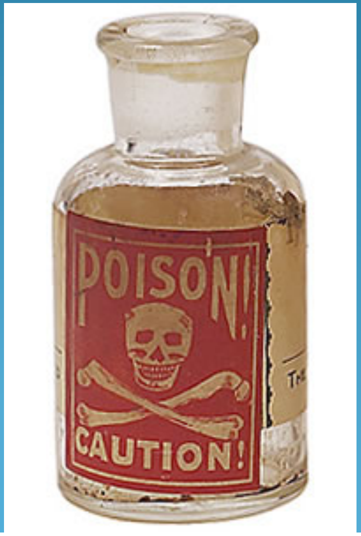
"Reliable Determination of Cyanide in Water—a Modest Proposal"

Mike Delaney and Chuck Blodget

Massachusetts Water Resources Authority (MWRA)



Reliable Determination of Cyanide in Water—a Modest Proposal

- Reliable determination of cyanide in water samples is important.
- Cyanide's diverse chemistry is problematic.
- A variety of chemical mechanisms can form or destroy cyanide. Some of these can occur within the sample container or during laboratory pretreatment and analysis, leading to biased results.
- Interferences can bias results high or low.
- *"There may be interferences that are not mitigated*"—EPA 2012 MUR.

MWRA
Deer Island Treatment Plant

Background: Cyanide Formation in Wastewater

- In 1997, we summarized our observations and experiments on cyanide determination in POTW wastewater. (WEF 1997: Delaney, *et al.* "Cyanide Formation from Chlorinated POTW Effluent", Proceedings of the "Environmental Laboratories" WEF Conference, Philadelphia, PA, August 1997.)
- In 1999, we amplified on this work: (WEFTEC 1999. Case Study: MWRA, Delaney, *et al.*)
  - Apparent cyanide formation in chlorinated wastewater is fairly common.
  - Negative amenable cyanide results are not unusual.
  - Is cyanide really forming or is it an interference?
  - Dechlorinating with ascorbic acid can be problematic.

Drinking Water

- Test DW treatment plant effluent for cyanide.
- "Detected Contaminants" (above the Lab's Reporting Limit) must be reported in the Consumer Confidence Report.
- In 2005 when our new plant came on line, we encountered some total cyanide detects. (10 hits in 50 samples.)
- These turned out to be false cyanide forming in the sample container ("false positives").
- Since 2007 we have been distilling quarterly samples on-site at CWTP to avoid false positives.

John J. Carroll Water Treatment Plant

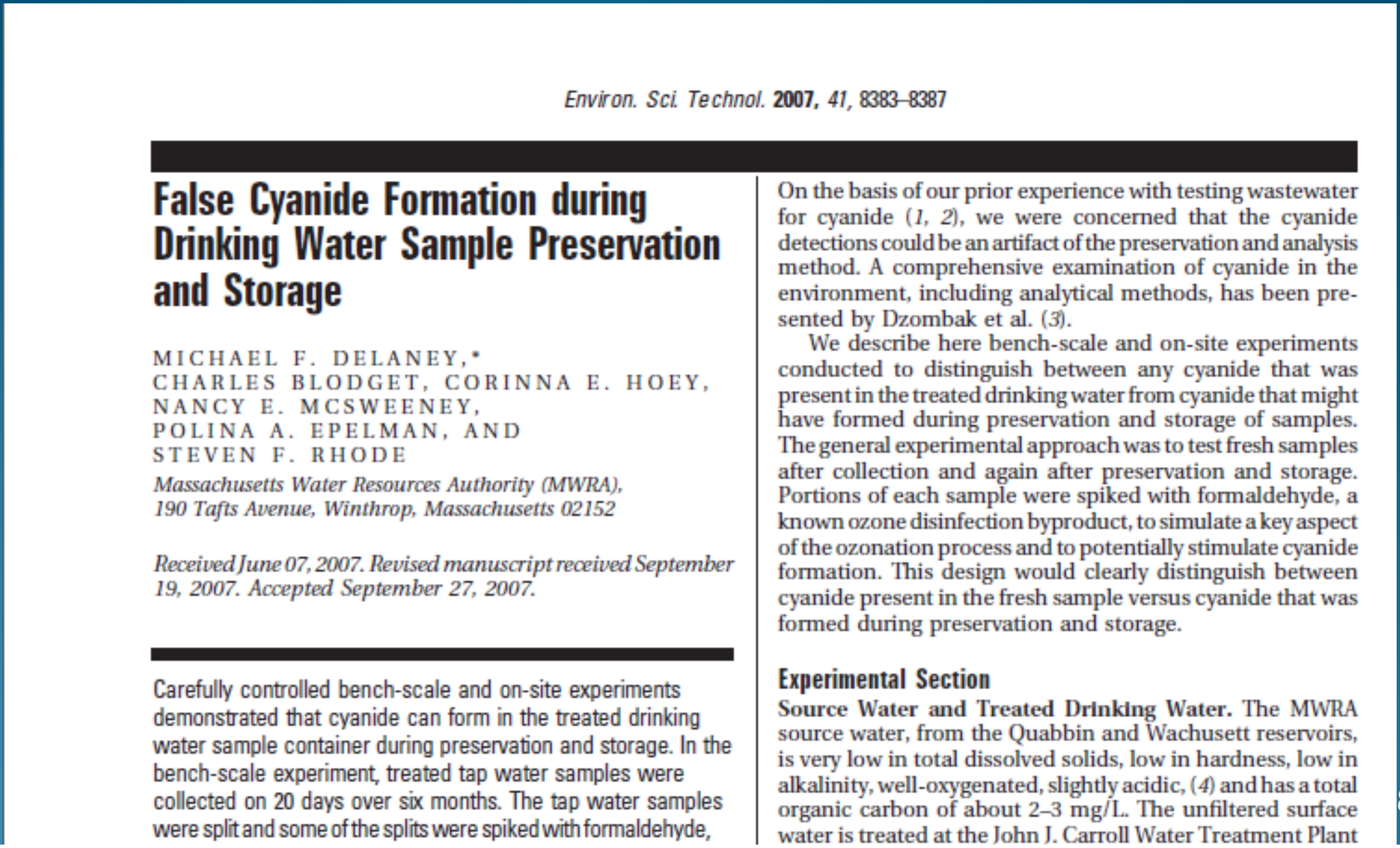
John J. Carroll Water Treatment Plant

Ozone

UV

False Cyanide Formation during Drinking Water Sample Preservation and Storage

- 2007, **Environmental Science and Technology**.
- Carefully controlled bench-scale and on-site experiments demonstrated that cyanide can form in the treated drinking water sample container during preservation and storage.



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False Cyanide Formation during Drinking Water Sample Preservation and Storage

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Carefully controlled bench-scale and on-site experiments demonstrated that cyanide can form in the treated drinking water sample container during preservation and storage. In the bench-scale experiment, treated tap water samples were collected on 20 days over six months. The tap water samples were split and some of the splits were spiked with formaldehyde,

