

Supplementary Data

Direct aqueous injection of the fluoroacetate anion in potable water for analysis by liquid chromatography tandem mass-spectrometry

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Table S1: Full gradient program

TIME	%A	%B	FLOW RATE (mL/min)	HPLC FLOW
0	95	5	0.5	Waste
1	95	5	0.5	
11	60	40	0.5	Instrument (10 to 21 min)
14	0	100	0.5	
19	0	100	0.5	
20	95	5	0.5	
21	80	20	1	Waste
24	0	100	1	
30	95	5	1	
30.5	95	5	0.5	Re-equilibration
32	95	5	0.5	

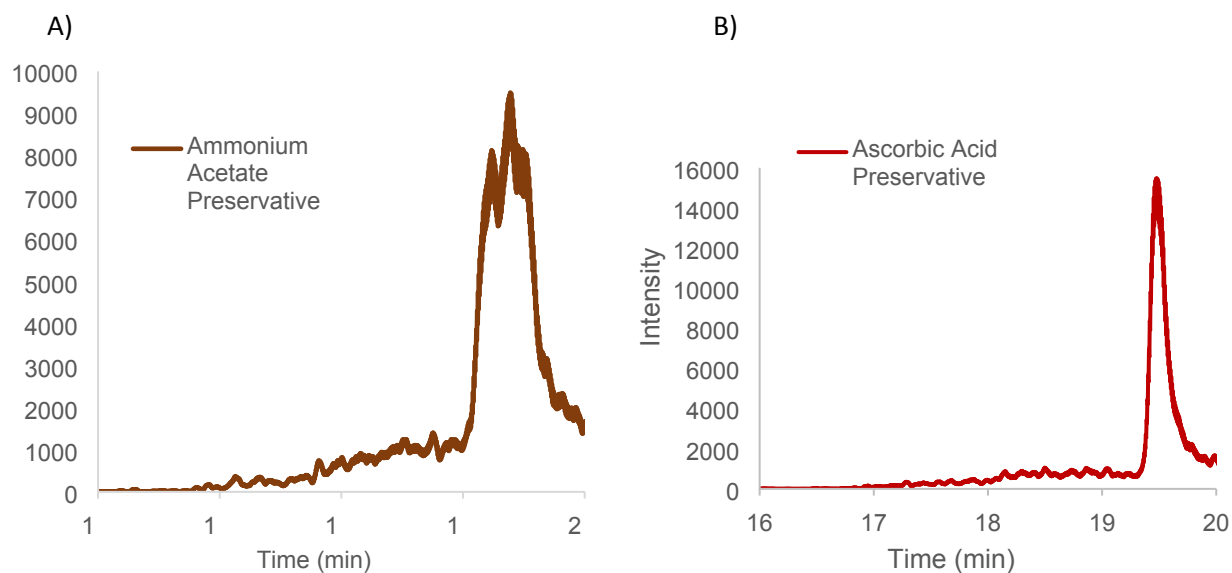


Figure S1: Effect of dechlorination agents on FAA chromatography. A) Extracted Ion Chromatogram (EIC) profile of mass 57.26 of a reagent water sample containing 20 mM ammonium acetate and 64 mg/L sodium omadine. B) EIC 57.26 of reagent water sample containing 250 mg/L ascorbic acid and 64 mg/L sodium omadine.

Table S2: Sample Filtration

Condition		Low Concentration <sup>a</sup>	High Concentration <sup>b</sup>
	Unfiltered	Average <sup>c</sup>	3.4
Std. dev.		0.84	2.22
RSD		25%	6%
Filtered	Average <sup>c</sup>	3.0	38.5
	Std. dev.	0.61	3.33
	RSD	20%	9%
<b>p-value<sup>d</sup></b>		0.25	0.29

<sup>a</sup>Low concentration = 4 µg/L

<sup>b</sup>High concentration = 40 µg/L

<sup>c</sup>n = 4

<sup>d</sup>One-tailed t-test,  $\alpha = 0.05$

*Discussion S1. Regression between conductivity and RT*

*Methods:* Retention times (RTs) were segregated by water type from four different water utilities (WS1-4) and averaged across all stability study samples. Conductivity was available for each water type and was natural log normalized for the regression analysis. Figure 2A shows the untransformed data.

