Gardenside Spring recession characterization and chloride-bromide analysis for sanitary sewage contamination.

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Introduction

Gardenside Spring, located in Gardenside Park, Lexington, KY, discharges into the Wolf Run tributary of the South Elkhorn Creek Basin. The park is located within the Inner Bluegrass Physiographic region typified by low-relief rolling hills (Blair, 2009). Prior efforts have indicated the spring behaves as a karst spring but no typical point sources for recharge (swallets, sinkholes) have been located. As such, further investigation of the springshed required the exploration of additional methods. Recession curve and chloride/bromide analyses, combined, may provide insights into flow regimes within the conduit network, nature of surface recharge, and presence of anthropogenic recharge from black water sources. Recession curve analysis (Bonacci, 1993) has been shown to reveal changes between flow regimes from conduit dominated (quick flow) and sediment filled/epikarst dominated (slow flow). Given the likely significant reworking of landforms within the suburban/urban watershed, slow flow domination of discharge may indicate recharge is predominantly due to infiltration as opposed to point sources (sinks, swallets, etc.). Chloride/bromide ratio analysis, while likely underutilized (Davis et al., 1998), has been used to indicate mixing of freshwater with brines, domestic effluent, and animal waste leachate (Davis et al., 1998; Katz et al., 2011). Domestic sewage contamination could explain the *E.Coli* impairment without the need for a surface source and provide baseflow maintenance observed over extended dry periods. Using previous water quality analysis (Blair, 2009), prior Cl/Br studies (Davis et al., 1998; Vengosh and Pankratov, 1998; Katz et al., 2011), and sampled water, a comparison of Cl/Br ratios for Gardenside Spring, springs within Fayette, Co, KY, and local surface water was conducted. End members were used to construct binary chemical mixing and precipitation models were constructed to aid in interpretation of current data. This was combined with confirmation of the presence of *E.Coli* in Gardenside Spring, comparable springs, and potential recharge sources.

Setting

Karst is prevalent throughout the region and the surface watershed of Wolf Run abuts the groundwater basins of McConnell Springs and Kenton's Bluehole. Interaction between surface and subsurface watersheds are common and karst groundwater basins regularly cross surface watershed divides (Currens and Paylor, 2009). The spring is located within the Ordovician-age Lexington Limestone, which has two principal facies, the Grier and Tanglewood Limestone members. These are interfingered by the minor shale and limestones of the Millersburg, Devils Hollow, Brannon members, and Macedonia Bed. The Lexington Limestone is overlain by the Clays Ferry Formation. The spring rises along a contact of interbedded minor shales (Blair, 2009) within the Tanglewood. Down cutting of Wolf Run, immediately up - and downstream of the spring, has been slowed by this minor shale. The immediate area surrounding the spring is dominated by ridges capped by the silty, weather resistant Brannon member.

Background

Introduced by Ognjen Bonacci (Bonacci, 1993), recession curve analysis can be used to determine changes in flow characteristics within the conduit system feeding a karst spring. Based on analytical descriptions of spring recession (post-storm event reduction from peak flow), the analysis uses the presence or absence of inflection points within a hydrograph to indicate variation between flow regimes. These regimes are turbulent flow (quick flow) in large conduits and diffuse flow (slow flow) in smaller and/or sediment filled conduits. A thorough understanding of local geology and spring response is important in the analysis as conduit morphology, subsurface variation in basin extent, or storm event intensity may influence storage. Accurate discharge measurements across analyzed events are also required, either through field measurement or calculation from a rating curve. And even with accurate measurements, assumptions required by the analysis may not be applicable to the aquifer in question. Despite the limited applicability, the method may provide a means of better describing parameters controlling karst spring response when tracer tests have been unsuccessful. As no rating exists for the spring, recession analysis requires the establishment of a rating curve (relating water depth to discharge) to estimate discharge over the study period.

Analysis of chloride/bromide ratios has been in use since the late 1960's to determine the evolution and potential mixing of brines and subsurface seawater (Rittenhouse, 1967). Within the past thirty years the analysis has been expanded into hydrogeology, specifically, as a proxy for mixing between low-Cl/Br ratio waters (precipitation, shallow groundwater, fresh surface water) and high-Cl/Br ratio waters (seawater, brines, deep groundwater, domestic and animal wastewater) (Davis et al., 1998; Vengosh and Pankratov, 1998; Katz et al., 2011). In their review of the application of Cl/Br techniques, Davis et al (1998) summarize the underlying behaviors of chlorine and bromine in natural systems that enables the ratio analysis. First, the analysis is based on the tendency of both chlorine and bromine to occur as monovalent anions (Cl^- and Br^-) in natural systems (Hem, 1985). Chlorine, when ionized as chloride, does not show absorptive tendencies, has a low abundance in rock-forming minerals, has a high stability, is non-volatile/lacks volatile compounds in natural compounds (outside of hydrothermal settings), and has a low bioconcentration in aqueous systems (Feth, 1981). Additionally, both species behave conservatively in solution (Fuge, 1969). Some important differences do exist, and as bromide is generally found in low concentrations, a slight variation can quickly alter Cl/Br values. Those differences aside, Cl/Br has been used successfully in a number of studies seeking to determine contamination sources of potable and freshwaters, and when coupled with additional lines of evidence is a useful tool for determining interaction with wastewater (Davis et al., 1998).

Methods

Rating curve construction

A total of thirty-one spring discharge measurements were taken from February to July of 2017 using a Sontek Flomaster water-flow meter along a cross-section of the channel fed by the spring. Discharge measurements were made generally at the same location but were adjusted pending flow conditions. Two measurements were discarded due to software or operator error. The remaining measurements were divided into three time periods: Oct. – April, April 8 – 9th, and April – July due to the water level instrument being disturbed, resulting in three separate curves.

Convention generally dictates that rating curves are established by plotting discharge versus stage, often in log-log space, then describing the relationship using a trendline. The established equation can then be solved to estimate discharge based on recorded stage. However, a comparison of discharge estimates using equations created from discharge versus stage, and stage versus discharge plots, indicated that stage versus discharge based equations produced discharge estimates closer to measured values. As such, rating curves were established and subsequent discharge estimates were made based on a stage versus discharge relationship.

Stage and temperature data were sampled at 15-minute intervals across the study period using an In-Situ Aqua Troll. Once collated by month and checked for erratic jumps or unexpected variation, stage was then used to estimate discharge.

Recession curve analysis

A storm event preceded by a recorded rain event was selected for each month across the study period. October and April were excluded due to low rainfall and the disturbance of the instrument. For each event, the falling limb of the hydrograph was plotted in semi-log space from peak discharge to trough or return to baseflow (estimated at 0.05 cfs). Following Bonnaci (1993), each recession was examined for variations in lines tangent to discharge across the recession.

Major Ion and *E. Coli*

Major ion and *E. Coli* analyses were conducted at the University of Kentucky Environmental Research and Training Lab using Ion Chromatography and IDEXX Collilert. Gardenside Spring, McConnell Springs, Kenton's Bluehole, a storm sewer outlet (Beacon Hill Rd. culvert), and Wolf Run (upstream of spring) were sampled during higher than baseflow and baseflow conditions at Gardenside Spring. Three, sterile 50 ml polypropylene and two, triple DI rinsed 250 ml bottles were taken at each site. Bottles were then kept on ice or refrigerated until they could be analyzed. *E. Coli* and major ion analyses were conducted within twenty-four hours of sampling. *E. Coli* analysis was conducted using a 10 times dilution or straight sample. Diluted water was mixed with a 90ml prepackaged solution per IDEXX instructions. Collilert media was then applied to both treatments. Prepared samples were then incubated for twenty-four hours at 35° C. The colony count was then determined using IDEXX guidelines under a UV light. One sample of influent from the Town Branch Water Treatment Facility was provided by ERTL and was run without dilution, at 100 times and 10 times dilution for major ions.

Chloride-Bromide Ratio

A literature review was conducted to determine Cl/Br mass ratios of typical natural waters and potential contaminant sources (Appendix, Table. 1). Chloride, bromide, fluoride, and alkalinity values for local surface waters, well water, and springs within Fayette county, KY and Gardenside Spring were obtained where available (Table. 2; USGS, 1986; Blair, 2008; KGS, 2016). Water quality data for spring water included maximum, most recent, and the median value for each species over the total number of samples for each site. These values were sorted by date and winter months (December, January, February, and March) for most recent and maximum values were excluded to prevent runoff contamination. Chloride and bromide values were then averaged across all remaining values and values with sample frequencies larger than one.

Values were again sorted by spring ID and shared most recent and maximum reported value date for both chloride and bromide. Again, average values were calculated. It is important to note that the water quality data gathered generally had no description of the reason it was gathered. This leaves open the possibility that predominantly low-water quality springs are overrepresented. Mixing models were then created using reported and sample values for local waters and those of typical endmembers i.e. sewage, brines, and seawater (Appendix, Table. 1) gathered from literature review. End members were selected for the species in question and then the proportion of the dilute solution was reduced to create a mixing curve. Reported and measured values for sampled locations and other local springs were then plotted on the constructed mixing curves.

Results

E. Coli was present in all samples tested in both high- and low-flow conditions. At high flow, Gardenside Spring had the lowest colony count of between 41 and 54 colonies per 100 ml and McConnell Springs had the highest colony count of between 2416 and 5172 colonies per 100 ml. At low flow, McConnell Springs had the lowest colony count of between 75 and 122 colonies per 100 ml and runoff from the Beacon Hill Road culvert had the highest of between 2419 and 2909 colonies per 100 ml. Runoff from the Beacon Hill Road culvert was also the second highest colony count under high-flow conditions at 794 and 1119 colonies per 100 ml. Comparing high-to low-flow conditions, Gardenside Spring had a higher colony count at low flow of between 153 and 216 colonies per 100 ml.

Three rating curves were established. Differing number of measurements and recorded flow conditions between the curves resulted in trends of varying fit (R^2). As no obvious non-linear trend was apparent, linear trends were used to establish the rating curves. Equations describing the linear trends were then used to estimate discharge from recorded water depth. The April through July period had the most measurements and the greatest R^2 at 0.4766 (Fig. 1), as such the recession analysis was focused on events within that time period.