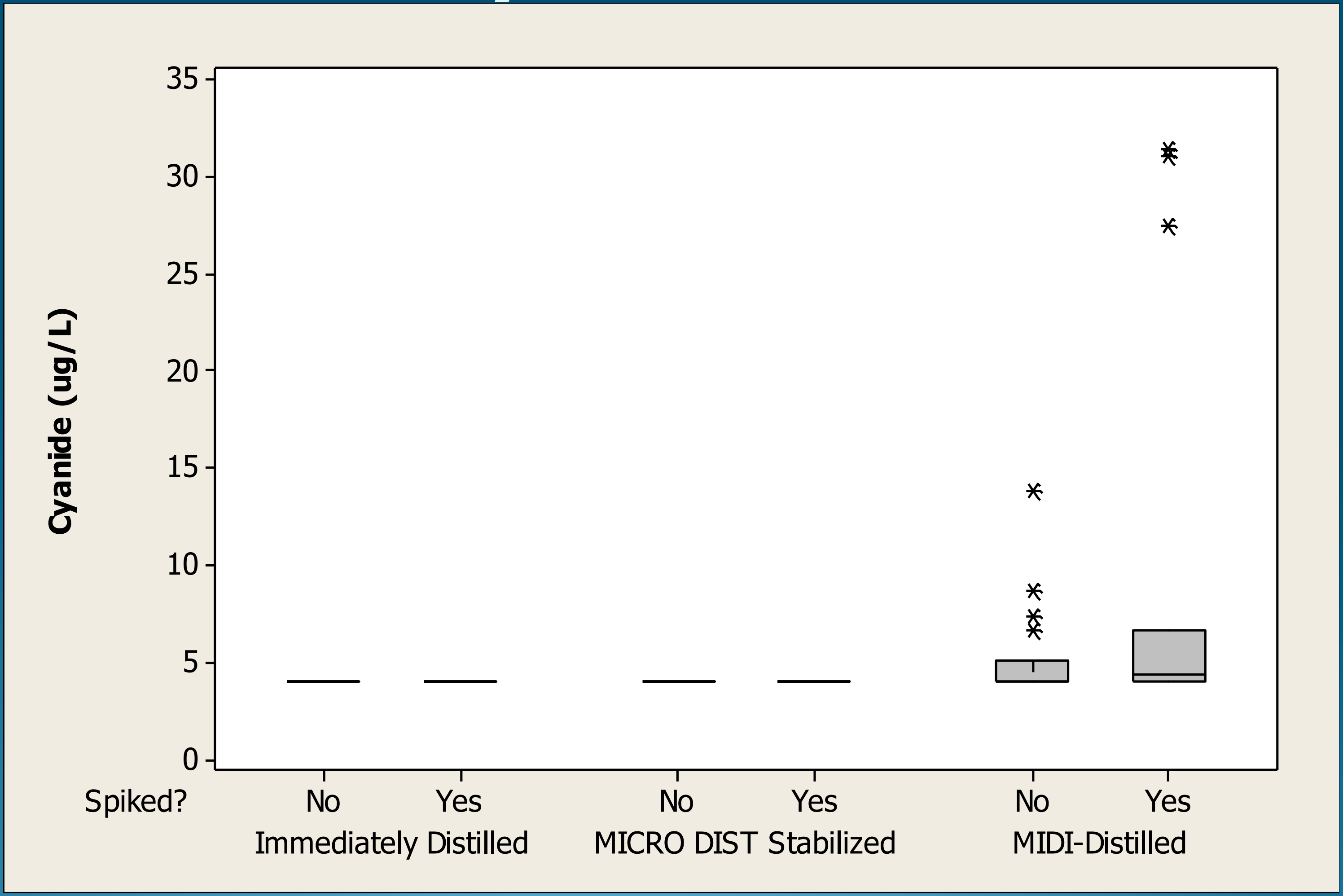
On the basis of our prior experience with testing wastewater for cyanide (*1*, *2*), we were concerned that the cyanide detections could be an artifact of the preservation and analysis method. A comprehensive examination of cyanide in the environment, including analytical methods, has been presented by Dzombak et al. (*3*).

We describe here bench-scale and on-site experiments conducted to distinguish between any cyanide that was present in the treated drinking water from cyanide that might have formed during preservation and storage of samples. The general experimental approach was to test fresh samples after collection and again after preservation and storage. Portions of each sample were spiked with formaldehyde, a known ozone disinfection byproduct, to simulate a key aspect of the ozonation process and to potentially stimulate cyanide formation. This design would clearly distinguish between cyanide present in the fresh sample versus cyanide that was formed during preservation and storage.

Experimental Section

Source Water and Treated Drinking Water. The MWRA source water, from the Quabbin and Wachusett reservoirs, is very low in total dissolved solids, low in hardness, low in alkalinity, well-oxygenated, slightly acidic, (*4*) and has a total organic carbon of about 2–3 mg/L. The unfiltered surface water is treated at the John J. Carroll Water Treatment Plant

NaOH causes Cyanide to form; Formaldehyde makes it worse.



Outcome: On-Site Distillation without NaOH.

Wastewater:
2007 EPA Method Update Rule

- Faced with the difficulties of getting accurate and precise results for total cyanide in wastewater, the 2007 EPA CWA Method Update Rule detailed the voluminous and proscriptive required procedures for testing and treating for potential cyanide positive and negative interferences.

2007 Cyanide Footnote, page 1

- This Footnote goes on for 7 pages!
- Add a reducing agent only if an oxidant (e.g., chlorine) is present. Reducing agents shown to be effective are sodium thiosulfate ($Na_2S_2O_3$), ascorbic acid, sodium arsenite ($NaAsO_2$), or sodium borohydride ($NaBH_4$). However, some of these agents have been shown to produce a positive or negative cyanide bias, depending on other substances in the sample and the analytical method used. Therefore, do not add an excess of reducing agent. Methods recommending ascorbic acid (e.g., EPA Method 335.4) specify adding ascorbic acid crystals, 0.1 - 0.6 g, until a drop of sample produces no color on potassium iodide (KI) starch paper, then adding 0.06 g (60 mg) for each liter of sample volume. If $NaBH_4$ or $NaAsO_2$ is used, 25 mg/L $NaBH_4$ or 100 mg/L $NaAsO_2$ will reduce more than 50 mg/L of chlorine (see method "Kelada-01" and/or Standard Method 4500-CN^- for more information). After adding reducing agent, test the sample using KI paper, a test strip (e.g. for chlorine, SenSafe™ Total Chlorine Water Check 480010) moistened with acetate buffer solution (see Standard Method 4500-Cl.C.3e), or a chlorine/oxidant test method (e.g., EPA Method 330.4 or 330.5), to make sure all oxidant is removed. If oxidant remains, add more reducing agent. Whatever agent is used, it should be tested to assure that cyanide results are not affected adversely.

2012 EPA Method Update Rule

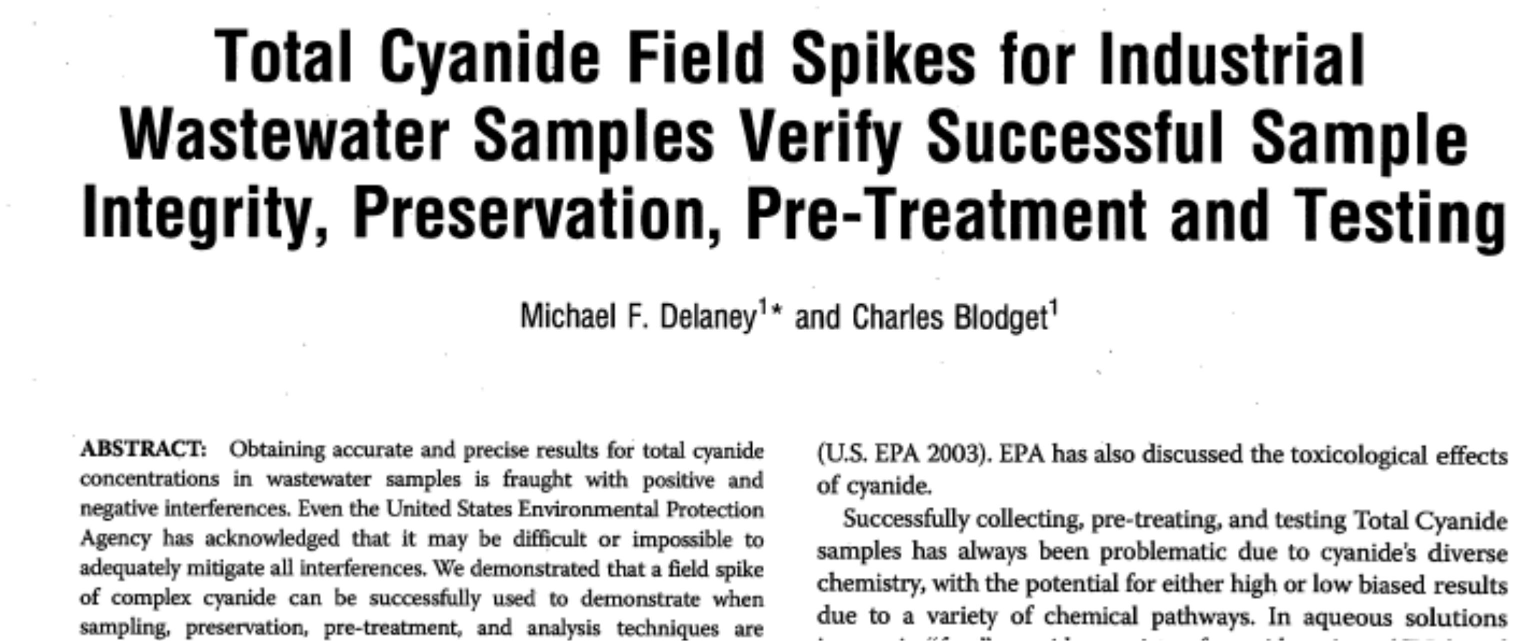
- Revised footnote for cyanide preservation:
  - *"There may be interferences that are not mitigated …any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method."*
- Use ASTM D7365–09a.