WS	RT (std. dev)	Conductivity	Ln Conductivity
WS 1	19.44 (0.052)	348	2.541579
WS 2	19.44 (0.041)	287	2.4578
WS 3	19.14 (0.095)	1124	3.050766
WS 4	19.33 (0.086)	388	2.588832
<b>Regression</b>			
$\beta$	Std. Error	p-value	R <sup>2</sup>
-1.818	0.3122	0.0282	0.944

Table S3: Stability study represents four different water utility sources (WS) and reagent water (RW).

	Day 0	Day 1	Day 3	Day 7	Day 14	Day 21	Day 28/31 <sup>a</sup>
<b>RW Low<sup>1</sup> Average (µg/L)</b>	3.3	3.7	3.9	3.7	3.7	3.5	3.5
% RSD	5	9	6	8	11	5	12
% of day 0	ref	112	120	114	111	107	108
<b>RW High Average (µg/L)</b>	44.9	39.0	43.4	39.0	40.0	41.9	38.2
% RSD	8	3	6	13	8	4	13
% of day 0	ref	87	97	87	89	93	85
<b>WS 1 Low<sup>1</sup> Average (µg/L)</b>	3.9	3.9	3.3	4.3	3.7	3.5	3.5
% RSD	13	8	10	5	9	7	8
% of day 0	ref	101	86	110	94	89	91
<b>WS 1 High<sup>1</sup> Average (µg/L)</b>	41.1	39.5	36.9	39.0	41.8	38.0	44.2
% RSD	4	5	7	2	3	2	11
% of day 0	ref	96	90	95	102	92	107
<b>WS 2 Low<sup>1</sup> Average (µg/L)</b>	4.0	3.8	3.7	3.8	3.2	3.3	3.0
% RSD	15	7	2	10	15	10	26
% of day 0	ref	94	92	95	80	81	76
<b>WS 2 High<sup>1</sup> Average (µg/L)</b>	41.5	39.2	37.6	40.2	38.3	36.8	45.3
% RSD	2	4	1	4	1	4	8
% of day 0	ref	94	91	97	92	89	109
<b>WS 3 Low Average (µg/L)</b>	4.0	3.6	2.5	3.1	3.0	3.1	2.4
% RSD	5	13	13	6	33	14	15
% of day 0	ref	89	63	76	74	78	59
<b>WS 3 High Average (µg/L)</b>	40.3	38.5	36.2	40.0	38.4	44.4	44.2
% RSD	11	3	3	9	8	9	3
% of day 0	ref	96	90	99	95	110	110
<b>WS 4 Low Average (µg/L)</b>	4.00	3.99	3.94	4.02	3.97	3.52	3.58
% RSD	1	10	21	11	20	9	29
% of day 0	ref	100	99	101	99	88	90
<b>WS 4 High Average (µg/L)</b>	40.6	37.3	36.6	41.3	37.4	39.8	37.4
% RSD	3%	2%	5%	6%	3%	2%	5%
% of day 0	ref	92%	90%	102%	92%	98%	92%

<sup>a</sup> Final measurement was conducted after 31 days

All values are calculated from three replicates.

RSD = relative standard deviation.

Ref = Day 0 was the comparison value, so recovery is considered 100%.

Table S4: Calibration curve concentrations for fluoroacetate (FAA) and fluoroacetate internal standard (FAA\_L).