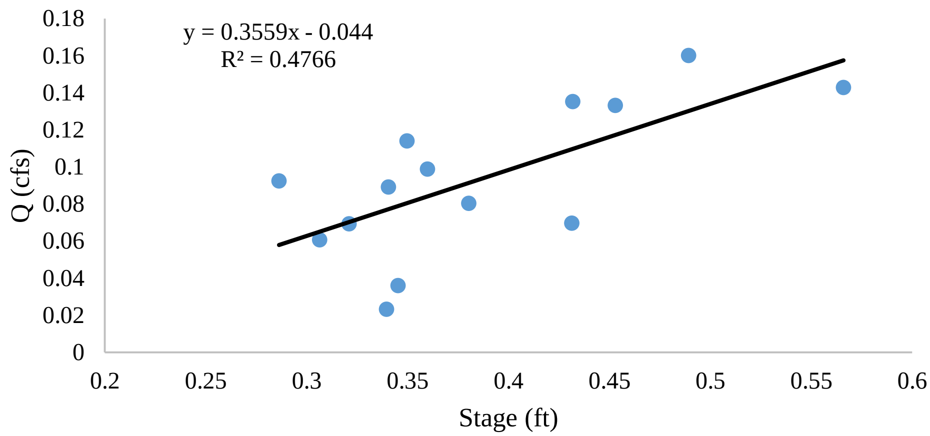

Fig. 1 - Gardenside Rating, April 14th - July, 2017

Estimated, non-negative discharge from May through July ranged from 0.007 to 0.67 cfs. Of the seventeen total rain event and spring responses observed, recession from three events were examined for abrupt shifts in recession trend: May 3rd -5th, June 25th – 30th, and July 7th – 13th (Fig. 2, 3, and 4). Across the recessions observed a strong linear trend was present with R^2 ranging from 0.7665 to 0.9846. Minor variation in discharge was present but no systematic change in lines tangent to the slope were observed.

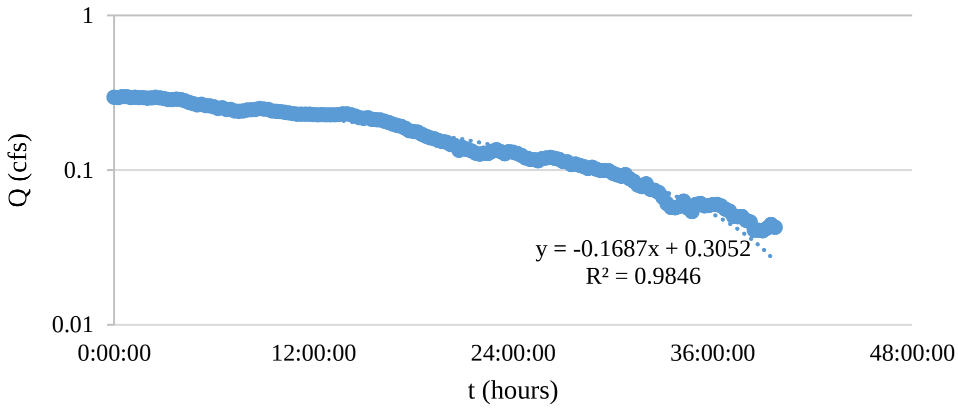

Fig. 2 - Gardenside Recession, May 3 - 5, 2017

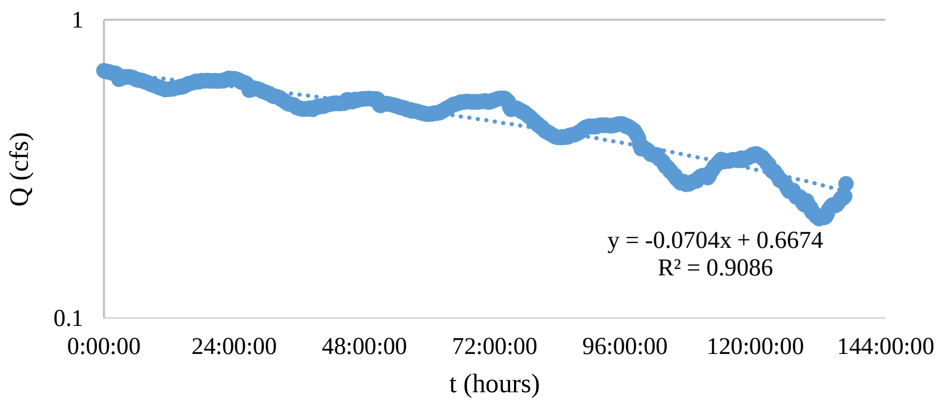

Fig. 3 - Gardenside Discharge, June 25 - 30, 2017

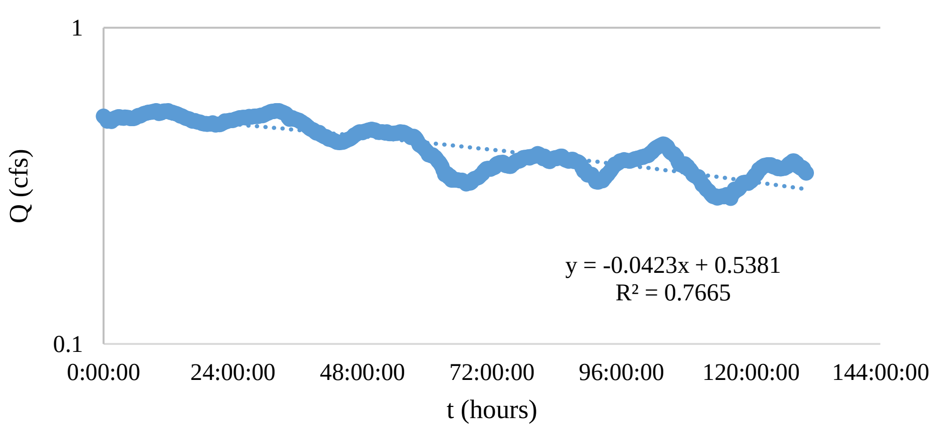

Fig. 4 - Gardenside Discharge, July 7 - 14, 2017

Ion Analysis

Values reported from sixteen Fayette Co. springs met the sorting requirements. These sites represent a total of 222 samples. Reported, non-winter month, maximum chloride values ranged from 27.8 to 442.0 mg/l, most recent values fell between 13.3 and 442 mg/l, and median values ranged from 27.75 to 442 mg/l. Several springs had only one reported sample leading to maximum, most recent, and reported median values to be the same. The average maximum reported chloride value was 163.0 mg/l across the 7 included springs comprising 13 samples. Average maximum for the two sites with more than one sample was 49.8 mg/l representing 8 samples. The average most recent reported values for non-winter months (11 sites) was 121.32 mg/l representing 191 samples. Only including sites with multiple samples reduced the average of most recent values to 48.85 mg/l (3 sites, 71 samples). The average median value reported across all sites, including winter months, was 98.35 mg/l, and for multi-sampled sites only, 39 mg/l (16 sites, 222 samples). The only reported chloride value for Gardenside Spring was a maximum of 51 mg/l. Measured chloride was higher and was relatively consistent at 67 mg/l during high flow, and 66.8 mg/l at low flow. The sampling period for prior work at GSS includes winter months but the date of the maximum value is not reported. New samples were taken in April and July, respectively. Several significant rain events had occurred prior to sampling in April and coupled with a mild winter, recent input of road salt was likely minimal. Town Branch water treatment plant influent chloride was 129 mg/l. No seasonal comparison was available but, seasonal variation is possible if sections of the storm and sanitary sewer are shared.

Reported, non-winter month, maximum bromide values for Fayette Co. springs ranged from 0.040 to 0.104 mg/l, most recent values fell between 0.033 and 0.104 mg/l, and median values ranged from 0.023 to 0.104 mg/l. As with chloride, several springs had only one reported sample leading to maximum, most recent, and reported median values to be the same. The average maximum bromide value was 0.758 mg/l across the 10 included springs comprising 71 samples. Average maximum for the sites with more than one sample was 0.0675 mg/l representing 65 samples. The average most recent values for non-winter months (11 sites) was 0.0634 mg/l representing 131 samples. Only including sites with multiple samples reduced the average of most recent values to 0.042 mg/l (3 sites, 71 samples). The average median value across all reported sites, including winter months, was 98.35 mg/l, and for multi-sampled sites only, 39 mg/l (5 sites, 125 samples). The only reported bromide value for Gardenside Spring was a maximum of 0.254 mg/l. Sampled values were significantly lower at 0.019 mg/l (high flow) and 0.027 mg/l (low flow). It is important to note that sampled values of bromide are close to the detection limit of the instrument. While the presence of bromide is certain, no real comparison can be made between the two samples as error likely encompasses the difference between sampled concentrations. Again, the sampling period for prior work at GSS includes winter months but the date of the maximum value is not reported.

Mixing Models

Five chloride-bromide binary mixing models were created with varying end-members, these included: local surface water (Elkhorn Creek, KY; Smoot, 1986) and seawater, surface water and effluent, average median Fayette Springs and effluent, and sampled values of Fayette Springs and Town Branch influent. Chloride and bromide end-member models were treated as either constant or variable bromide concentration. When bromide is held constant, variation in Cl/Br ratios are chloride dependent. When bromide concentration varies in the mixing model, bromide increases faster than chloride resulting in an opposing Cl/Br trend to the fixed bromide model. Cl vs. Cl/Br for GSS from prior research falls closely along the variable bromide mixing curve. Sampled values do not, as bromide concentrations were lower than previously reported values (Fig. 5). Across Fayette County springs, no median spring Cl vs. Cl/Br value falls directly on the variable Br curve, but several fell along the fixed Br curve, and were close to the variable Br curve as well.

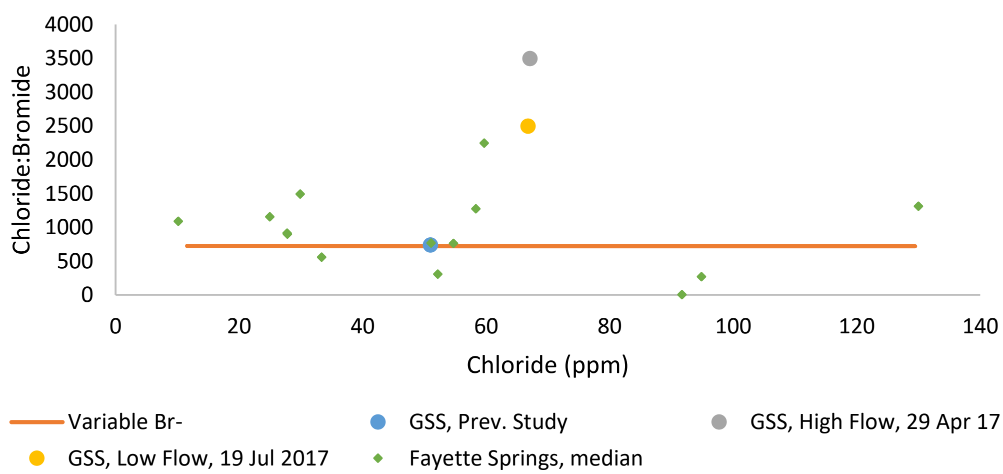

Fig. 5 – Combined chloride – bromide mixing curve (variable bromide), median spring and Gardenside Spring Cl vs. Cl/Br.