How do you do this?

- “Quality Control in the method” is generally lab-based QC:
  - Method Blank
  - Laboratory Control Sample
  - Duplicate or Matrix Spike/Matrix Spike Duplicate.
- Lab QC doesn’t address field sampling, preservation, transport, and storage.
- What about using Field Spikes?
- A Field Spike will indicate whether cyanide is gained or lost.

2015 Field Spike Paper

- A Field Spike of complex cyanide can be successfully used to demonstrate when sampling, preservation, pre-treatment, and analysis techniques are working adequately to retain any cyanide present in the sample without causing false positives or false negatives.
- The Field Spike approach is general and should also work in a similar manner for raw and treated drinking water samples.
- **Water Environment Research**, June 2015.



Total Cyanide Field Spikes for Industrial Wastewater Samples Verify Successful Sample Integrity, Preservation, Pre-Treatment and Testing

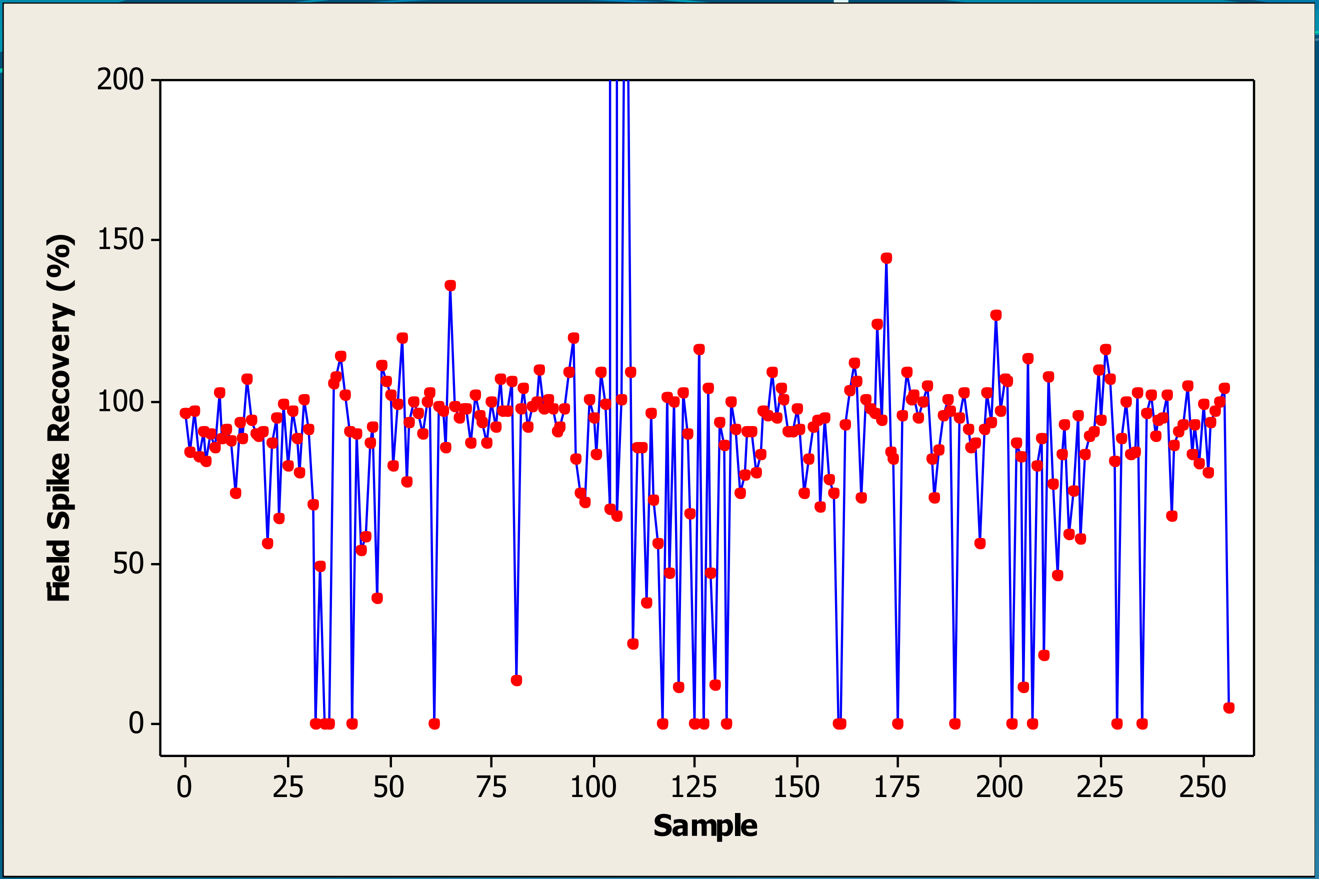
Michael F. Delaney[1]* and Charles Blodget[1]

ABSTRACT: Obtaining accurate and precise results for total cyanide concentrations in wastewater samples is fraught with positive and negative interferences. Even the United States Environmental Protection Agency has acknowledged that it may be difficult or impossible to adequately mitigate all interferences. We demonstrated that a field spike of complex cyanide can be successfully used to demonstrate when sampling, preservation, pre-treatment, and analysis techniques are

(U.S. EPA 2003). EPA has also discussed the toxicological effects of cyanide.

Successfully collecting, pre-treating, and testing Total Cyanide samples has always been problematic due to cyanide's diverse chemistry, with the potential for either high or low biased results due to a variety of chemical pathways. In aqueous solutions

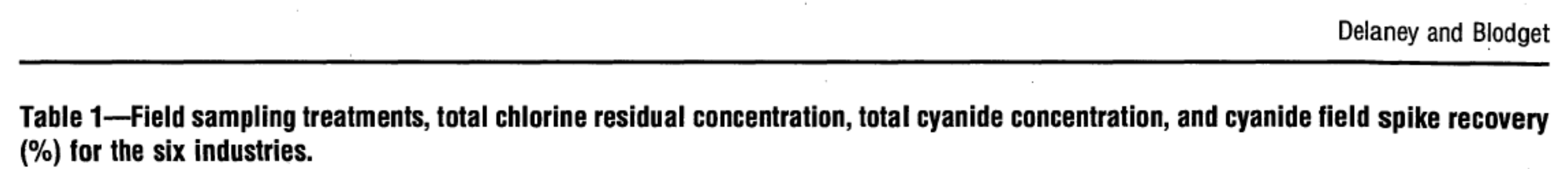
Field Spike Results



Deflated!

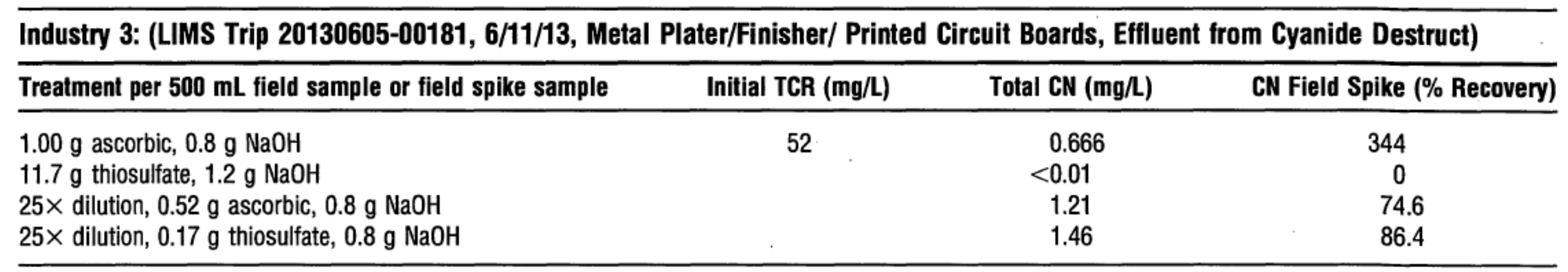
For 257 industrial wastewater effluent samples collected at a wide variety of Greater Boston industries, 237 (92.2%) had usable field spike recoveries, averaging 86.2% recovery.

Field Dilution as a treatment for matrix interferences (a solution to pollution)



Delaney and Blodget

Table 1—Field sampling treatments, total chlorine residual concentration, total cyanide concentration, and cyanide field spike recovery (%) for the six industries.



