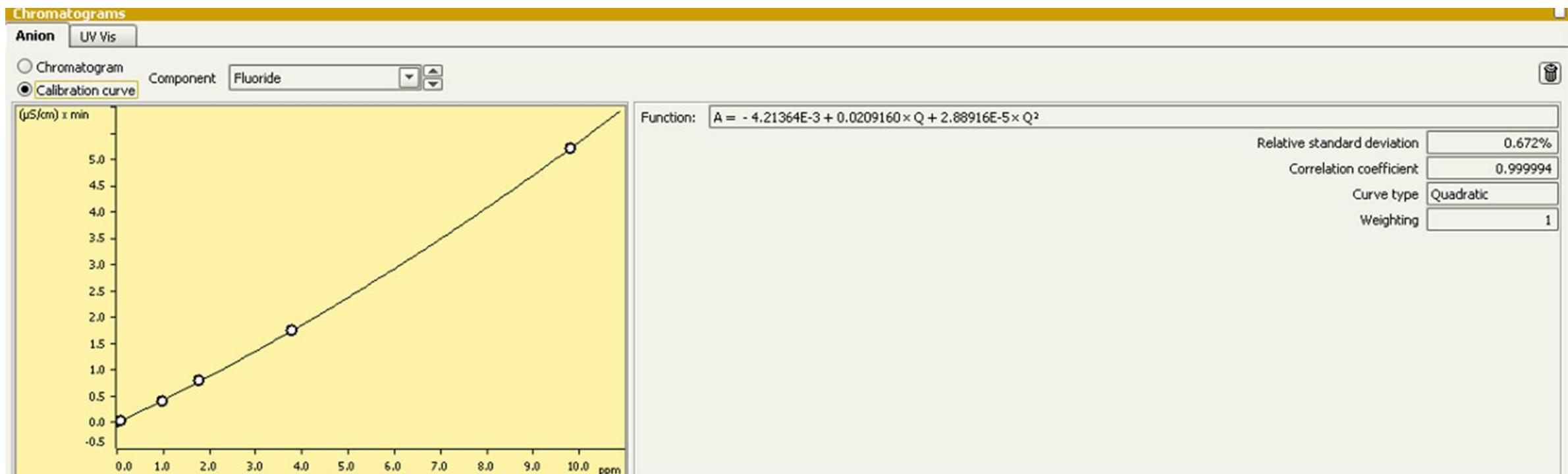
Standard Overlay Anion- Conductivity



Standard 1	20.0	1.0	1.0
Standard 2	20.0	1.0	1.0
Standard 3	20.0	1.0	1.0
Standard 4	20.0	1.0	1.0
Standard 5	20.0	1.0	1.0
Standard 6	20.0	1.0	1.0