Conclusions

One large feature (sinkhole along Stonewall Rd.) is suspected as a source of recharge to the spring. However, extensive reworking due to land use (suburban) and past construction in the catchement may have filled many sinks, or throats within sinks, supplying water to the spring. This could explain the lack of observed karst features and would make diffuse recharge (through soil overlying the epikarst connected to Gardenside Spring) the greatest contributor to discharge. The recession curve analysis agrees with this hypothesis. Specifically, through the apparent lack of an abrupt change in flow regime (conduit flow (quick flow) to diffuse flow (slow flow)) observed across the events analyzed.

If sanitary sewage contamination is the primary source of *E. Coli* impairment of the spring several observations were expected. First, an increased *E. Coli* colony count at baseflow when the dilution effect of storm response would be at its lowest. This was observed as the *E. Coli* colony count of Gardenside Spring did increase at baseflow. Second, increased chloride and bromide values should be seen at baseflow, again due to a decreased dilution effect. This did not occur and chloride concentrations increased at high flow. Furthermore, base level *E. Coli,* chloride, and bromide were comparable to another suburban/peri-urban karst spring (Kenton's Blue Hole). And, third, Gardenside Spring water chloride/bromide ratios falling close to the refined sanitary sewage and freshwater mixing model. This was not observed, despite prior reported values of Cl/Br and Cl/F ratios from Gardenside Spring falling closely along a mixing curve based on the local spring values and effluent values gathered during literature review. These results do not support sanitary sewage leakage as the source of *E. Coli* impairment.

Gathered data does provide an alternative hypothesis, however. Major ion and *E. Coli* concentrations are suggestive of another *E. Coli* source within the springshed. Storm water runoff chloride concentrations were the highest measured for both storm response and baseflow conditions. As storm sewer discharge also had very high *E. Coli* colony counts (956 colonies/100ml at high flow; 2661 colonies/100ml at base flow) this could provide a source of *E. Coli* and the associated increase in chloride concentration of Gardenside Spring at high flow.

While too many unknowns are present to make a strong conclusion, the sampled chloride-bromide ratio, change in major ion concentration, and overall chemical characteristics is inconsistent with sanitary sewage contamination. In contrast, the recession characterized flow regime, and measured chloride and *E. Coli* is suggestive of runoff as a potential source of *E. Coli* within Gardenside Spring.

References

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Appendix

Fluid	Cl/Br	Cl^-	Source
Summer Runoff	10 – 100		Davis et al.,1998
Winter Runoff, Urban (median)	1167		Davis et al., 1998
Precipitation	50 – 150		Davis et al., 1998
Groundwater	100 – 200, 172 – 293		Davis et al., 1998; Vengosh and Pankratov, 1998
Seawater	28 – 292	19000 – 20000	Davis et al., 1998
Lake Superior	120	0.5 – 2.8	Davis et al., 1998
Small Lake	151 – 244		Davis et al., 1998
Stream	~ local precipitation	< 100	Davis et al., 1998
Spring Water	145 – 440		Vengosh and Pankratov, 1998
Sewage	300 – 600, 410 – 873		Davis et al., 1998; Vengosh and Pankratov, 1998
NaCl Evaporite Dissolution	1000 - 10000		Davis et al., 1998
Sewage Contamination Groundwater	150 – 540		Vengosh and Pankratov, 1998
Cattle Waste	66.5 – 167		Hudak, 2002
Horse Waste	119 – 156		Hudak, 2002
Goat Waste	33.4 – 165		Hudak, 2002
Septic Tank Effluent	450	69	Thomas, 2000
Spetic Tank Effluent, Midwest	769	91	Panno, 2006
Septic Tank Effluent (median)	694	35	Katz, 2010

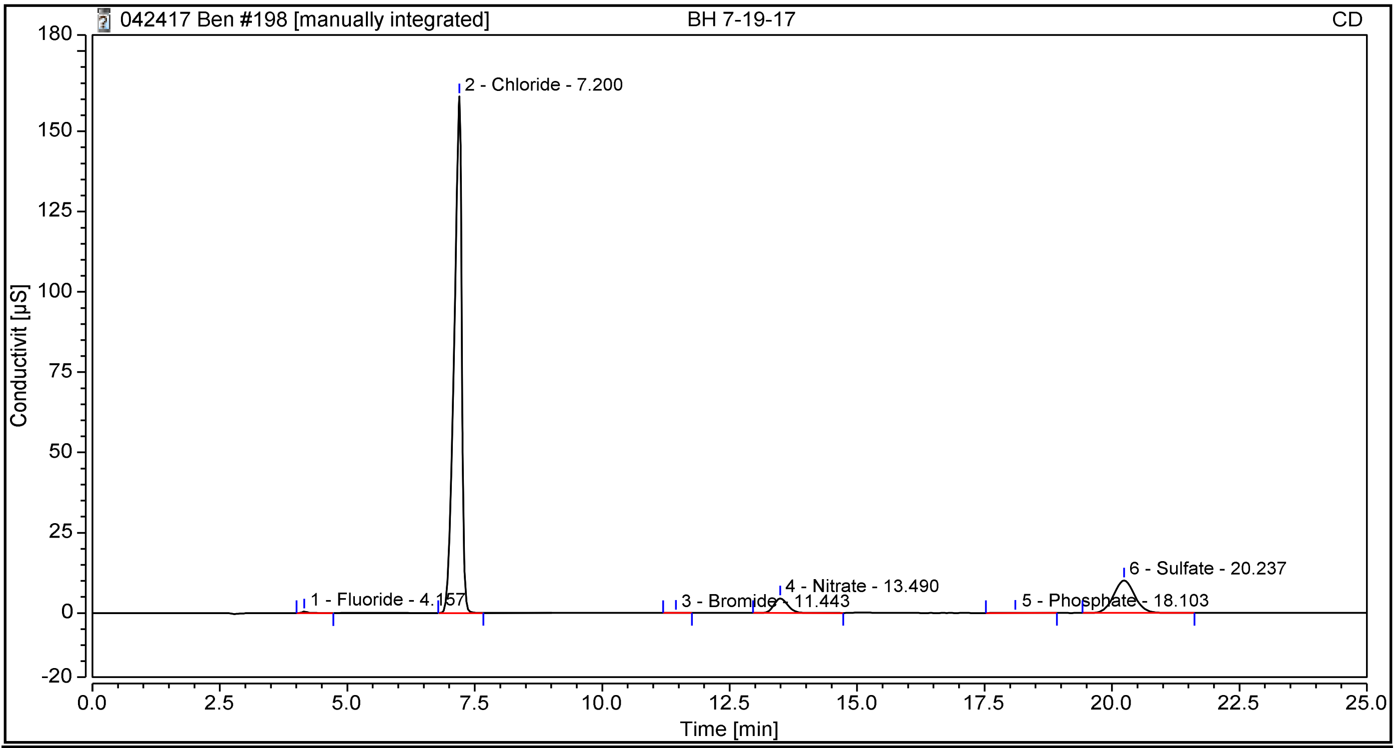
Table. 1 – Chloride/Bromide ratios and chloride values for common water and contaminant sources.

Chromatogram and Results

Injection Details

Injection Name:	**BH 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**11**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 18:15**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

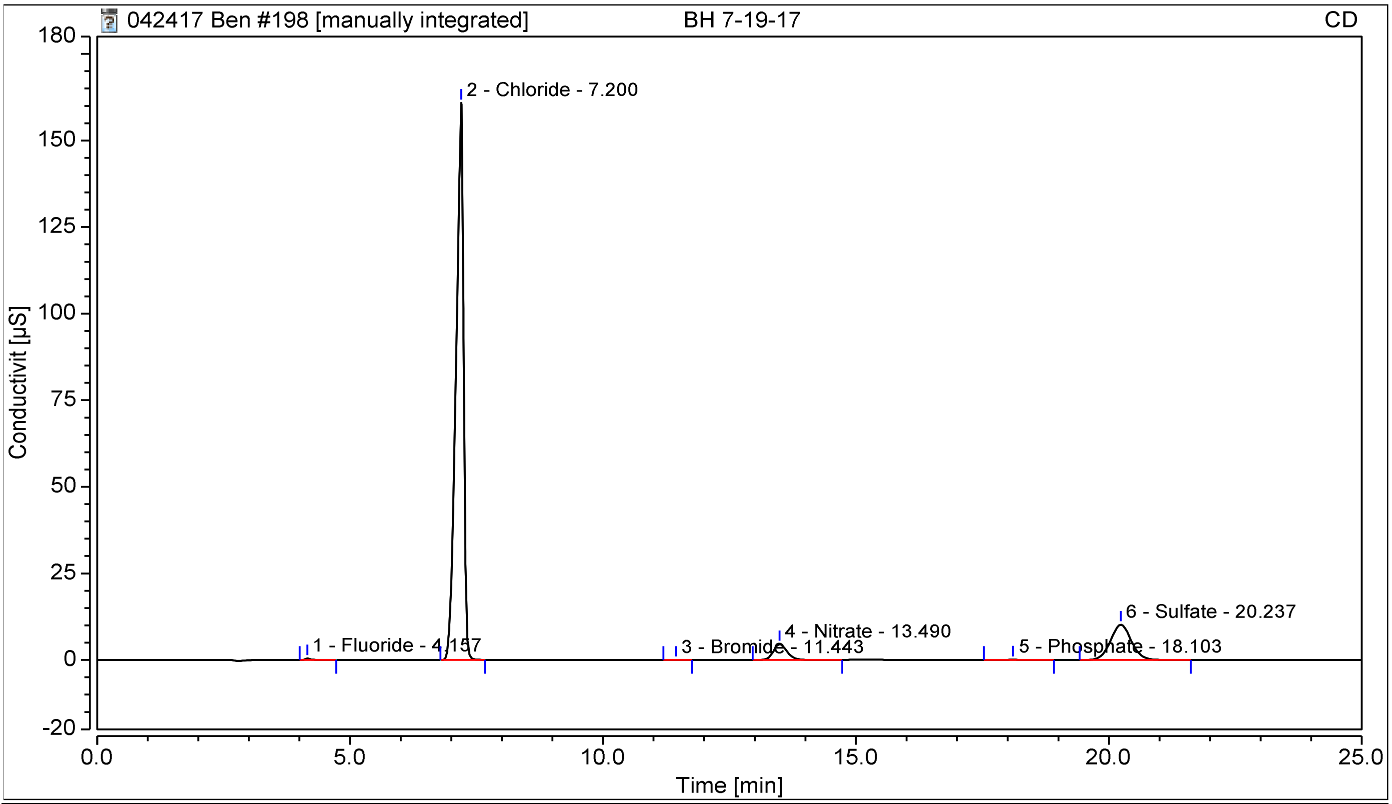
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.157	0.060	0.453	0.18	0.26	0.2304
2	Chloride	7.200	27.735	160.833	81.32	91.36	132.4454
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.443	0.004	0.018	0.01	0.01	0.0682
4	Nitrate	13.490	1.434	4.540	4.20	2.58	3.4383
5	Phosphate	18.103	0.026	0.053	0.08	0.03	0.6722
6	Sulfate	20.237	4.848	10.156	14.21	5.77	41.2528
Total:			**34.107**	**176.052**	**100.00**	**100.00**	