Industry 3: (LIMS Trip 20130605-00181, 6/11/13, Metal Plater/Finisher/ Printed Circuit Boards, Effluent from Cyanide Destruct)

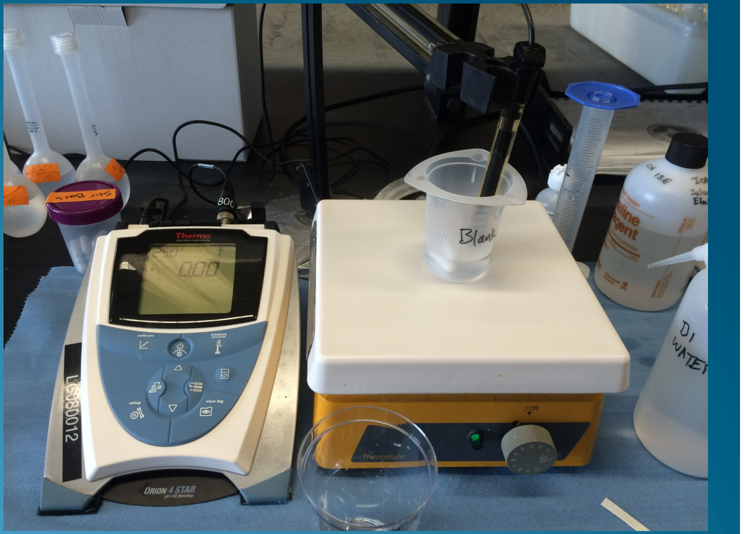
Treatment per 500 mL field sample or field spike sample	Initial TCR (mg/L)	Total CN (mg/L)	CN Field Spike (% Recovery)
1.00 g ascorbic, 0.8 g NaOH	52	0.666	344
11.7 g thiosulfate, 1.2 g NaOH		<0.01	0
25× dilution, 0.52 g ascorbic, 0.8 g NaOH		1.21	74.6
25× dilution, 0.17 g thiosulfate, 0.8 g NaOH		1.46	86.4

Field Spike recoveries for problematic industries that had very high or very low Field Spike recoveries showed when alternative preservations and Field Dilutions were successfully preserving total cyanide.

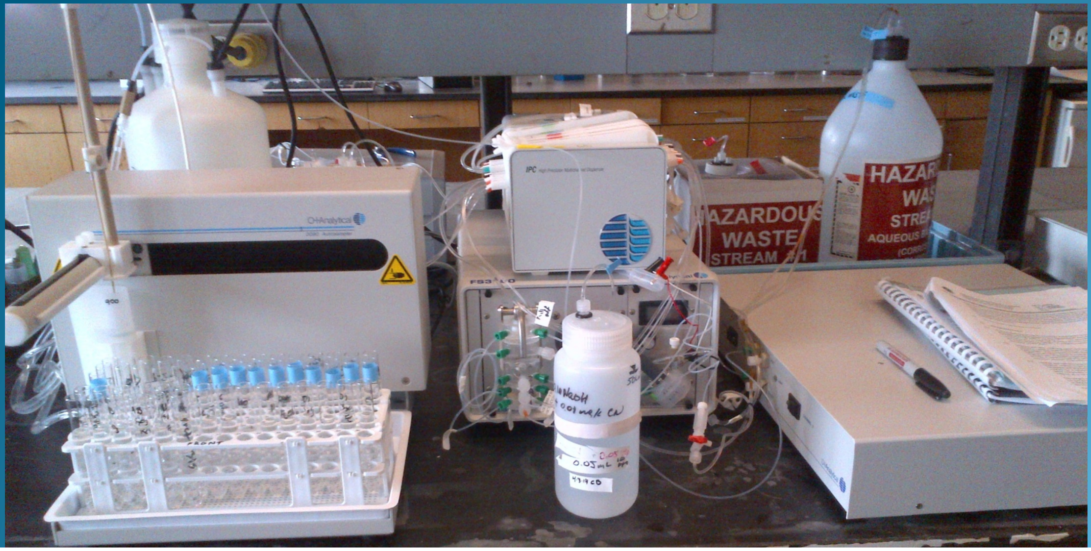
Cyanide Analysis Approaches

MicroDist Autoanalyzer (AAN)

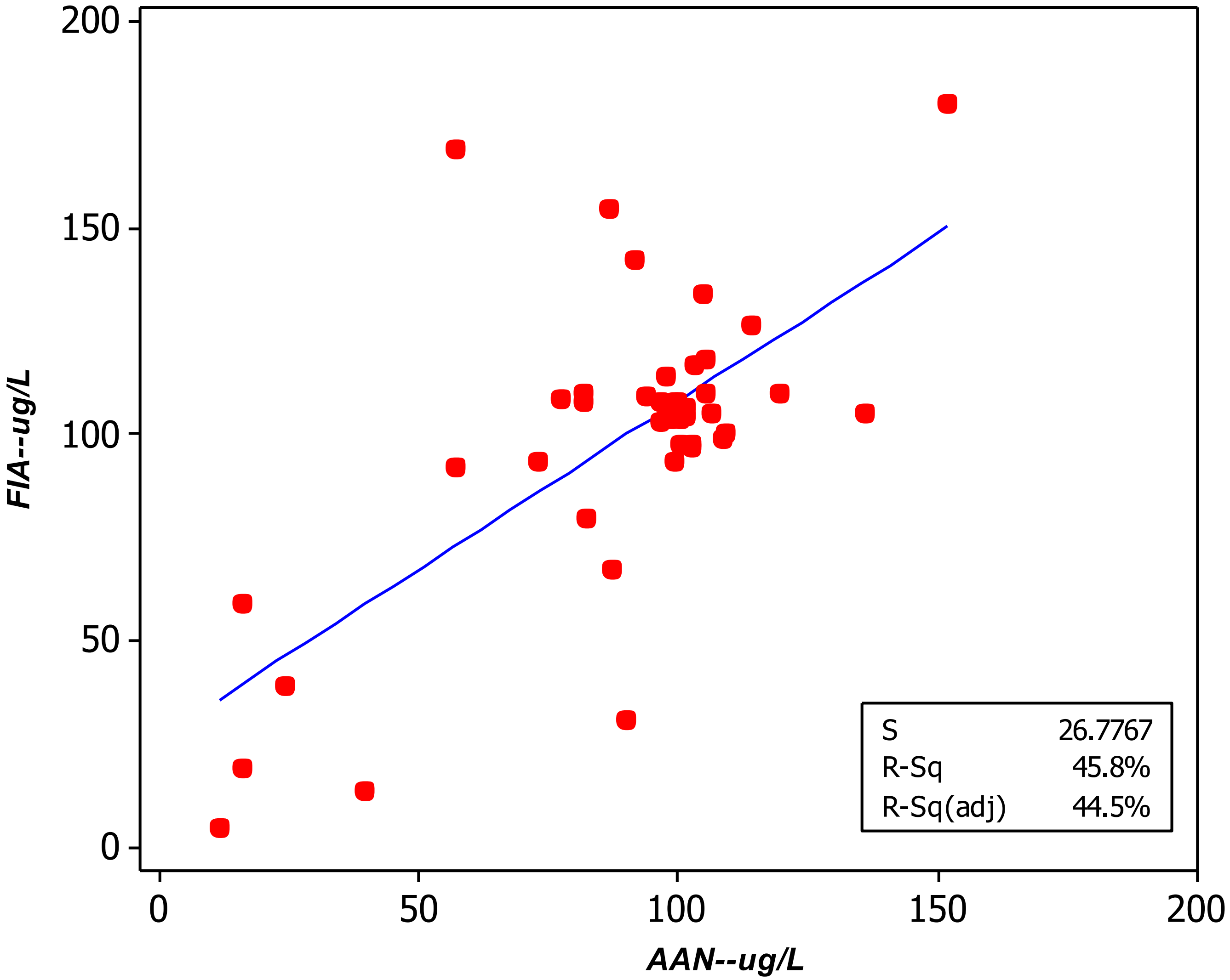
Ion Selective Electrode (ISE)



Flow Injection Analysis (FIA)



