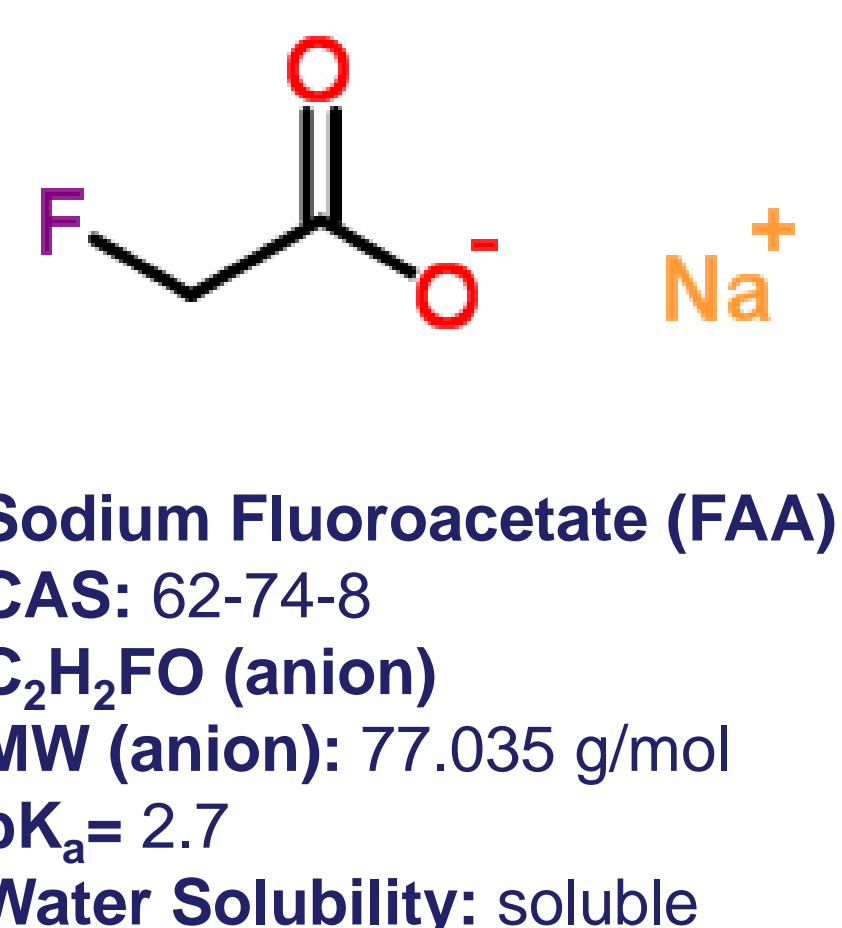


Introduction

In case of any large scale contamination incident, the US Environmental Protection Agency's (EPA) Homeland Security Research Program (HSRP) has developed the *Selected Analytical Methods for Environmental Remediation and Recovery (SAM)* document (<https://www.epa.gov/homeland-security-research/sam>) to provide recommended analysis methods for priority chemicals, radioisotopes, pathogens, and biotoxins in environmental matrices. SAM will assist in characterization and remediation following any large scale incident. Sodium fluoroacetate (FAA) is included in SAM but lacks an updated, verified analytical method for water. It has also been identified by other federal agencies as a compound of concern.

FAA, sometimes called Compound 1080, is a water soluble, acute mammalian pesticide. Its historical uses in the U.S. include rodent control and "toxic collars" worn by livestock to protect against predators such as wolves and coyotes. Most prominently, it is used in New Zealand for aerial control of possums. New Zealand faces unique pest control challenges with native ecosystems threatened by introduced possums. No natural predators are present with only two mammals (both species of bats) indigenous to the islands. Use of fluoroacetate as pest control in New Zealand has been controversial, culminating in an eco-terrorist threat to contaminate infant formula with FAA if its use was not stopped by March 2015. Fortunately, no contamination was detected, however the threat is still possible in any country.



Objective: Develop an analytical method to analyze FAA in water samples to assist local, state, and federal authorities in any large scale environmental response or remediation effort.

Method Considerations

Historically, FAA was analyzed by gas chromatography requiring time-consuming derivatization steps. Recent publications have taken advantage of liquid chromatography mass spectrometry (LC-MS) and highlighted methods for FAA in infant formula (Bessaire et al., 2015) and urine (Hamelin et al., 2010). Both methods require sample preparation steps. Drinking water is a less complex matrix and analysis time could be further reduced by the development of a direct aqueous injection (DAI) method.

In support of a large scale environmental response, EPA's HSRP supports emergency response by selecting methods that utilize **widely available equipment** and are able to be **high throughput** to ensure lab capability and capacity are possible.

Table 1. Fluoroacetate risk and toxicity values.