Chromatogram and SST Results

Injection Details

Injection Name:	**BH 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**11**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 18:15**	*Sample Weight:*	**1.0000**

Chromatogram



SST Results

No.	Name	Inj.Condition	Peak	Test Result	Injection

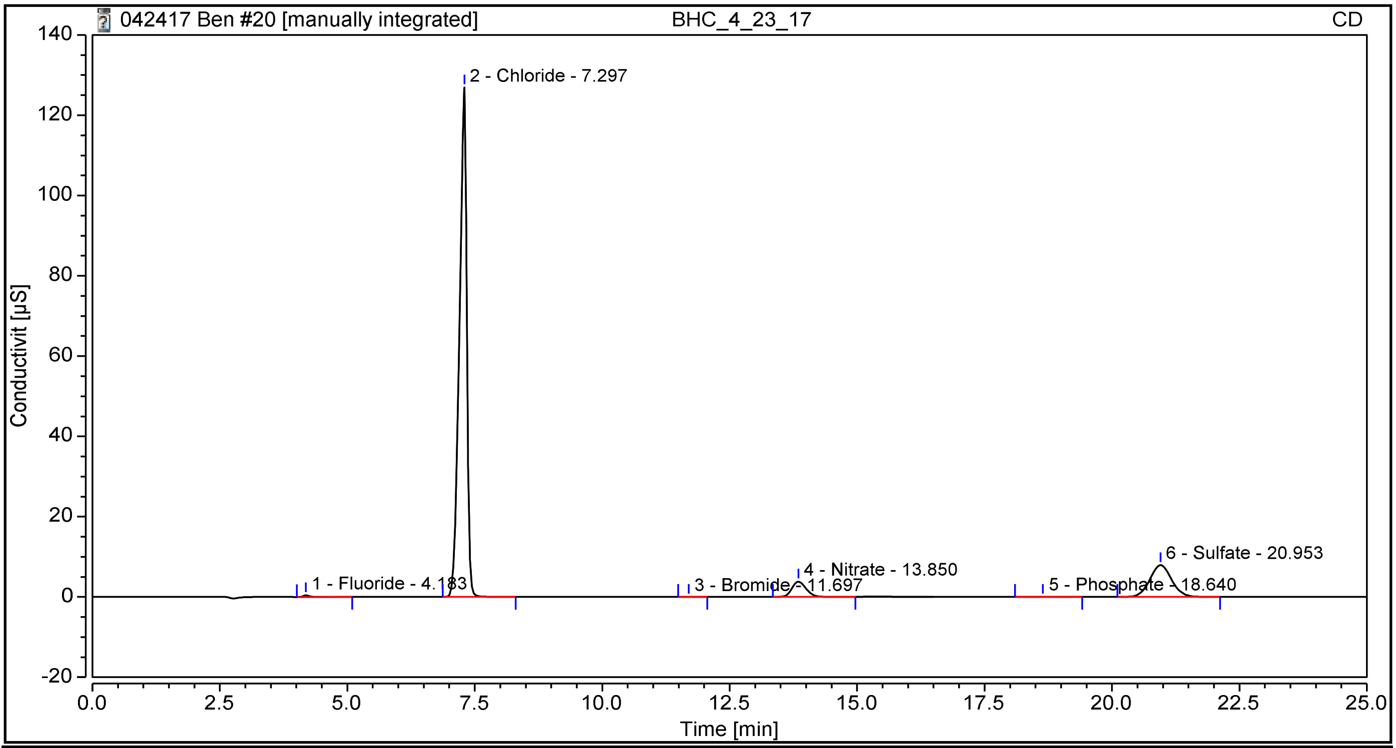
Number of executed test cases: **n.a.** **Total Result:** **Passed**

Chromatogram and Results

Injection Details

Injection Name:	**BHC_4_23_17**	*Run Time (min):*	**25.00**
Vial Number:	**8**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**24/Apr/17 21:06**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.183	0.057	0.429	0.22	0.31	0.2199
2	Chloride	7.297	21.234	126.893	80.09	91.21	104.2963
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.697	0.003	0.010	0.01	0.01	0.0434
4	Nitrate	13.850	1.238	3.816	4.67	2.74	2.9732
5	Phosphate	18.640	0.026	0.052	0.10	0.04	0.6736
6	Sulfate	20.953	3.955	7.928	14.92	5.70	33.9847
Total:			**26.513**	**139.128**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**GSS 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**10**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
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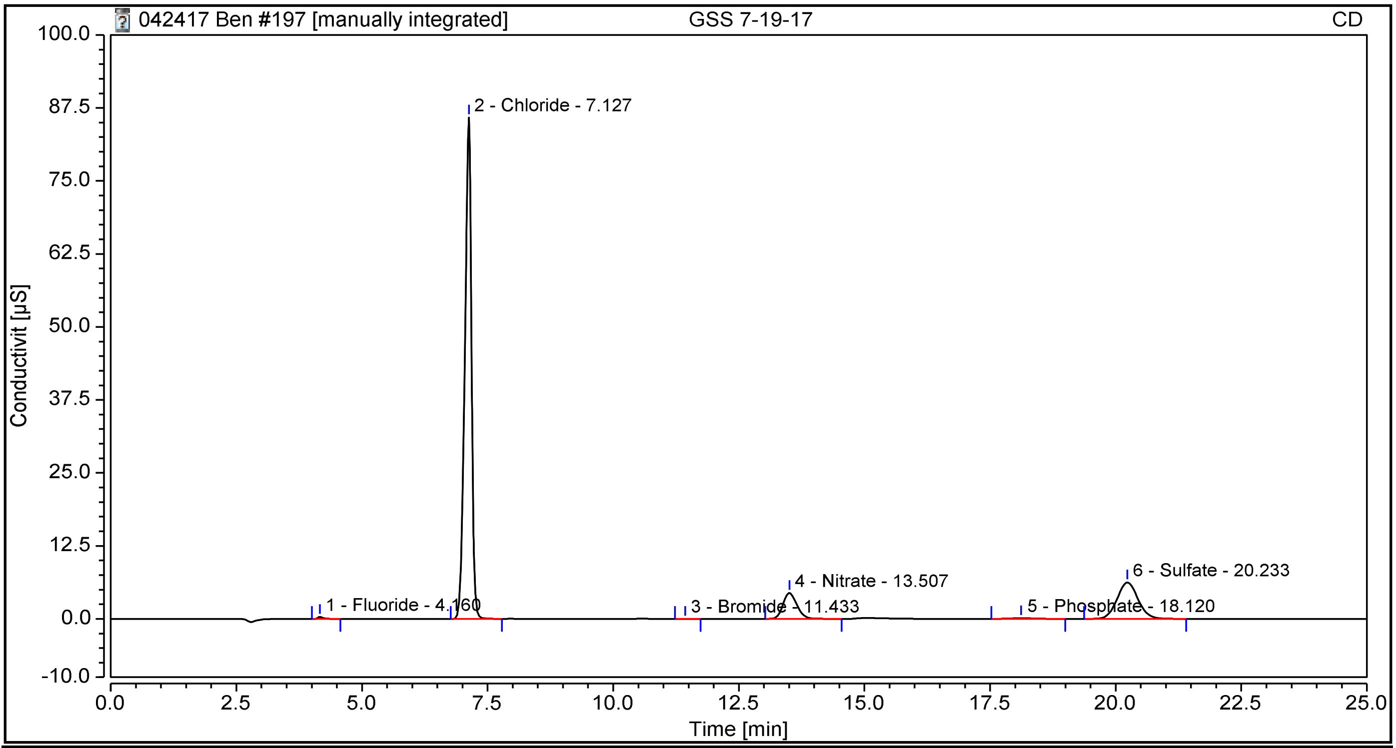
Chromatogram



Integration Results

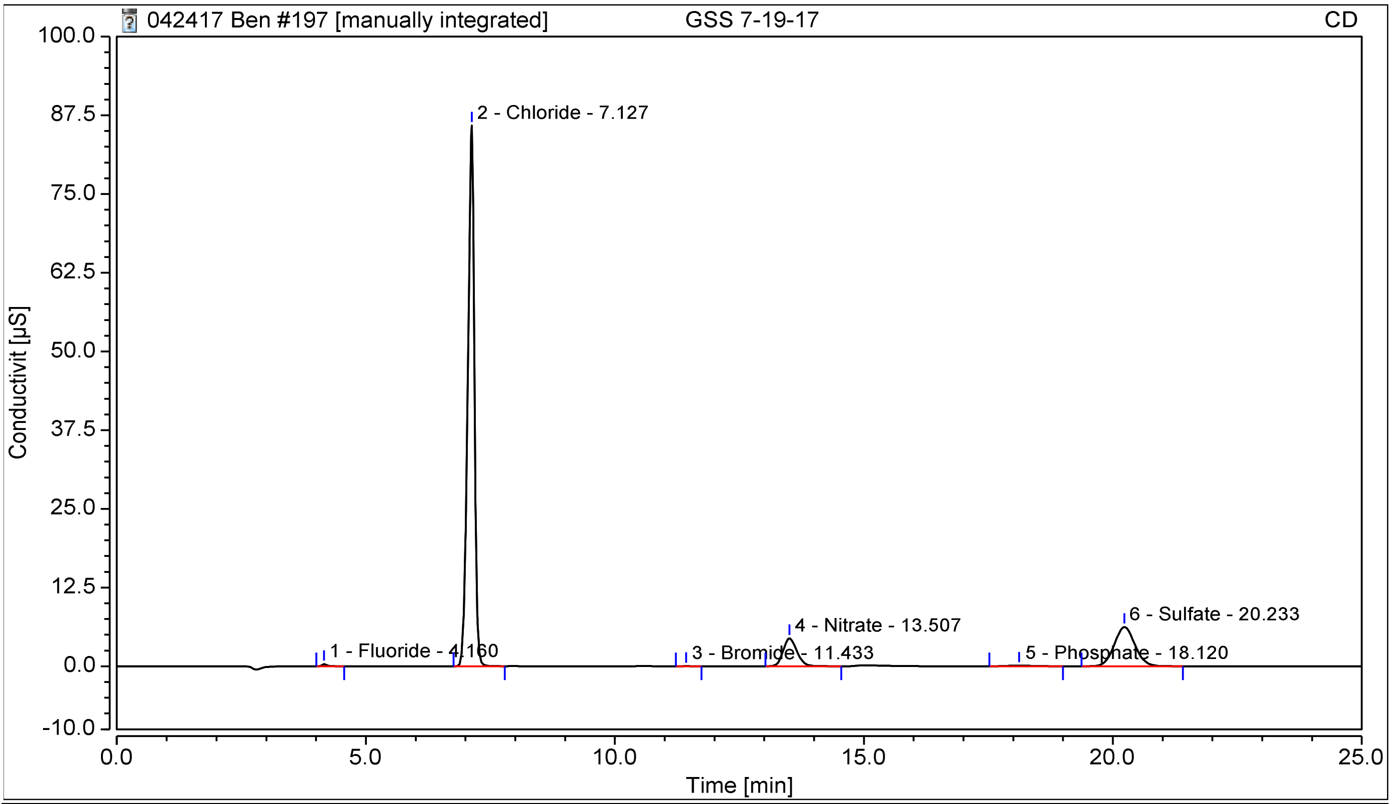
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.160	0.044	0.359	0.25	0.37	0.1714
2	Chloride	7.127	13.080	85.872	74.34	88.53	66.7895
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.433	0.002	0.008	0.01	0.01	0.0268
4	Nitrate	13.507	1.415	4.428	8.04	4.56	3.3941
5	Phosphate	18.120	0.052	0.104	0.30	0.11	1.3348
6	Sulfate	20.233	3.002	6.228	17.06	6.42	26.0700
Total:			**17.595**	**96.998**	**100.00**	**100.00**	