FIA versus Autoanalyzer for Total CN on industrial and POTW including spikes



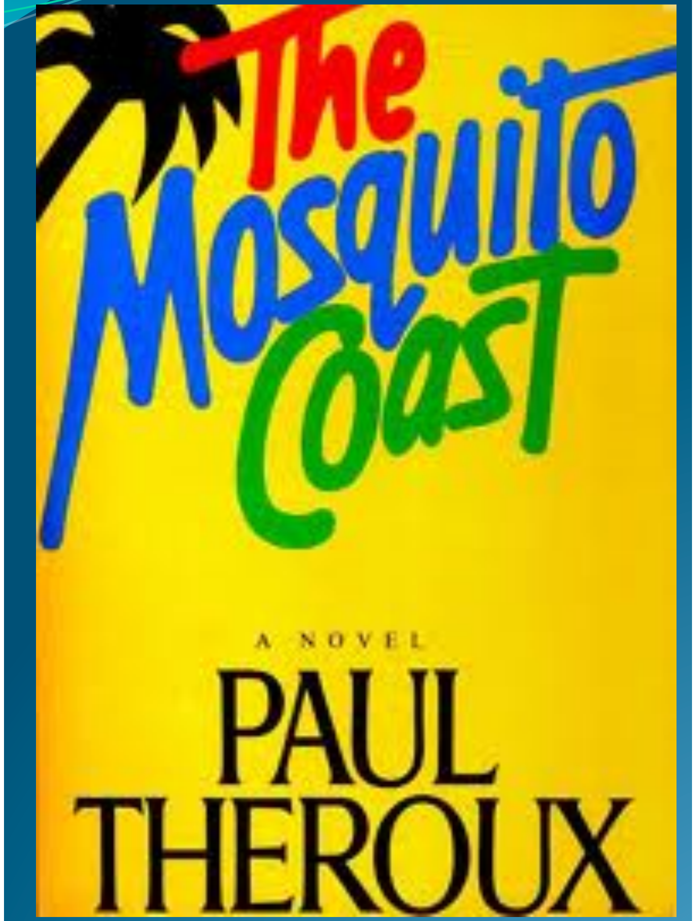
Drinking Water: Avoiding False Positives

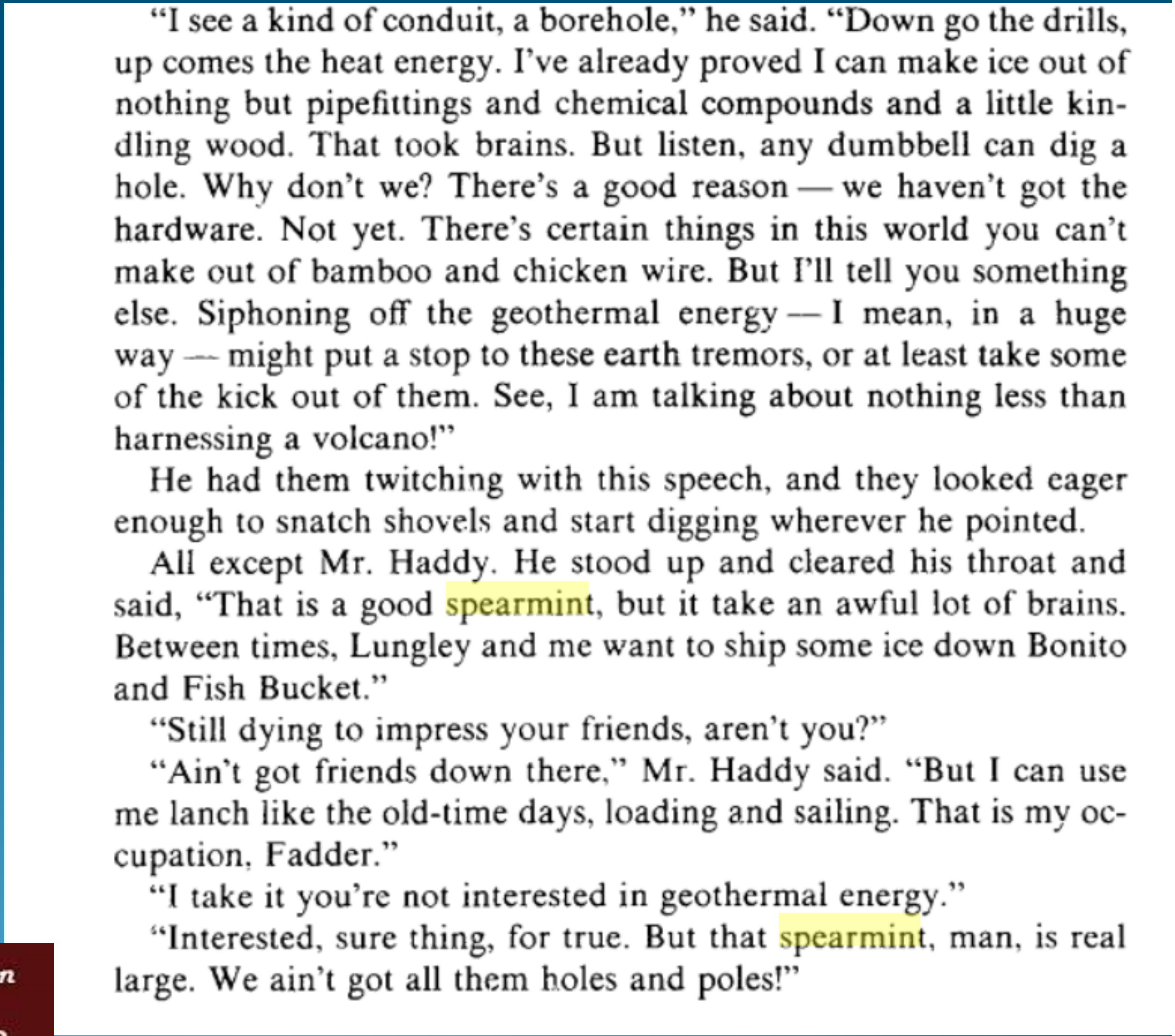
- Nobody wants "false positive" hits for cyanide at their drinking water plant.
- We know we can "stimulate" a false positive by raising the sample's pH.
  - Unpreserved: <0.5 ug/L
  - NaOH Preserved: 9.5 ug/L
- We are tired of doing on-site cyanide distillations to avoid false positives.
- The regulated parameter is "Free CN" and the MCL is 200 ug/L.
- We can't do a lot of investigatory testing on real samples from the permitted location using an approved method because we would have to report the results.

Drinking Water: Avoiding False Positives

- MassDEP decided they could certify us for Available Cyanide in drinking water.
- The Available Cyanide method can be used to measure Free Cyanide (without on-line UV digestion).
- NaOH preservation and vigorous acid distillation are problematic.
- How far can we push the envelope with not preserving and gently analyzing samples?

“Spearmints” (Mosquito Coast)





“I see a kind of conduit, a borehole,” he said. “Down go the drills, up comes the heat energy. I’ve already proved I can make ice out of nothing but pipefittings and chemical compounds and a little kindling wood. That took brains. But listen, any dumbbell can dig a hole. Why don’t we? There’s a good reason — we haven’t got the hardware. Not yet. There’s certain things in this world you can’t make out of bamboo and chicken wire. But I’ll tell you something else. Siphoning off the geothermal energy — I mean, in a huge way — might put a stop to these earth tremors, or at least take some of the kick out of them. See, I am talking about nothing less than harnessing a volcano!”

He had them twitching with this speech, and they looked eager enough to snatch shovels and start digging wherever he pointed.

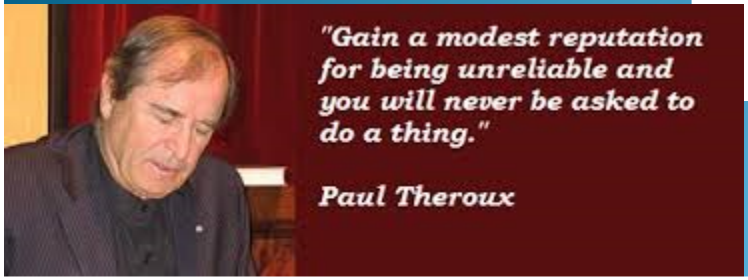
All except Mr. Haddy. He stood up and cleared his throat and said, “That is a good spearmint, but it take an awful lot of brains. Between times, Lungley and me want to ship some ice down Bonito and Fish Bucket.”

“Still dying to impress your friends, aren’t you?”

“Ain’t got friends down there,” Mr. Haddy said. “But I can use me lanch like the old-time days, loading and sailing. That is my occupation, Fadder.”