Parameter	Value	Source
EPA Reference Dose	0.00002 mg/kg/day	EPA 738-R-95-025 (1995)
LD ₅₀	2-5 mg/kg	Cited in Eason, et al., (2011)
EPA Regional Screening Levels (May 2016)	0.4 µg/L	https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables-may-2016

Method



Sample Preservation and Preparation

- Sample Preservation:
 - Ascorbic acid (dechlorination)
 - Sodium omadine (anti-microbial)
- Filtration with PDVF 0.22 µm filter
- Addition of labeled internal standard (IS)¹³C₂-Fluoroacetate

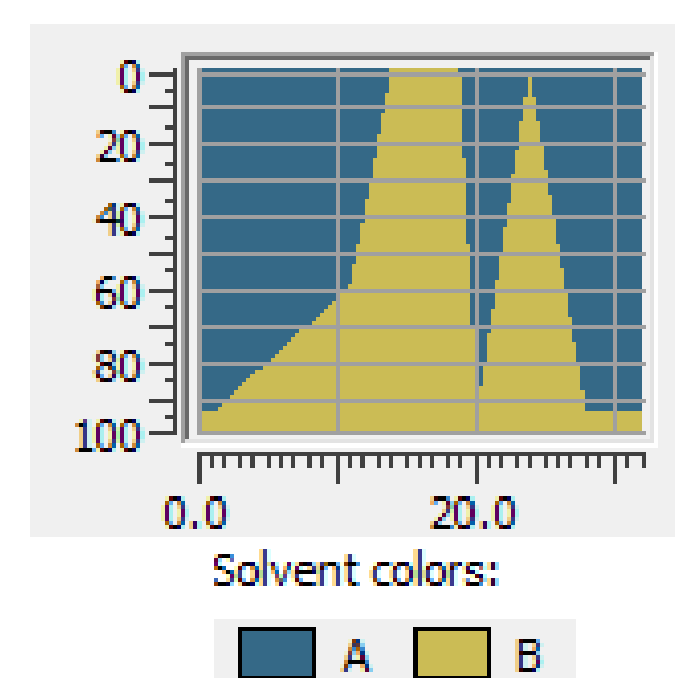


Figure 1. Gradient Diagram

Gradient elution

A: 0.005% Acetic Acid in water
B: 0.005% Acetic Acid in acetonitrile
Column: Sunfire™ C8 (150 mm x 4.5 mm, 5 µm)
Flow rate: 0.5 mL/min
Solvent Divert: 10 minutes
Retention Time: 19.4 minutes
Runtime: 32 minutes

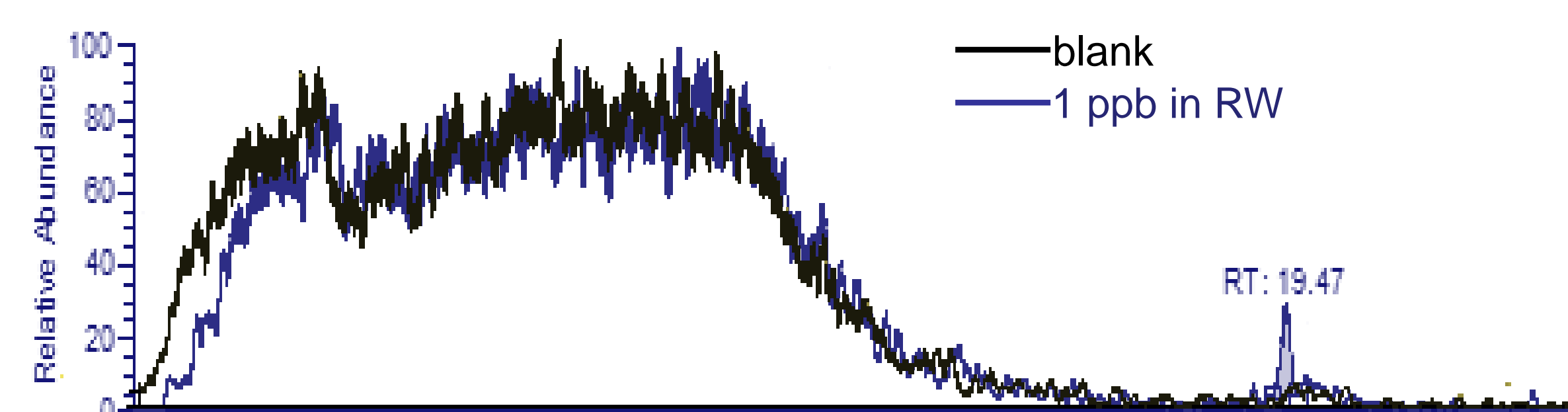
Table 2. Mass spectrometer parameters

Mass Spectrometer Parameters		
Polarity	ESI-	
Source Temperature	275 °C	
Capillary	3.3 kV	
Collision Energy	14 eV	
MS Dwell Time	100 ms	
Compound	Transition reactions (m/z)	
Compound	Quantification	Analyte Confirmation
Fluoroacetate (FAA)	76.97 > 56.96	76.97 > 32.98
¹³ C ₂ -Fluoroacetate (IS)	80.95 > 36.13	80.95 > 59.9



Thermo Accela HPLC
Thermo Quantum TSQ

Method Performance



Extracted chromatogram 1. Low standard in Reagent Water (RW) (blue) and blank water (black).