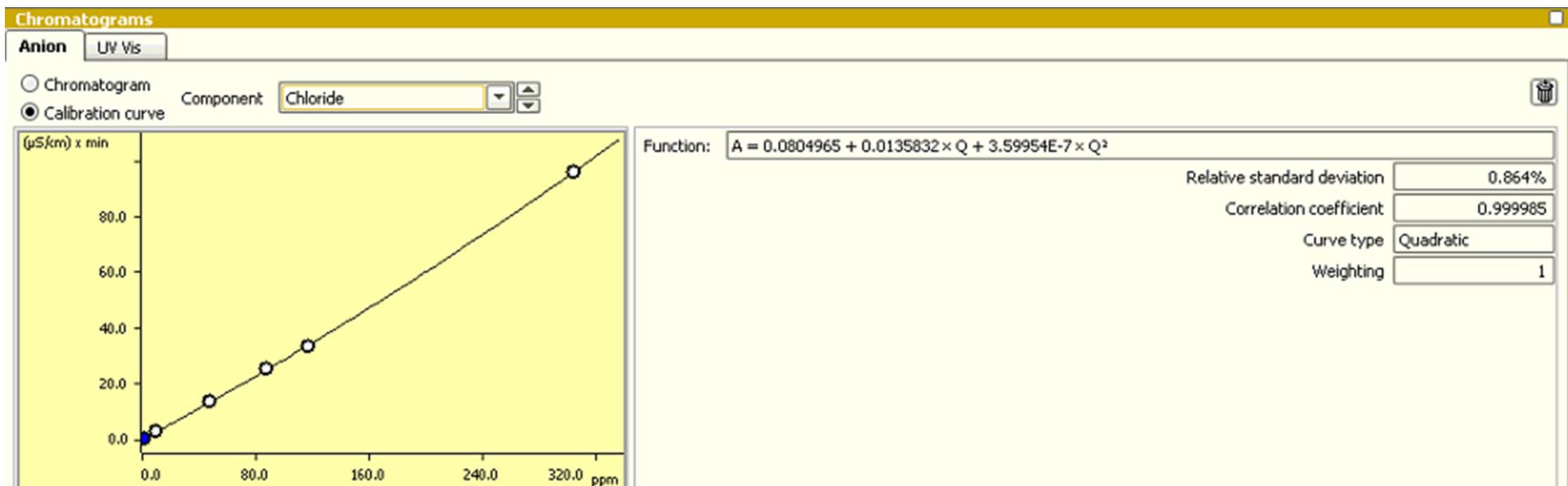
UV Vis	—

Standard: F-



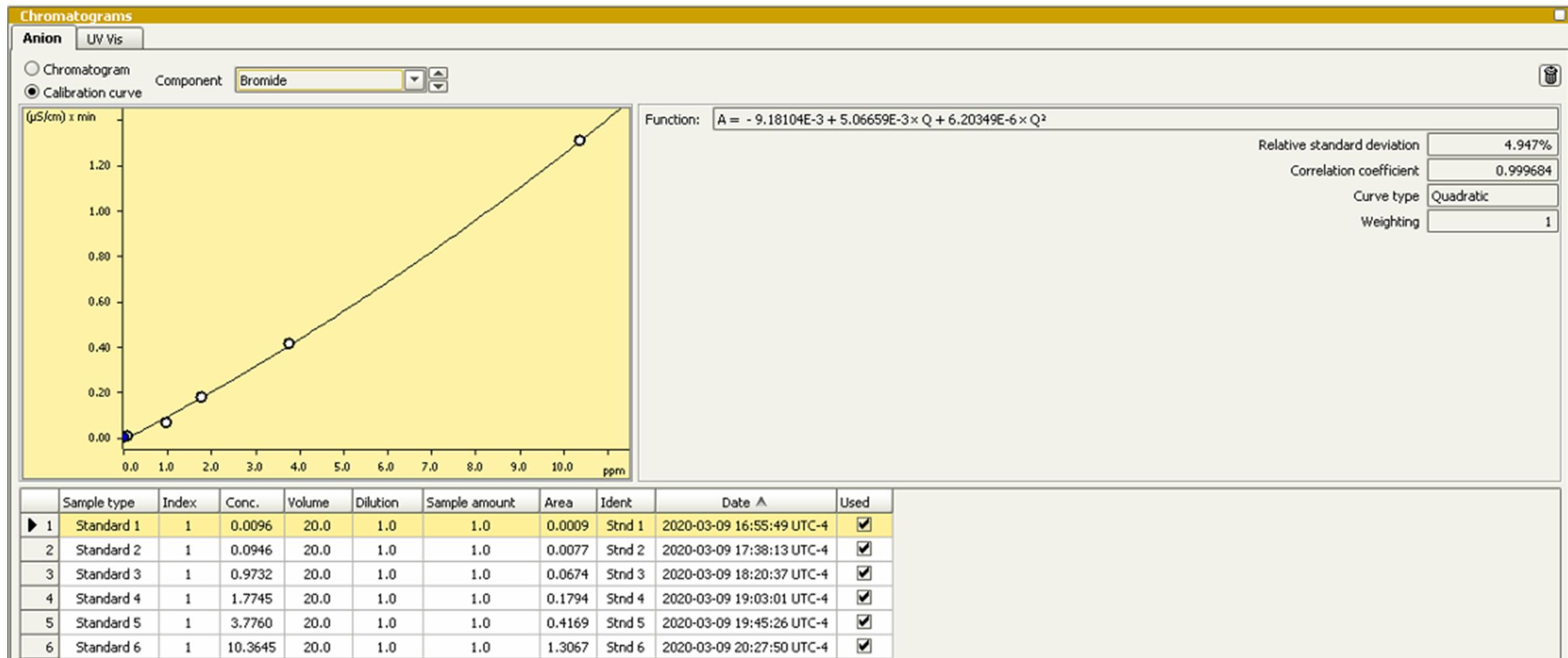
	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date ▲	Used
► 1	Standard 1	1	0.0096	20.0	1.0	1.0	0.0032	Stnd 1	2020-03-09 16:55:49 UTC-4	<input checked="" type="checkbox"/>
2	Standard 2	1	0.0949	20.0	1.0	1.0	0.0323	Stnd 2	2020-03-09 17:38:13 UTC-4	<input checked="" type="checkbox"/>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