“I take it you’re not interested in geothermal energy.”

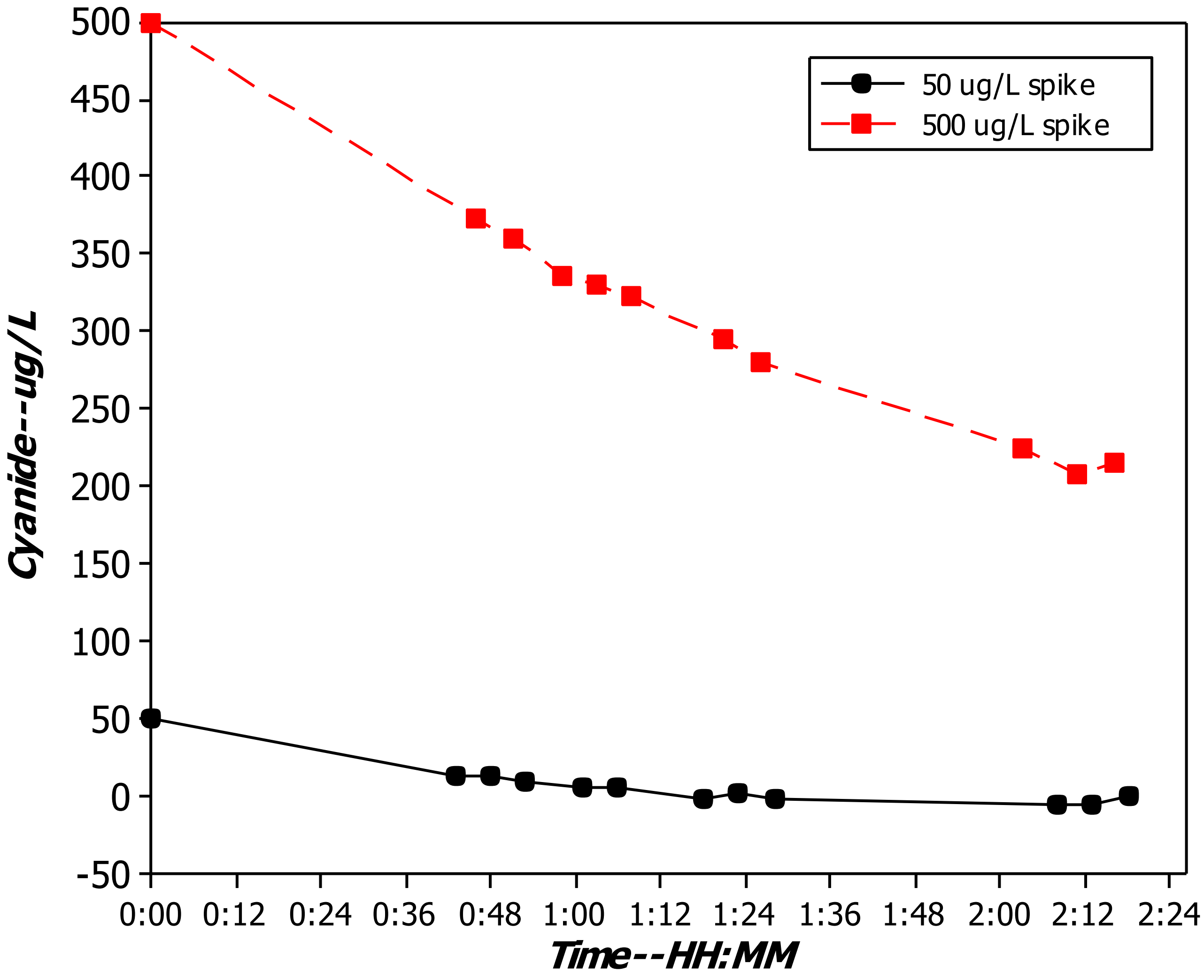
“Interested, sure thing, for true. But that spearmint, man, is real large. We ain’t got all them holes and poles!”



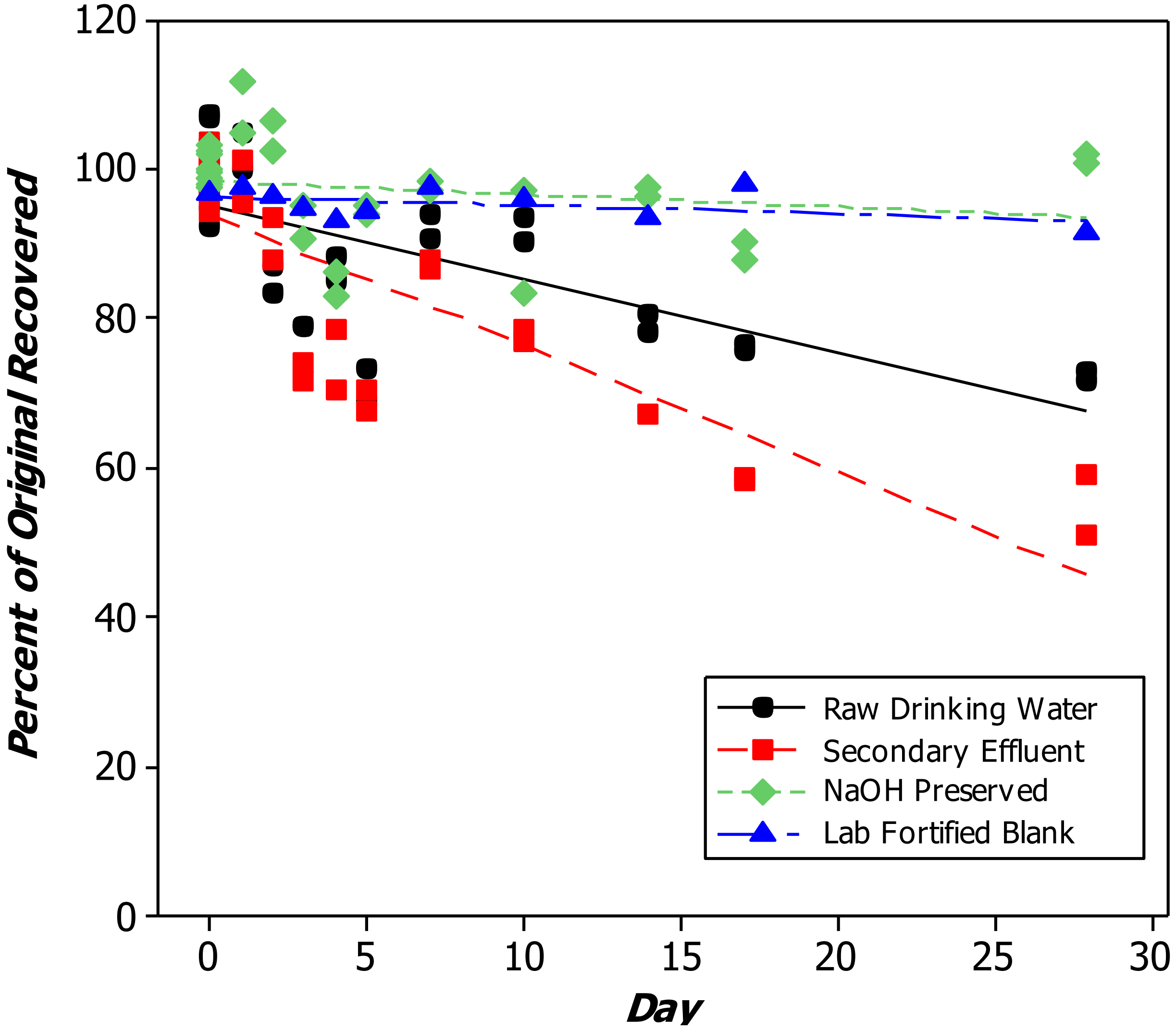
"Gain a modest reputation for being unreliable and you will never be asked to do a thing."