Table 3. Method limit of detection and range.

Analytical Parameter	Concentration (µg/L)
Method Limit of Detection (reagent water)	0.41
Linear Dynamic Range	1 – 100

The limit of detection (LOD) was determined by the standard deviation of the injection of 7 low-level, fortified reagent water (RW) replicates over the course of 3 days. The LOD was calculated as 0.4 ppb in reagent water. The primary degradation pathway appears to be biologically mediated processes (Northcott, et al. 2014) and has been stated to be chlorine resistant (EPA, 2012).

Method Performance continued

Water Sources and Parameters

Treated water was obtained from the following sources

- Reagent Water (RW) – Optima™ LC/MS Grade
- Water Source 1 (WS 1) – chlorinated drinking water, low organic content
- Water Source 2 (WS 2) – chlorinated drinking water, high organic content

Table 4. Water Sample Parameters

Parameter	WS 1	WS 2
pH	8.8	9.35
Turbidity (NTU)	0.05	0.27
Conductivity	287	348
Alkalinity (mg/L)	63	76
Hardness (mg/L)	114	76
Free Chlorine (mg/L)	1.3	0.03
Total Organic Content (mg/L)	1.13	7.85

Table 5. Method accuracy & precision

Water Source	Parameter	Accuracy & Precision
RW (n=7, 12 ppb)	Average	11.7
	Std. Dev	0.40
	Precision (RSD)	3.4%
	Accuracy (% RE)	2.5%
WS 2 (n=10, 10 ppb)	Average	9.9
	Std. Dev	0.87
	Precision	9%
	Accuracy (% RE)	1.1%

% RE= Relative Error; WS 1 results are pending

Table 6. FAA stability in RW and WS 1 with preservatives.

Day	Reagent Water + Preservatives			WS 1+ Preservatives		
	% Recovery	Standard deviation	% RSD	% Recovery	Standard deviation	% RSD
1	87%	3.6	8%	83%	4.7	12%
3	97%	1.0	3%	83%	1.6	3%
7	87%	2.8	6%	67%	4.4	14%
14	89%	5.0	13%	88%	9.9	24%
21	92%	2.7	7%	78%	4.4	12%
28	85%	2.0	5%	83%	0.4	1%

*n=3 at each time point; WS 2 results are pending.

Conclusions & Future Work

Initial demonstration of capability was evaluated with chromatographic separation on a Sunfire™ C8 column. Two identified fragments serve as quantitation and qualification ions for FAA. Quantitative analysis was completed by isotope dilution with a labeled internal standard. The LOD was in the low ppb range, similar to the recommended screening levels.

FAA appeared to be stable with/without (data not shown) preservatives over 30 days when stored at 4°C. Accuracy and precision were consistent across different water types. Future work will include additional stability studies with different water types.

References

- Bessaire, T., Tarres, A., Goyon, A., Mottier, P., Dubois, M., Tan, W.P., Delatour, T., 2015. Quantitative determination of sodium monofluoroacetate "1080" in infant formulas and dairy products by isotope dilution LC-MS/MS. *Food Addit. Contam. A* 32(11) 1885-1892.
- Eason, C., Miller, A., Ogilvie, S., Fairweather, A., 2011. An updated review of the toxicology and ecotoxicology of sodium fluoroacetate (1080) in relation to its use as a pest control tool in New Zealand. *New Zeal. J. Ecol.* 35 (1), 1-20.
- Environmental Protection Agency. (2012). Chemical Contaminant Persistence and Decontamination in Drinking Water Pipes (EPA publication No. 600/R/12/514). Washington DC: U.S. Environmental Protection Agency.
- Environmental Protection Agency. (1995). Reregistration eligibility decision Sodium Fluoroacetate. (EPA publication No. 738-R-95-025). Washington DC: U.S. Environmental Protection Agency.
- Hamelin, E.I., Mawhinney, D.B., Parry, R., Kobelski, R.J., 2010. Quantification of monofluoroacetate and monochloroacetate in human urine by isotope dilution liquid chromatography tandem mass spectrometry. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* 878, 1045-1050.
- Northcott, G., Jensen, D., Ying, L., Fisher, P., 2014. Degradation rate of sodium fluoroacetate in three New Zealand soils. *Environ. Toxicol. Chem.* 33 (5) 1048-1058.

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