Standard: Cl-

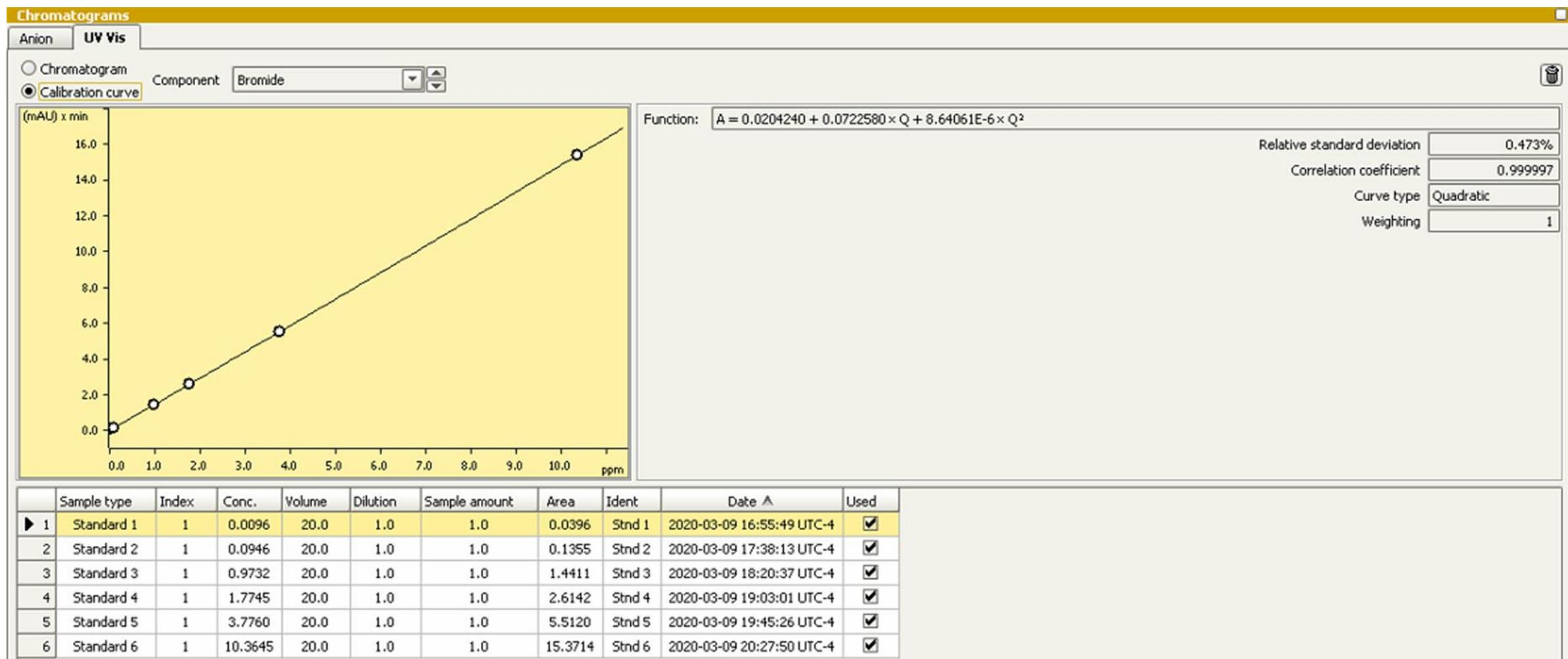


	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date ▲	Used
► 1	Standard 1	1	0.9488	20.0	1.0	1.0	0.2330	Stnd 1	2020-03-09 16:55:49 UTC-4	<input checked="" type="checkbox"/>
2	Standard 2	1	9.5667	20.0	1.0	1.0	2.6250	Stnd 2	2020-03-09 17:38:13 UTC-4	<input checked="" type="checkbox"/>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

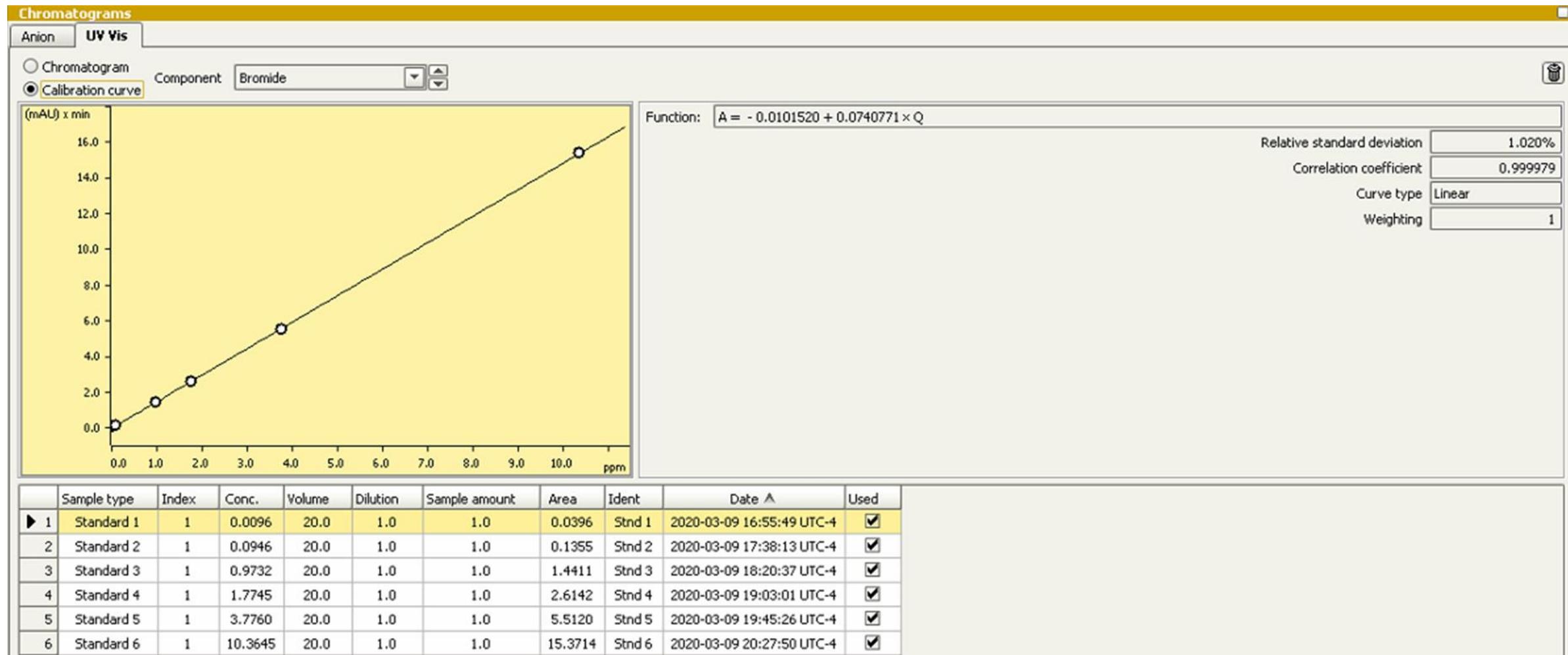
Standard: Br- (Conductivity)