Chromatogram and SST Results

Injection Details

Injection Name:	**GSS 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**10**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 17:48**	*Sample Weight:*	**1.0000**

Chromatogram



SST Results

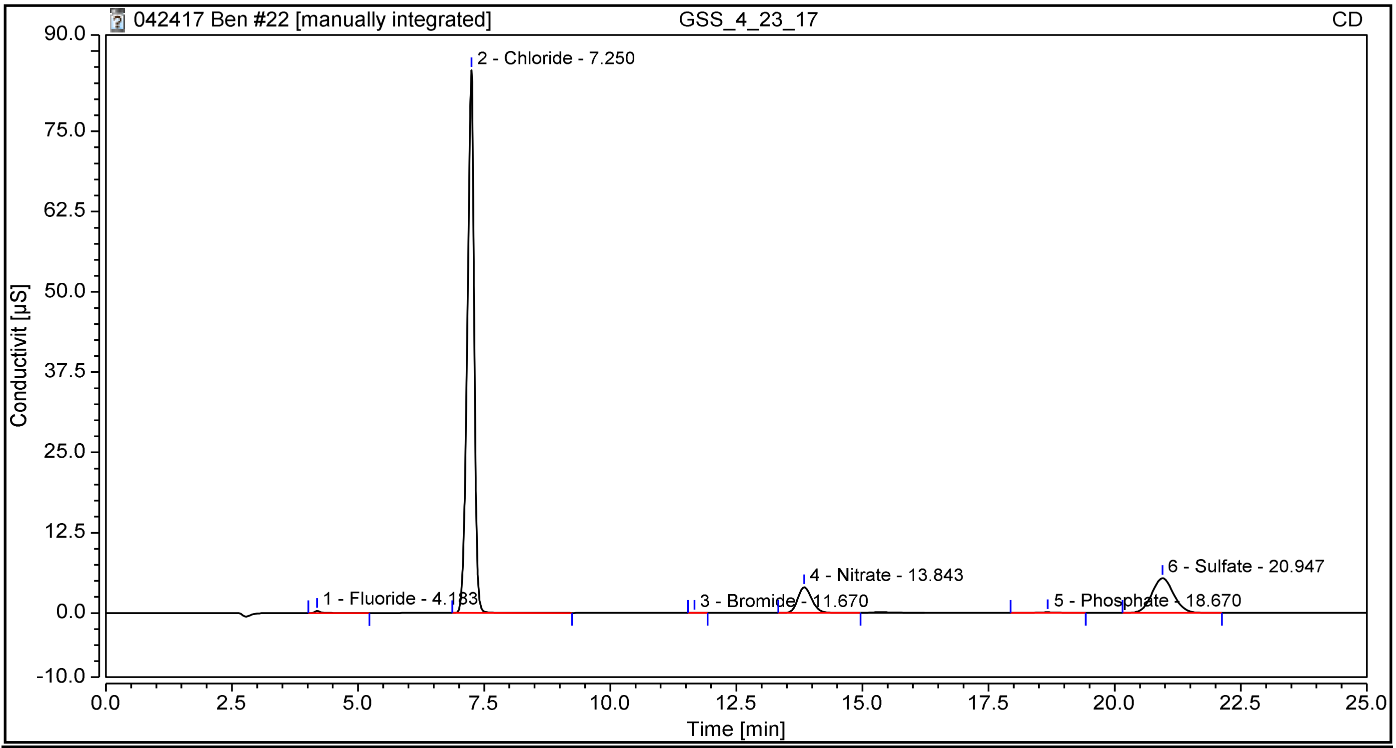
No.	Name	Inj.Condition	Peak	Test Result	Injection
Number of executed test cases:	**n.a.**		**Total Result:**	**Passed**	

Chromatogram and Results

Injection Details

Injection Name:	**GSS_4_23_17**	*Run Time (min):*	**25.00**
Vial Number:	**10**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**24/Apr/17 22:00**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

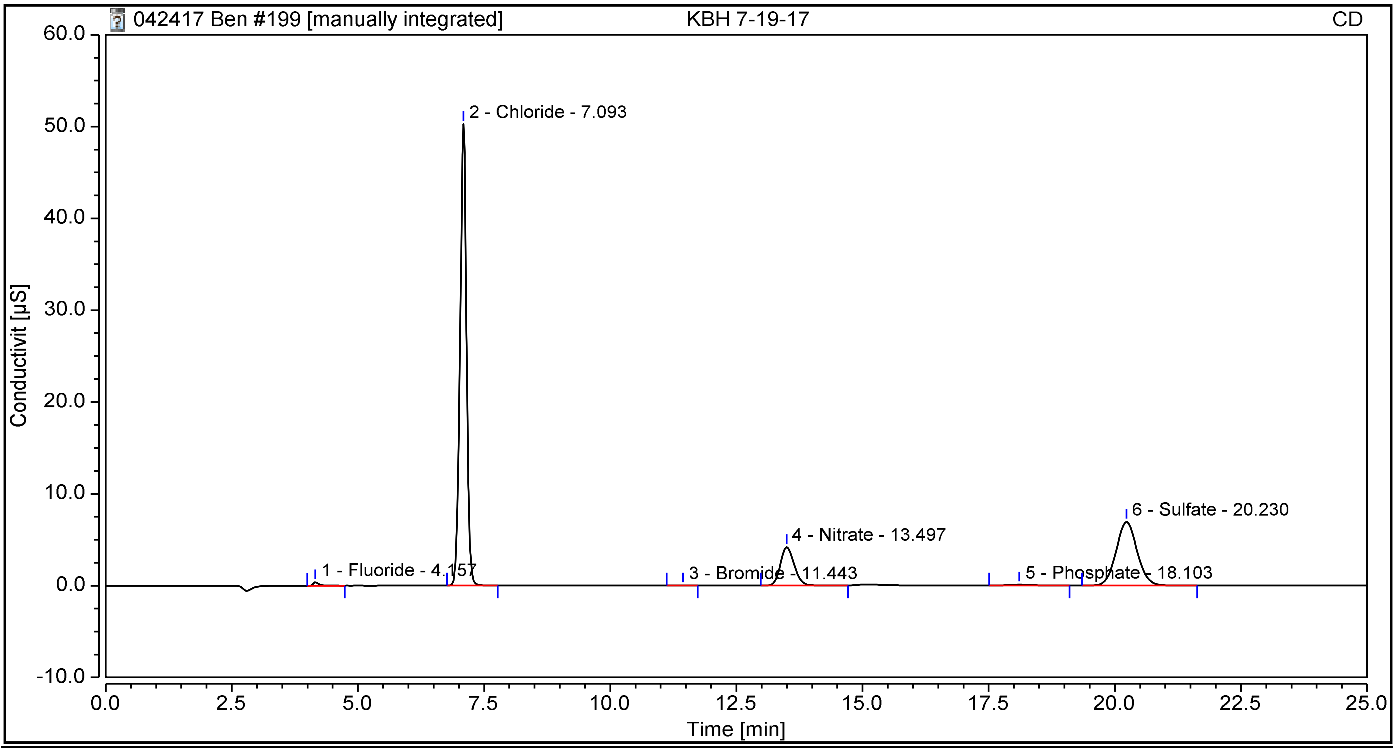
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.183	0.048	0.339	0.28	0.36	0.1859
2	Chloride	7.250	13.149	84.532	76.11	89.53	67.1180
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.670	0.001	0.005	0.01	0.01	0.0192
4	Nitrate	13.843	1.297	4.015	7.51	4.25	3.1134
5	Phosphate	18.670	0.051	0.101	0.29	0.11	1.3054
6	Sulfate	20.947	2.729	5.424	15.80	5.74	23.7712
Total:			**17.275**	**94.417**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**KBH 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**12**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 18:42**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.157	0.051	0.395	0.42	0.64	0.1968
2	Chloride	7.093	7.457	50.273	60.89	81.17	39.2202
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.443	0.002	0.007	0.02	0.01	0.0317
4	Nitrate	13.497	1.339	4.204	10.93	6.79	3.2119
5	Phosphate	18.103	0.052	0.103	0.42	0.17	1.3319
6	Sulfate	20.230	3.346	6.951	27.32	11.22	28.9435
Total:			**12.247**	**61.932**	**100.00**	**100.00**	