Paul Theroux

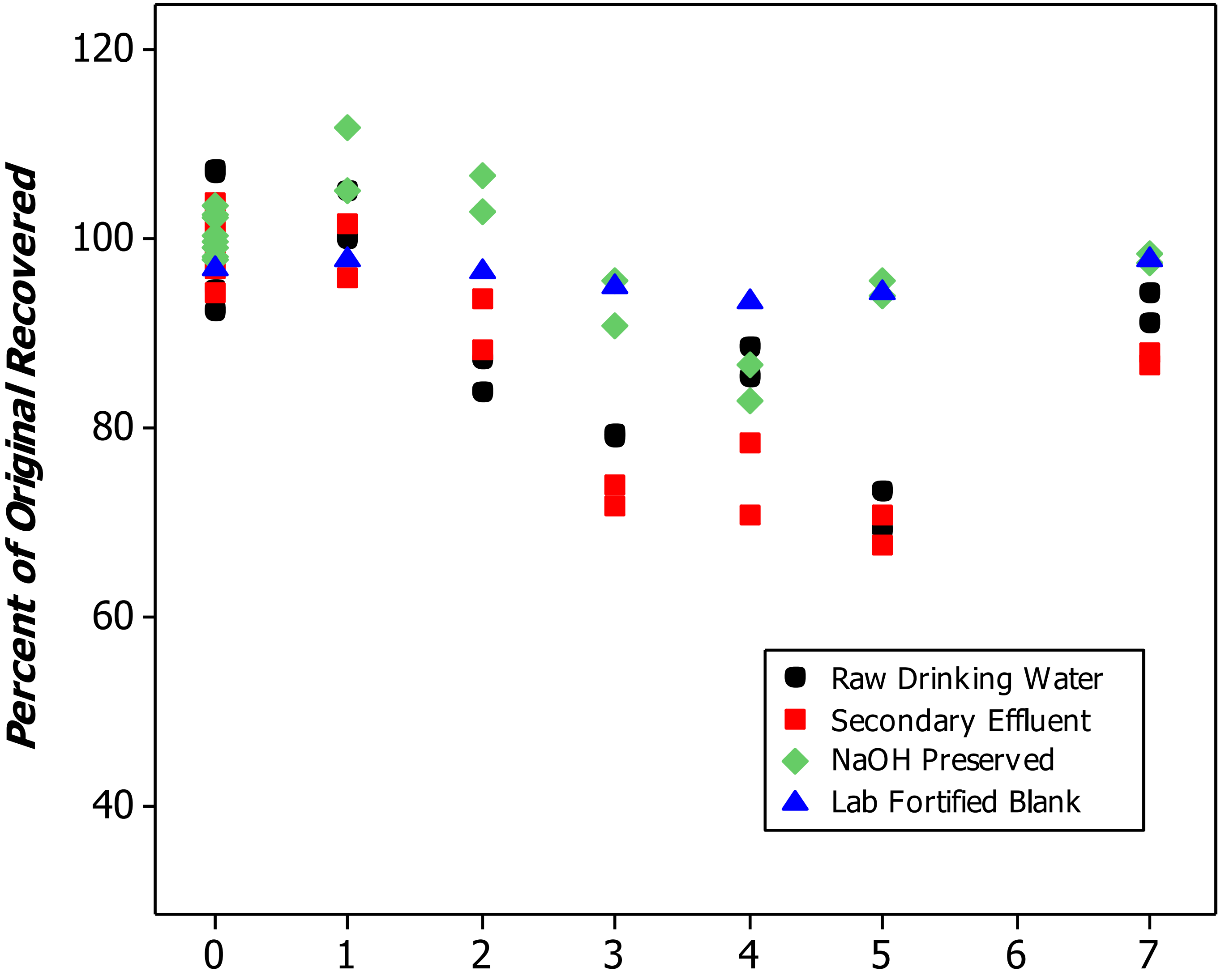
Unpreserved Undechlorinated Drinking Water: Half-life ~1.5 hours



Unpreserved "No Chlorine" Holding Time Results
Half-life: >28 days



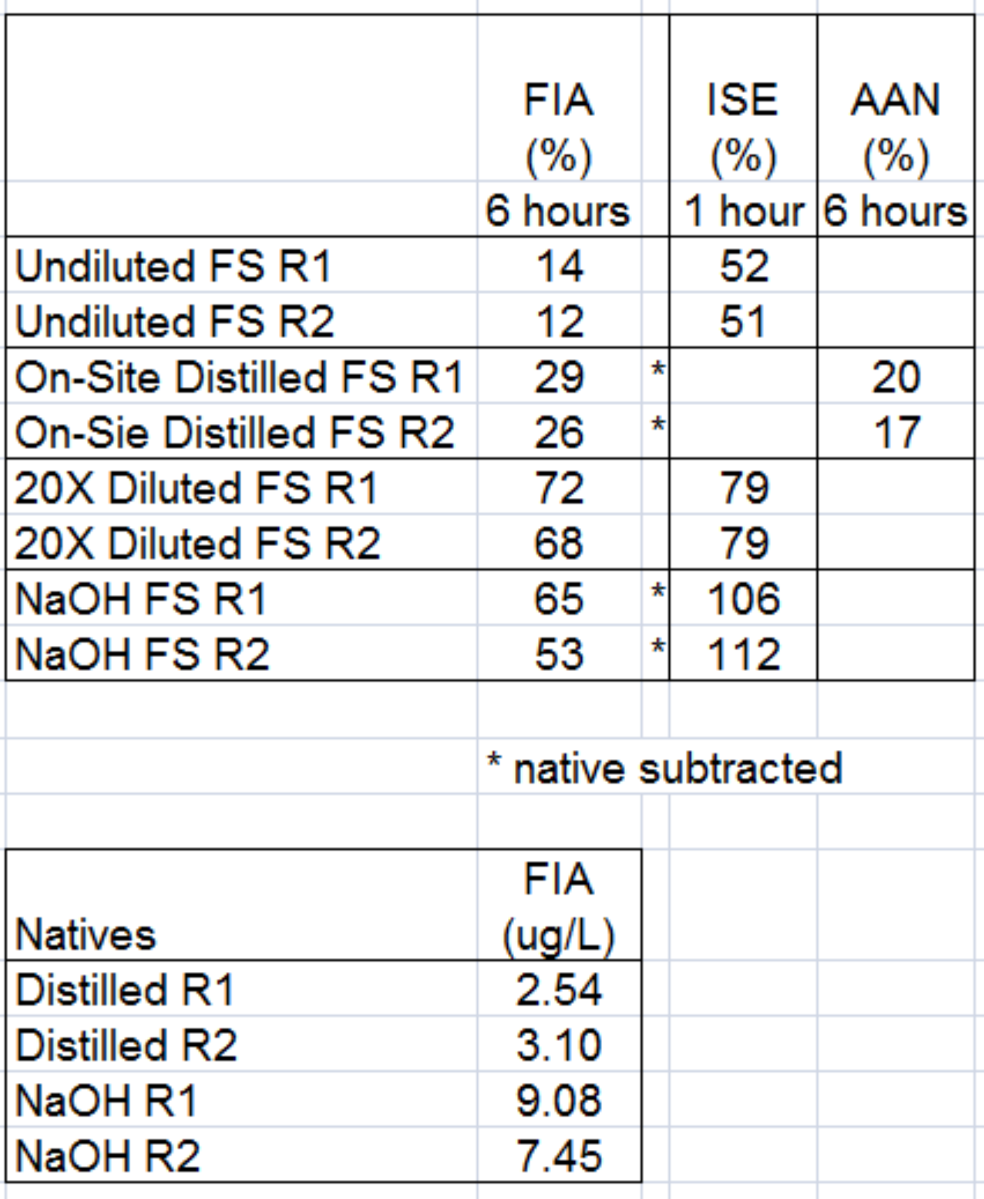
Unpreserved "No Chlorine" Holding Time Results (Days 0 to 7)



Dechlorinated Drinking Water Free Cyanide Results

Sample Type	**FIA** µg/L (6 hours)	**ISE** µg/L (1 hour)	**AAN** µg/L (6 hours)
Undiluted R1	<2	<20	
Undiluted R2	<2	<20	
Distilled On-Site R1	2.54		<10
Distilled On-Site R2	3.10		<10
20X Diluted R1	<40	<400	
20X Diluted R2	<40	<400	
NaOH R1	9.08	<20	
NaOH R2	7.45	<20	

Dechlorinated Drinking Water Field Spike Results



	FIA (%) 6 hours		ISE (%) 1 hour	AAN (%) 6 hours
Undiluted FS R1	14		52	
Undiluted FS R2	12		51	
On-Site Distilled FS R1	29	*		20
On-Sie Distilled FS R2	26	*		17
20X Diluted FS R1	72		79	
20X Diluted FS R2	68		79	
NaOH FS R1	65	*	106	
NaOH FS R2	53	*	112	