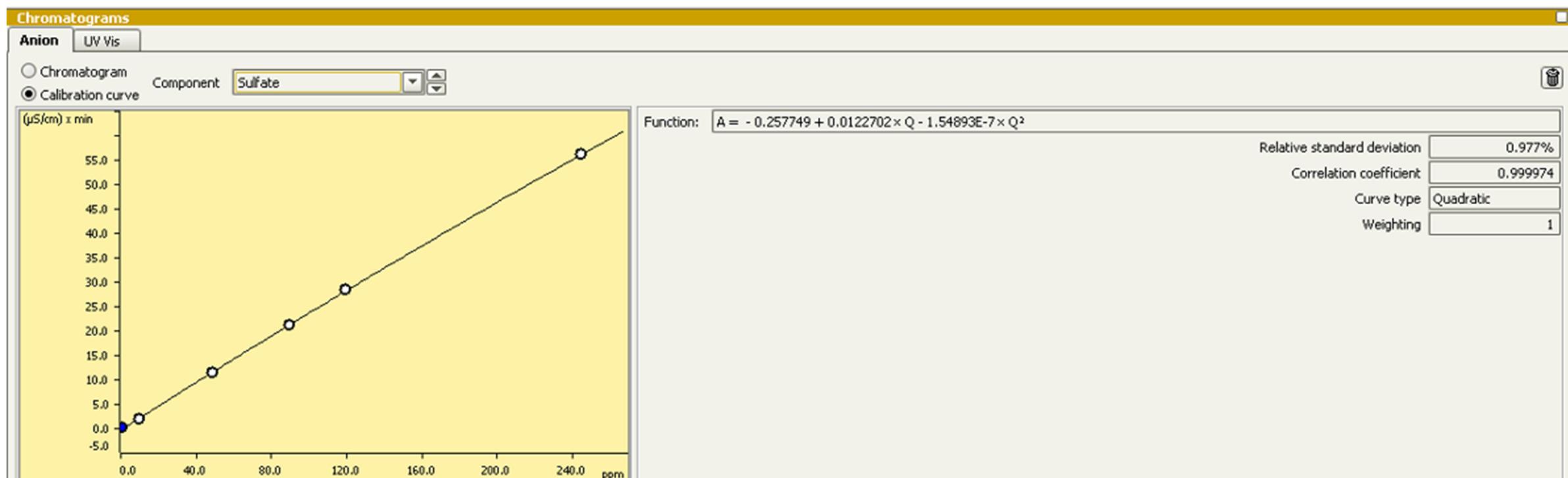
Standard: Br- (UV/Vis)- Quadratic Fit



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



Standard: SO₄²⁻



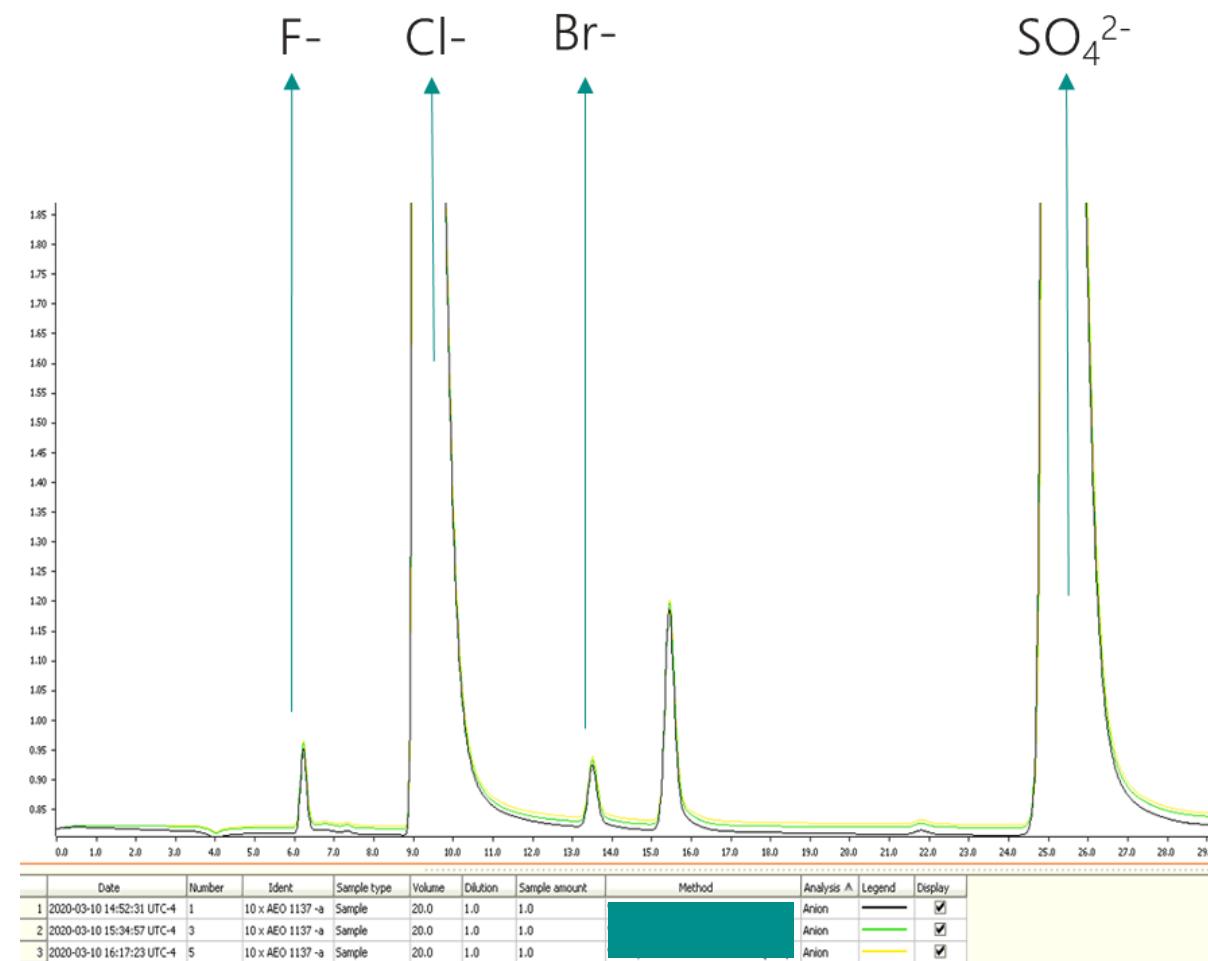
	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date ▲	Used
► 1	Standard 1	1	0.9702	20.0	1.0	1.0	0.1598	Stnd 1	2020-03-09 16:55:49 UTC-4	<input checked="" type="checkbox"/>
2	Standard 2	1	9.7823	20.0	1.0	1.0	2.0512	Stnd 2	2020-03-09 17:38:13 UTC-4	<input checked="" type="checkbox"/>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