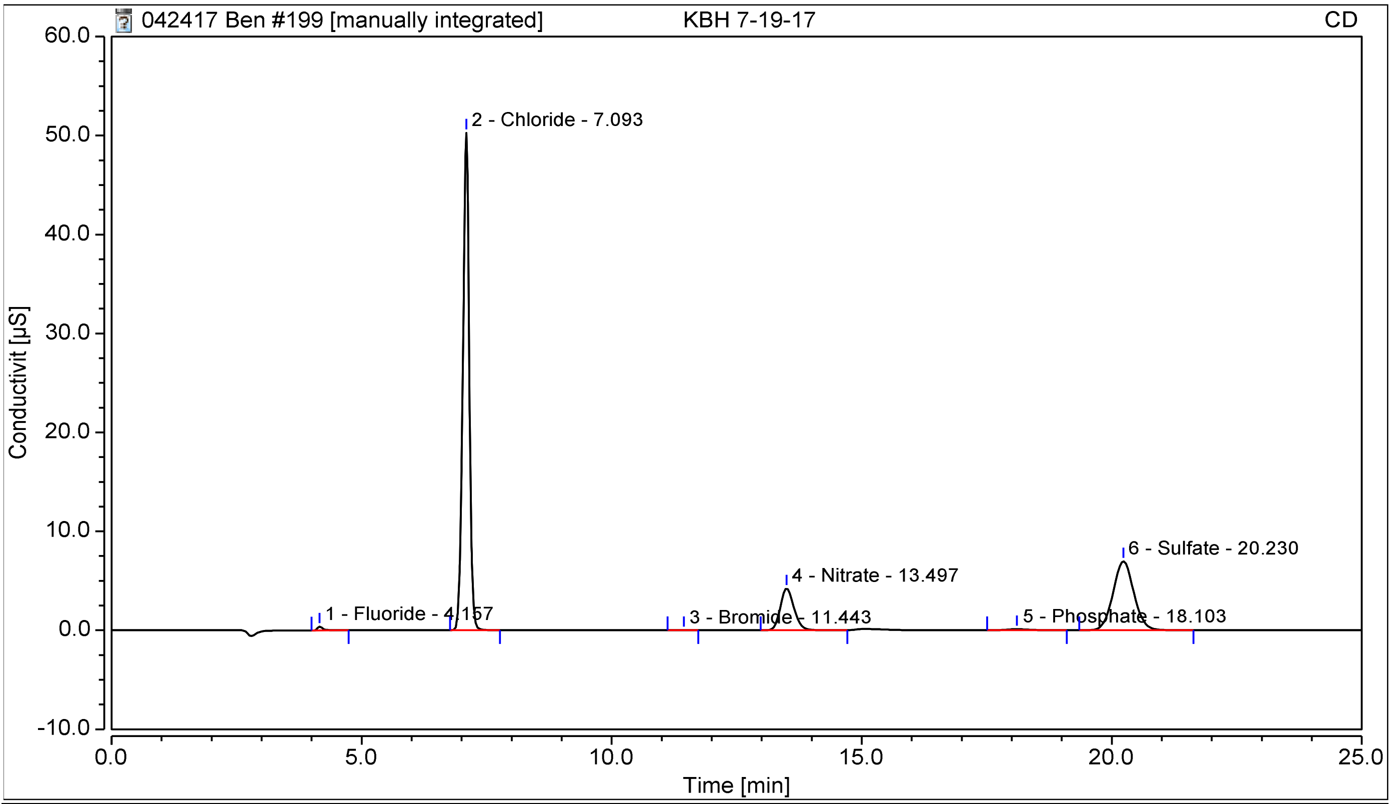
Chromeleon (c) Dionex
Version 7.2.4.8179

Chromatogram and SST Results

Injection Details

Injection Name:	**KBH 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**12**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 18:42**	*Sample Weight:*	**1.0000**

Chromatogram



SST Results

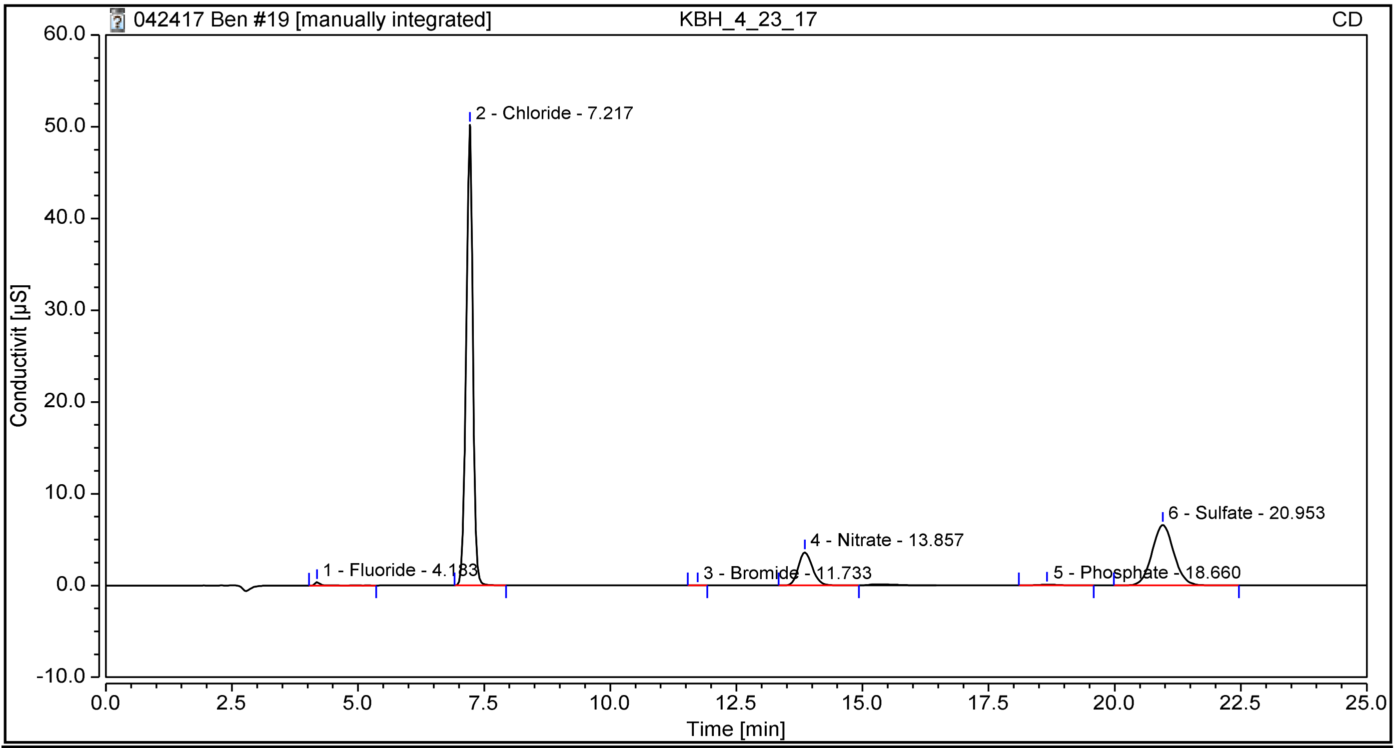
No.	Name	Inj.Condition	Peak	Test Result	Injection
Number of executed test cases:	**n.a.**		**Total Result:**	**Passed**	

Chromatogram and Results

Injection Details

Injection Name:	**KBH_4_23_17**	*Run Time (min):*	**25.00**
Vial Number:	**7**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**24/Apr/17 20:40**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

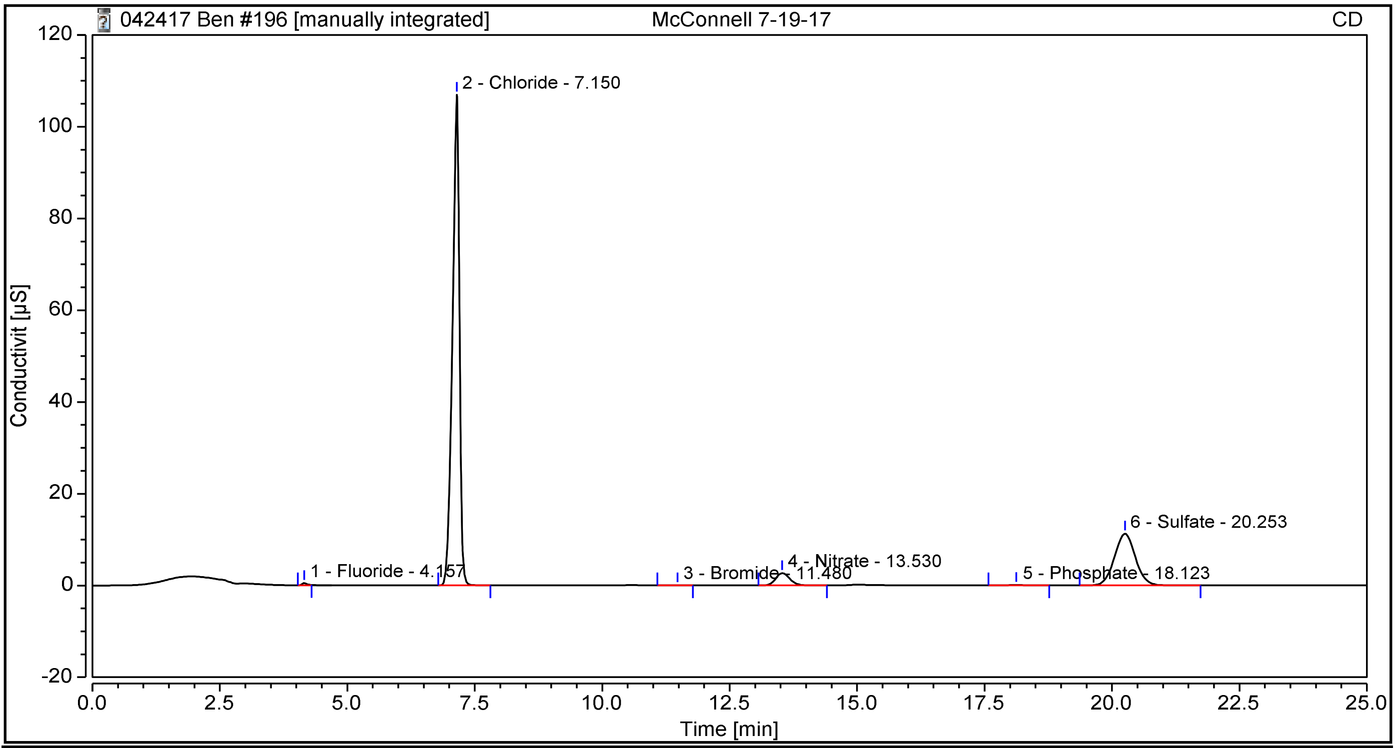
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.183	0.050	0.365	0.41	0.60	0.1940
2	Chloride	7.217	7.609	50.186	62.47	82.49	39.9847
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.733	0.001	0.006	0.01	0.01	0.0202
4	Nitrate	13.857	1.176	3.611	9.65	5.93	2.8241
5	Phosphate	18.660	0.043	0.086	0.36	0.14	1.1123
6	Sulfate	20.953	3.301	6.585	27.10	10.82	28.5740
Total:			**12.181**	**60.839**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**McConnell 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**9**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 17:21**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