* native subtracted

Natives	FIA (ug/L)
Distilled R1	2.54
Distilled R2	3.10
NaOH R1	9.08
NaOH R2	7.45

Dechlorination Agent Comparison: Native Samples (FIA)

			TCR Before (mg/L)	TCR After (mg/L)	TCR (mg/L)	FCN (µg/L)	TCR (mg/L)	FCN (µg/L)	FCN (µg/L)	FCN (µg/L)
Sample Location	**Dechlorination Treatment**	**Time (hours):**	**0**	**0**	**6**	**6**	**24**	**24**	**72**	**96**
Before ammonia and hypochlorite treatment	**No TCR present**		<0.02			<2		<2	<2	<2
"	"					<2		<2	<2	<2
After ammonia and hypochlorite treatment	**No Dechlorination**		2.6		2.2	<2	2.2	<2	<2	<2
"	"					<2		<2	<2	<2
"	**Ascorbic Acid - Low**			<0.02	<0.02	<2	<0.02	<2	<2	<2
"	"					<2		<2	<2	<2
"	**Ascorbic Acid - High**					<2		<2	<2	<2
"	"					<2		<2	<2	<2
"	**Thiosulfate - Low**			<0.02	<0.02	<2	<0.02	<2	<2	<2
"	"					<2		<2	<2	<2
"	**Thiosulfate - High**					<2		<2	2.3	<2
"	"					<2		<2	<2	<2
"	**Arsenite - Low**			0.7	0.37	<2	0.21	<2	<2	<2
"	"					<2		<2	<2	<2
"	**Arsenite - High**			0.31	0.04	<2	<0.02	<2	2.2	<2
"	"					<2		<2	2.2	<2

Apparent cyanide formation after 3 days.

Dechlorination Agent Comparison Field Spikes (FIA)

			TCR Before (mg/L)	TCR After (mg/L)	TCR (mg/L)	FS (%)	TCR (mg/L)	FS (%)	FS (%)	FS (%)
Sample Location	**Dechlorination Treatment**	**Time (hours):**	**0**	**0**	**6**	**6**	**24**	**24**	**72**	**96**
Before ammonia and hypochlorite treatment	**No TCR present**		<0.02			95		74	29	20
"	"					96		72	23	16
After ammonia and hypochlorite treatment	**No Dechlorination**		2.6		2.2	<4	2.2	<4	<4	<4
"	"					<4		<4	<4	<4
"	**Ascorbic Acid - Low**			<0.02	<0.02	<4	<0.02	<4	<4	<4
"	"					<4		<4	<4	<4
"	**Ascorbic Acid - High**					66		38	13	7
"	"					49		27	10	5
"	**Thiosulfate - Low**			<0.02	<0.02	71	<0.02	38	12	8
"	"					79		41	11	7
"	**Thiosulfate - High**					69		36	11	8
"	"					67		36	13	10
"	**Arsenite - Low**			0.7	0.37	14	0.21	<4	<4	<4
"	"					13		<4	<4	<4
"	**Arsenite - High**			0.31	0.04	60	<0.02	23	13	8
"	"					60		22	11	9

Thiosulfate Dechlorination: ISE vs FIA

			ISE FCN (µg/L)	ISE FS (%)	FIA FCN (µg/L)	FIA FS (%)	FIA FCN (µg/L)	FIA FS (%)	FIA FCN (µg/L)	FIA FS (%)
Sample Location	**Dechlorination Treatment**	**Time (hours):**	18	18	18	18	72	72	96	96
After ammonia and hypochlorite treatment	**Thiosulfate - Low**		65	86	<2	43	10.8	38	10.8	39
"	"		65	78	<2	46	10.7	42	11.8	42
"	**Thiosulfate - High**		165	66	<2	39	9.8	37	11.2	36
"	"		157	76	<2	40	11.1	26	11.9	27

NaOH added after 18 hours for BOTH ISE and FIA.

Thiosulfate interference for ISE is probably due to sulfide.

Justification for Free Cyanide by FIA

- Free Cyanide is the regulated form of cyanide.
- OIA-1677 (2004) and ASTM D6888-04 are approved method for drinking water. (though the 2009 versions aren't).
- FIA can be used for Free Cyanide *("4 Measures "free" cyanides when distillation, digestion, or ligand exchange is omitted.")*.
- Analyzing an unpreserved sample within 24 hours is allowed (8.3: *"Unpreserved samples must be analyzed within 24 hours, or sooner if a change in cyanide concentration will occur."* 1677-04).

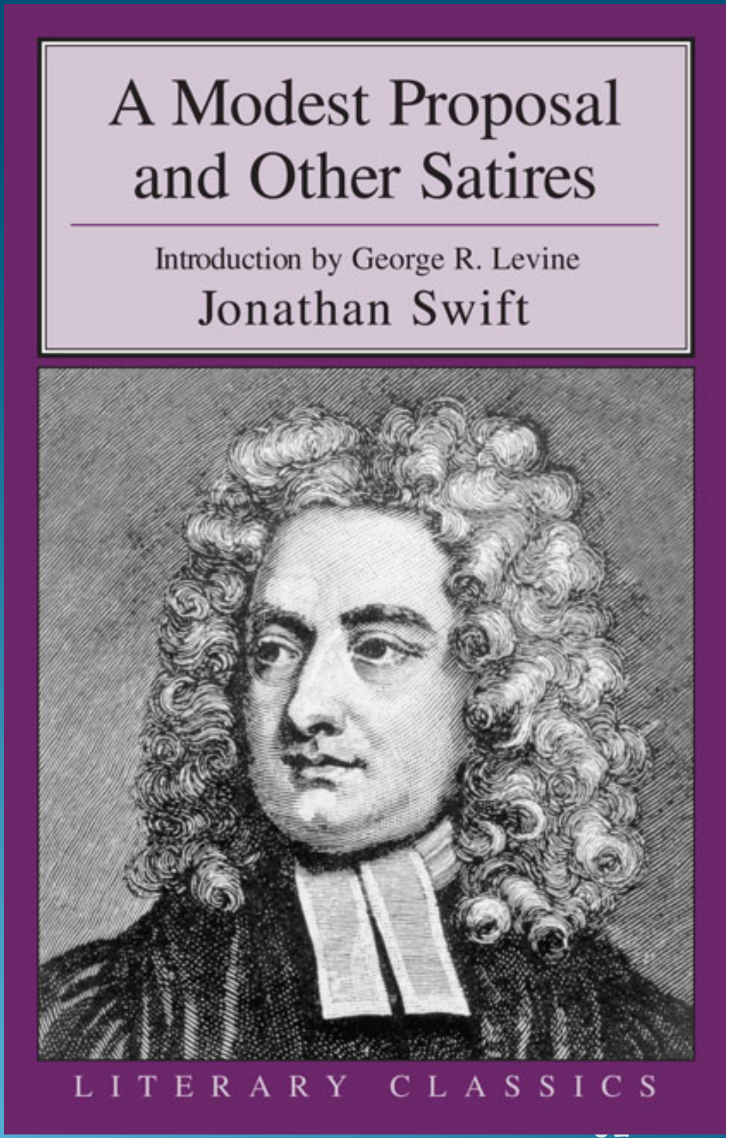
Justification for Free Cyanide by FIA

- Avoiding NaOH for preservation is reasonable.
  - *8.4 Do not add NaOH if the cyanide concentration would change as a result of the addition. (1677-09.).*

- Field dilution is reasonable to reduce interferences.
  - *8.5.1.1 If sulfide is detected by the lead acetate test strip (sulfide > 50 ppm), dilute sample so that sulfide is below amount detected by test strips. (1677-09.).*

Conclusions: A Modest Proposal

- Drinking Water:
  - Measure Free Cyanide for DW.
  - Use ISE on-site for Free Cyanide in the Standard Addition mode down to 20 µg/L.
- General:
  - Be careful how you dechlorinate.
  - Avoid NaOH.
  - Avoid distillation.
  - Use FIA without NaOH if sample can be tested within about 24 hours.
  - Use Field Dilution to reduce matrix effects.
  - Use Field Spikes to show it all worked.



A Modest Proposal
and Other Satires

Introduction by George R. Levine
Jonathan Swift

LITERARY CLASSICS

Thank you!

- Ed Caruso (ISE), Kevin Constantino (FIA), Tamara Smirnova (AAN) and MWRA employees from the Toxic Reduction and Control Department and Laboratory Services (sampling).