Sample Summary: F-, Cl-, Br- and SO₄²⁻

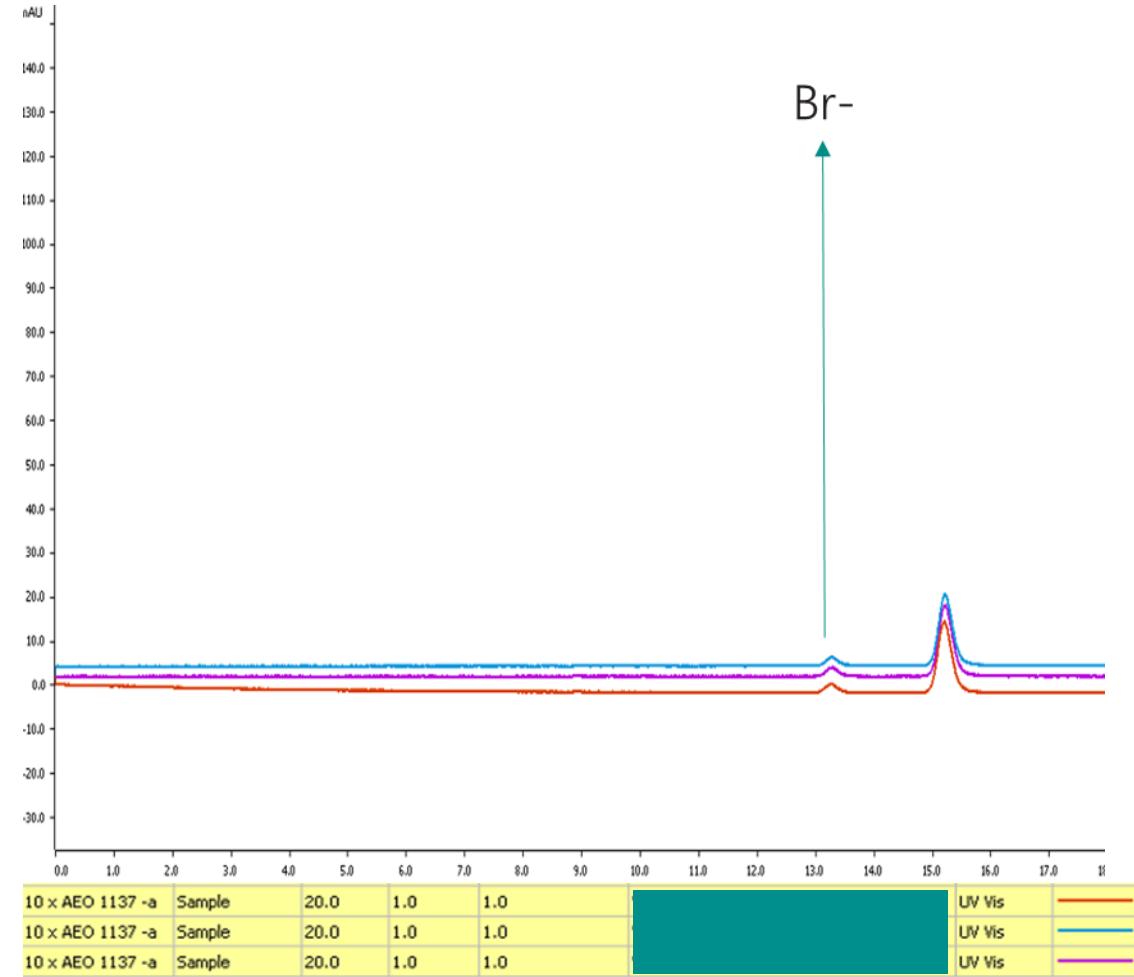
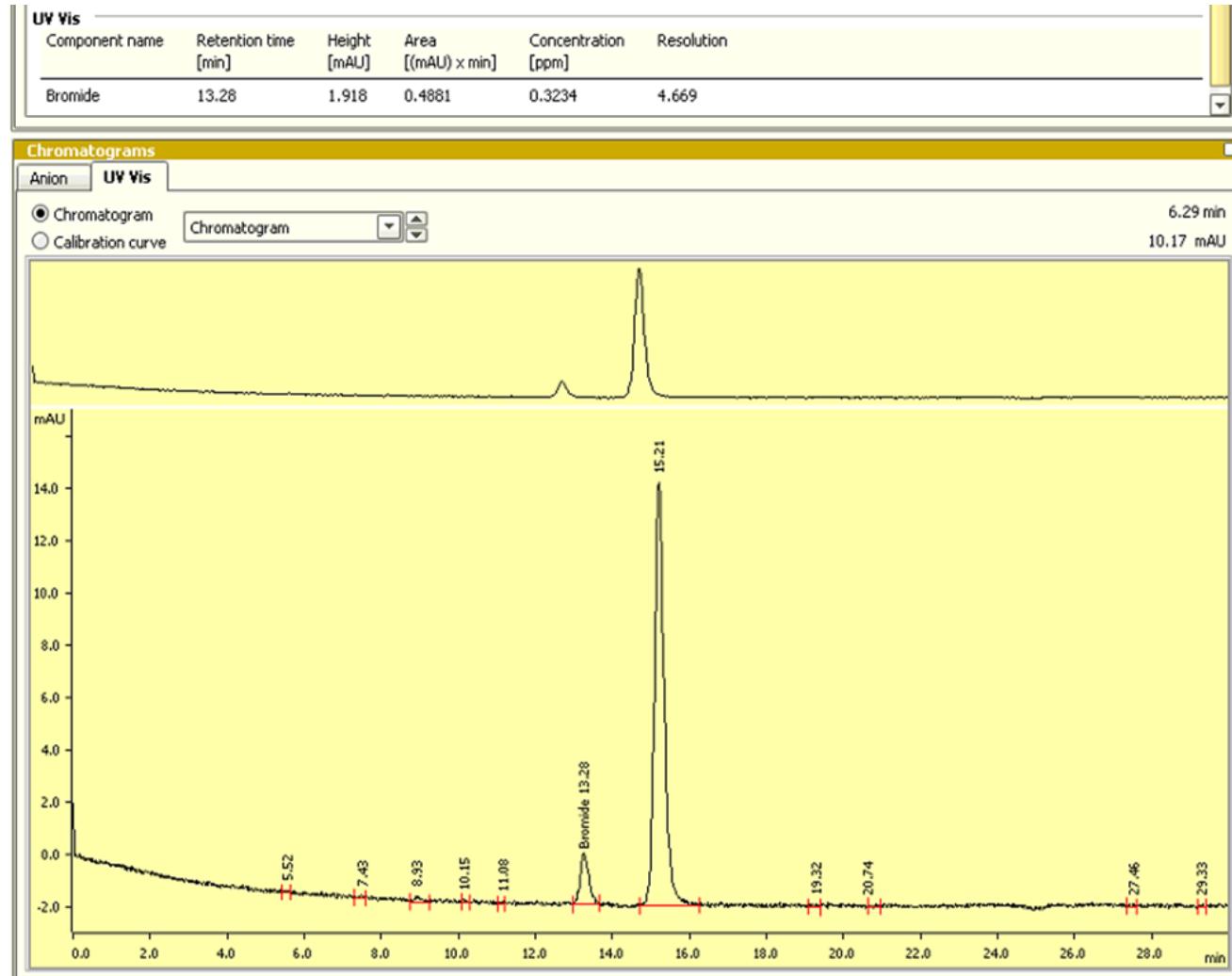
Sample	Anions	Average Concentration (ppm)	% RSD (X3)
AEO-1137	F-	0.758	0.3044
	Cl-	451.158	0.0539
	Br-	3.929	0.2333
	SO ₄ ⁻	658.285	0.0148
	UV Br-	3.334	2.1762
AEO-1367	F-	3.159	0.4275
	Cl-	2930.159	0.1709
	Br-	19.921	0.0100
	SO ₄ ⁻	75.737	0.0374
	UV Br-	19.884	0.2481

Dilution factor included (10X)