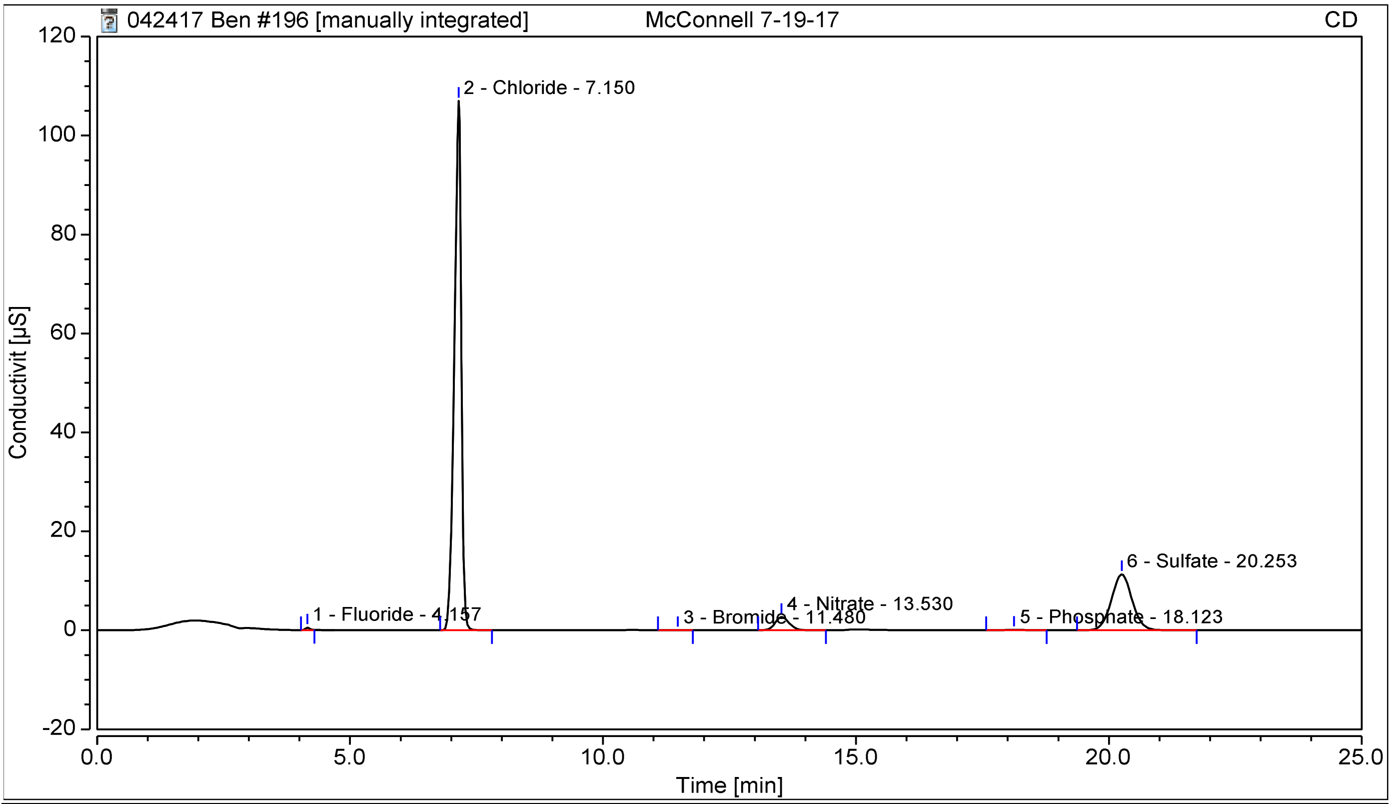
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.157	0.058	0.504	0.25	0.41	0.2250
2	Chloride	7.150	16.840	106.958	72.66	88.00	84.4179
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.480	0.005	0.019	0.02	0.02	0.0756
4	Nitrate	13.530	0.864	2.681	3.73	2.21	2.0786
5	Phosphate	18.123	0.035	0.074	0.15	0.06	0.9098
6	Sulfate	20.253	5.374	11.306	23.19	9.30	45.4698
Total:			**23.176**	**121.540**	**100.00**	**100.00**	

Chromatogram and SST Results

Injection Details

Injection Name:	**McConnell 7-19-17**	*Run Time (min):*	**25.00**
Vial Number:	**9**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 17:21**	*Sample Weight:*	**1.0000**

Chromatogram



SST Results

No.	Name	Inj.Condition	Peak	Test Result	Injection

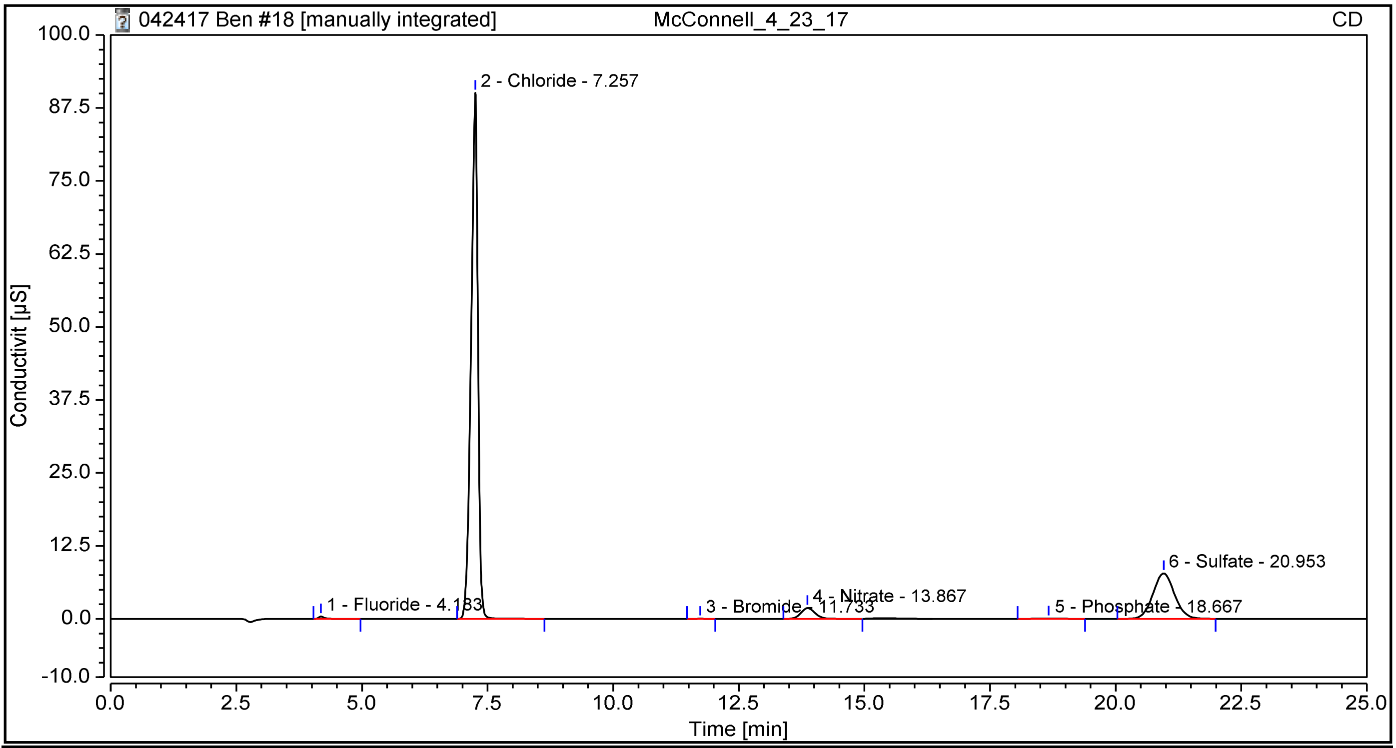
Number of executed test cases: **n.a.** **Total Result:** **Passed**

Chromatogram and Results

Injection Details

Injection Name:	**McConnell_4_23_17**	*Run Time (min):*	**25.00**
Vial Number:	**6**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**24/Apr/17 20:13**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

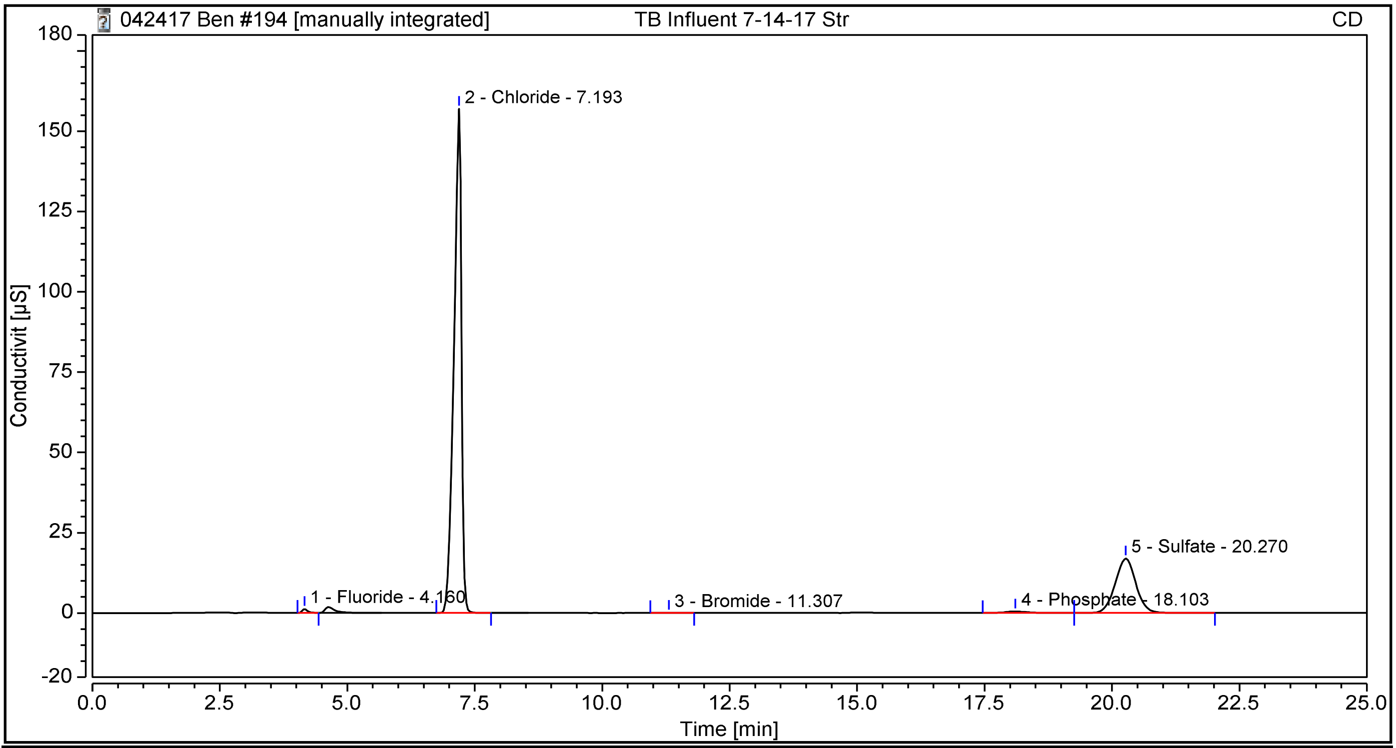
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.183	0.055	0.429	0.30	0.43	0.2129
2	Chloride	7.257	14.155	90.073	75.58	89.90	71.8895
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.733	0.003	0.011	0.02	0.01	0.0445
4	Nitrate	13.867	0.596	1.830	3.18	1.83	1.4369
5	Phosphate	18.667	0.030	0.060	0.16	0.06	0.7789
6	Sulfate	20.953	3.888	7.792	20.76	7.78	33.4284
Total:			**18.727**	**100.196**	**100.00**	**100.00**	