Calibration Solution Name	Source Solution	Source Solution Volume (µL)	2.5 g/L Ascorbic Acid Solution Volume (µL)	3.2 g/L Sodium Omadine Solution (µL)	2.5 mg/L FAA_L Standard Solution (µL)	Final Volume of Solution (mL)	Nominal Calibration Solution Conc. (µg/L)
CAL 1	0.05 mg/L FAA	20	100	20	10	1	1
CAL 2	0.05 mg/L FAA	40	100	20	10	1	2
CAL 3	0.05 mg/L FAA	80	100	20	10	1	4
CAL 4	0.05 mg/L FAA	160	100	20	10	1	8
CAL 5	1 mg/L FAA	12	100	20	10	1	12
CAL 6	1 mg/L FAA	20	100	20	10	1	20
CAL 7	1 mg/L FAA	40	100	20	10	1	40
CAL 8	1 mg/L FAA	60	100	20	10	1	60
CAL 9	1 mg/L FAA	100	100	20	10	1	100

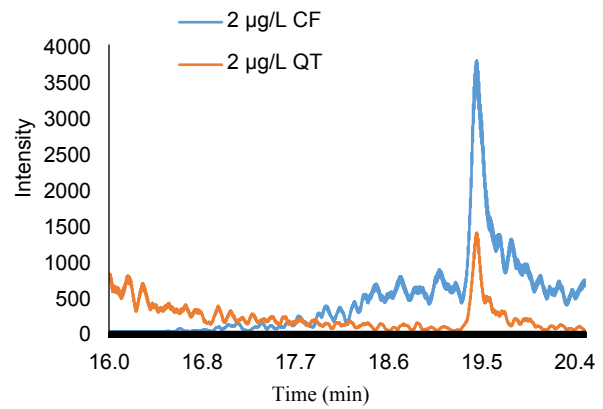
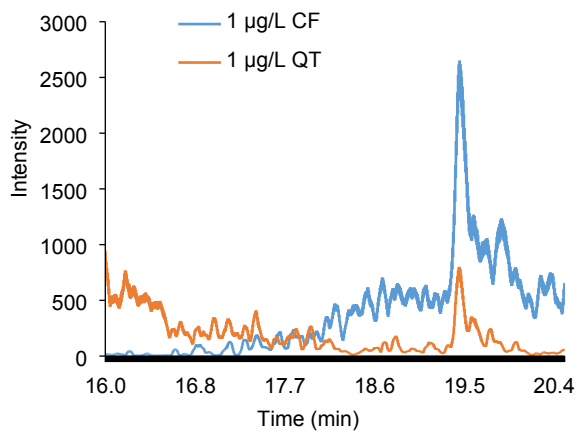
FAA detection limit was determined from seven replicates of samples at the CAL 3 level, with batches prepared over three days. The DL was calculated to be 0.4 µg/L, using a t value of 3.143 for n=7. The DL calculation is presented in Table S5. The MRL was determined from seven replicates of samples at the CAL 2 level. The HR<sub>PIR</sub> was determined to be 0.65 µg/L. Based on this result, the lower PIR was calculated to be 57.0% and the upper PIR to be 122%. These values meet both the upper and lower PIR limit requirements of ≤ 150% for the upper PIR and ≥ 50% for the lower PIR. The MRL confirmation is shown in Table S6. Representative chromatograms of both 1 µg/L and 2 µg/L, the MRL, are shown in Figure S2.

Table S5: DL Calculation

Sample	Nominal Concentration (µg/L)	Determined Concentration (µg/L)
DL CAL 3 Day 1		4.2
DL CAL 3 Day 2		4.1
DL CAL 3 Day 2		3.8
DL CAL 3 Day 2	4	4.2
DL CAL 3 Day 3		4.0
DL CAL 3 Day 3		4.1
DL CAL 3 Day 3		4.0
	Average	4.0
	s	0.13
	Calculated DL	0.4

**Table S6: Half-Range Prediction Interval Calculation**

Sample Name	Nominal Concentration Level ( $\mu\text{g/L}$ )	Determined Concentration ( $\mu\text{g/L}$ )
DL CAL 2_1	2	1.7
DL CAL 2_2		2.0
DL CAL 2_3		2.0
DL CAL 2_4		1.7
DL CAL 2_5		1.6
DL CAL 2_6		1.9
DL CAL 2_7		1.6
	<b>Average</b>	1.8
	<b>s</b>	0.2
	<b>HR<sub>PIR</sub></b>	0.65



**Figure S2: Low Standard Chromatograms for FAA**