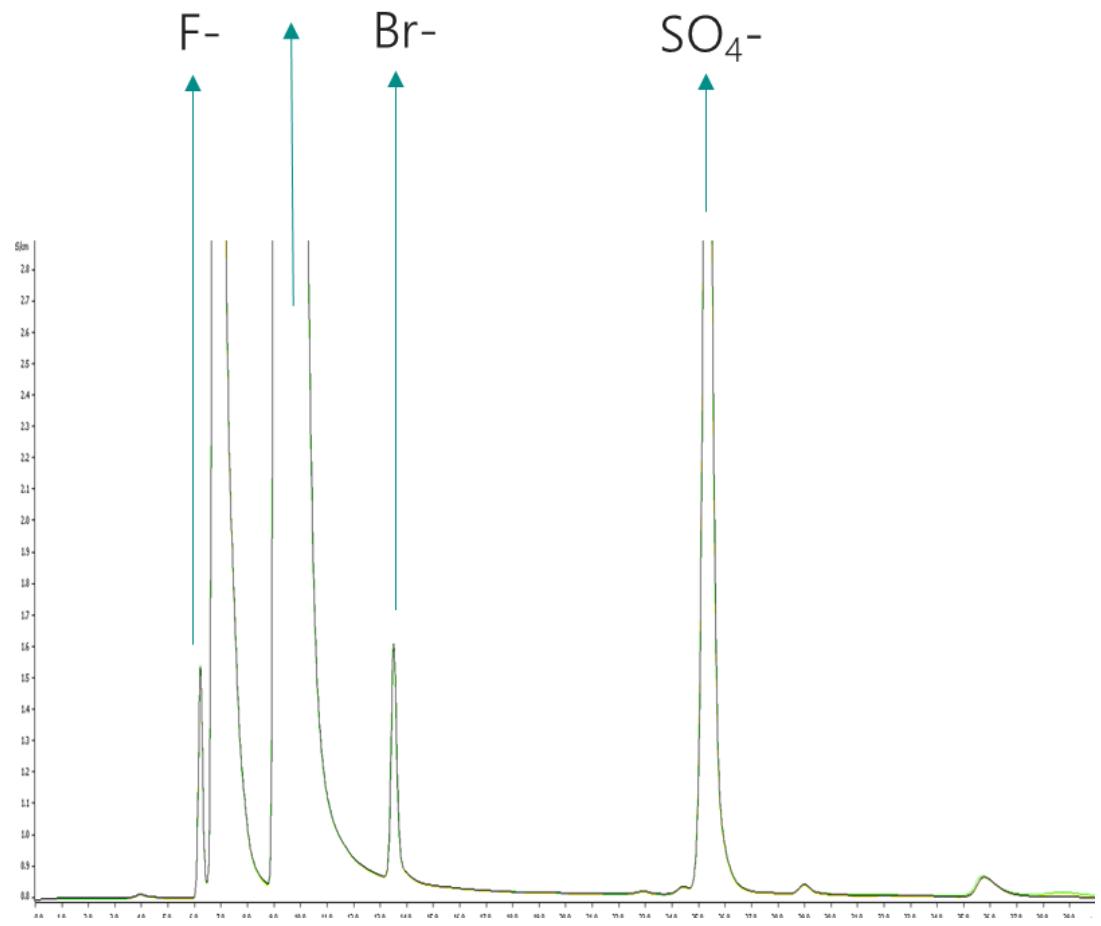
Sample AEO1137: F-, Cl-, Br- and SO₄²⁻



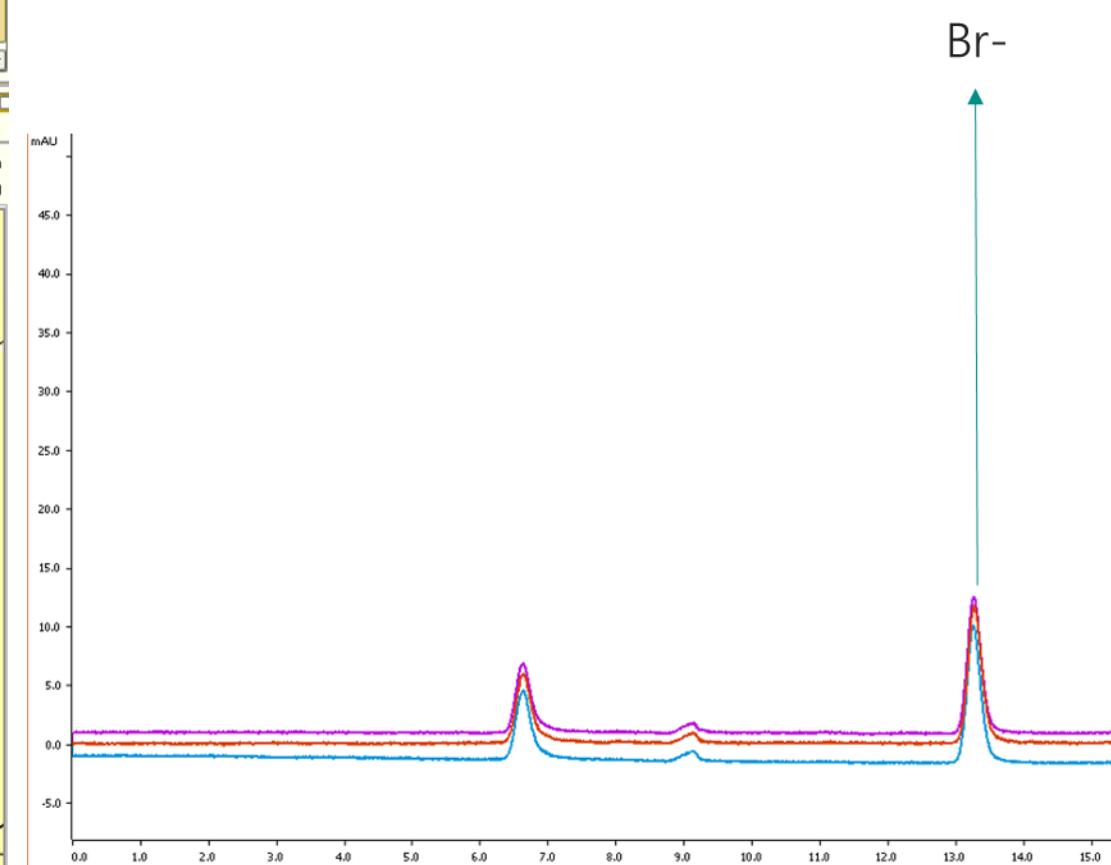
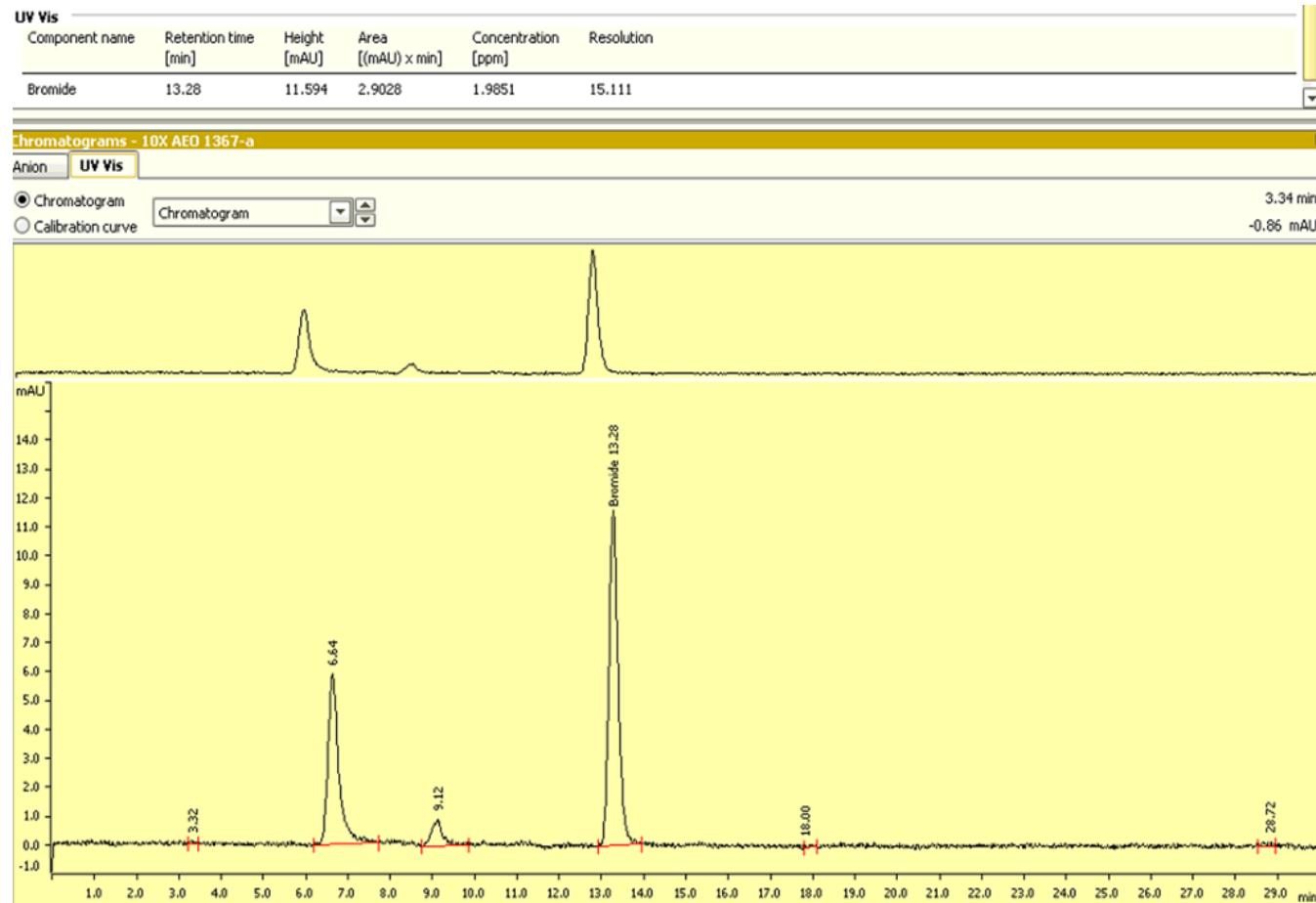
Sample AEO1137: Br- (UV/Vis)



Sample AEO1367: F-,Cl-,Br- and SO₄²⁻



Sample AEO1137: Br- (UV/Vis)



Sample Spike Summary: all samples were spiked with 5 ppm of Br-

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

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

Dilution factor not included

Conclusion

- Ability to detect F-,Cl-,Br- and SO_4^{2-} in samples
 - Shows repeatability with RSD (< 5%) values
- % Recovery for spiked samples at 5 ppm were excellent
 - Br- within 90-100% for both conductivity and UV detection