Chromatogram and Results

Injection Details

Injection Name:	**TB Influent 7-14-17 Str**	*Run Time (min):*	**25.00**
Vial Number:	**20**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 16:27**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

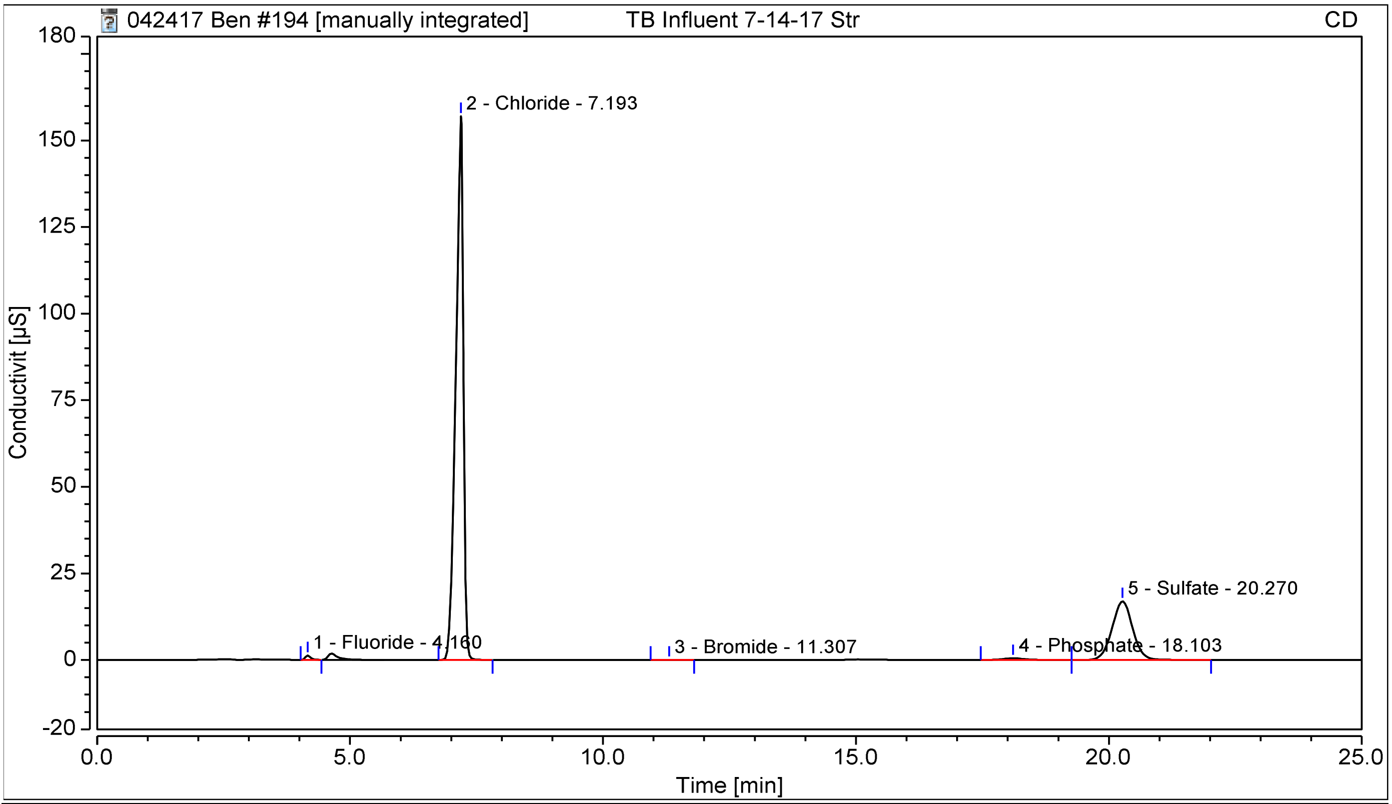
No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.160	0.151	1.244	0.43	0.71	0.5802
2	Chloride	7.193	27.018	156.943	76.32	89.36	129.4073
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.307	0.012	0.029	0.03	0.02	0.1852
n.a.	Nitrate	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4	Phosphate	18.103	0.233	0.469	0.66	0.27	5.9239
5	Sulfate	20.270	7.989	16.936	22.57	9.64	65.8218
Total:			**35.401**	**175.622**	**100.00**	**100.00**	

Chromatogram and SST Results

Injection Details

Injection Name:	**TB Influent 7-14-17 Str**	*Run Time (min):*	**25.00**
Vial Number:	**20**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**19/Jul/17 16:27**	*Sample Weight:*	**1.0000**

Chromatogram



SST Results

No.	Name	Inj.Condition	Peak	Test Result	Injection

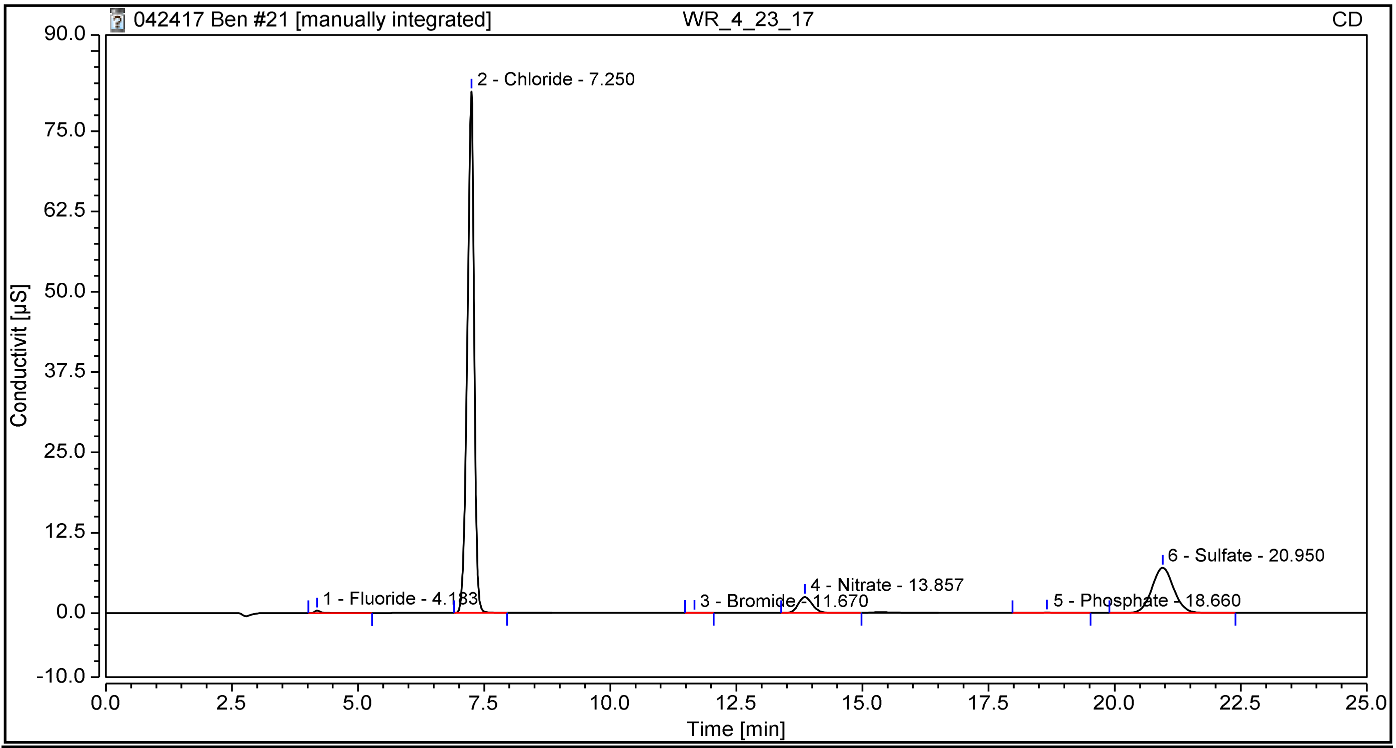
Number of executed test cases: **n.a.** **Total Result:** **Passed**

Chromatogram and Results

Injection Details

Injection Name:	**WR_4_23_17**	*Run Time (min):*	**25.00**
Vial Number:	**9**	*Injection Volume:*	**25.00**
Injection Type:	**Unknown**	*Channel:*	**CD**
Calibration Level:		*Wavelength:*	**n.a.**
Instrument Method:	**Carb_Bicarb_AS23_25min**	*Bandwidth:*	**n.a.**
Processing Method:	**Carb_Bicarb**	*Dilution Factor:*	**1.0000**
Injection Date/Time:	**24/Apr/17 21:33**	*Sample Weight:*	**1.0000**

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area µS*min	Height µS	Relative Area %	Relative Height %	Amount ppm
1	Fluoride	4.183	0.054	0.406	0.32	0.44	0.2081
2	Chloride	7.250	12.605	81.196	74.01	89.02	64.5186
n.a.	Nitrite	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
3	Bromide	11.670	0.003	0.008	0.01	0.01	0.0398
4	Nitrate	13.857	0.810	2.497	4.75	2.74	1.9491
5	Phosphate	18.660	0.027	0.052	0.16	0.06	0.6906
6	Sulfate	20.950	3.533	7.055	20.75	7.73	30.5016
Total:			**17.032**	**91.214**	**100.00**	**100.00**	