Testing for Cyanide in Drinking Water

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1. Executive Summary

This report comprises a detailed examination of issues regarding testing for cyanide in drinking water.

The determination of cyanide concentrations in drinking water is problematic due to its diverse chemistry. Cyanide exists in simple, uncomplexed forms, known as free cyanide (FCN) as well as complexed forms. Cyanide can be formed and destroyed by a variety of chemical reactions, which makes collecting, preserving, and testing drinking water samples difficult.

While cyanide is acutely toxic, its toxicology is well known. It doesn't bioaccumulate and is not known to be carcinogenic. This resulted in cyanide having a drinking water Maximum Contaminant Level (MCL) equal to its non-zero Maximum Contaminant Level Goal (MCLG) of 200 ug/L. Since the MCLG concentration is regarded as "safe", there is no particular need to test drinking water samples much below 200 ug/L. It is also unlikely that EPA will propose to lower the MCLG.

For Public Water Supplies (PWS), detecting cyanide is drinking water is problematic because detected contaminants must be reported in the PWS' annual Consumer Confidence Report (CCR). However, the terminology of detection and quantitation is ambiguous and confusing, which makes what needs to go into the CCR less than

obvious. This report contends that CCRs shouldn't include any cyanide results below 100 ug/L, which EPA regards as the Practical Quantitation Limit (PQL).

To make matters worse, we have shown that cyanide can form from treated drinking water when it is preserved and tested for CN. This is particularly problematic because drinking water testing is prescriptive—you are required to follow the sampling, preservation, and testing procedures specified in the regulations and approved method. So, it leaves a PWS with few viable options.

This report ends with detailed recommendations to EPA.

2. Cyanide Toxicology and the Maximum Contaminant Level Goal

"Everybody knows" that cyanide is acutely toxic and its toxic effects are well studied. Cyanide is present naturally in the blood, while its concentration can be elevated from exposure in water, food, and air, including cigarette smoke and fires. Cyanide's lethal dose, as an LD50, is reported to be 1.52 mg/kg for the oral exposure (ATSDR, 2006). At the current drinking water cyanide MCL of 200 ug/L, it would take a 70-kg adult 525 L to drink the LD50.

For chronic exposure, ATSDR (2006) has established an intermediate duration oral minimal risk level of 0.05 mg/Kg/day. For a 70-kg adult drinking 2.4 L/day, this works out to a cyanide concentration of 1.5 mg/L, which is 7.5 times higher than the MCL.

EPA proposed the drinking water MCL and MCLG for cyanide in 1990 and finalized the limits for both at 200 ug/L in 1992 (EPA, 1992) as Free Cyanide. Samples could be screened using Total Cyanide, but the definitive test was Free Cyanide by Cyanide Amenable to Chlorination (CATC). There were some comments on the proposed rule, but EPA reexamined the available toxicology studies and concluded that the MCL and MCLG were sufficiently protective of both acute and chronic effects of cyanide in drinking water.

EPA recently revised the human health ambient water quality criterion for Cyanide in 2015 (EPA, 2015). There were comments on the proposed criteria concerning free versus total cyanide methods (EPA, 2015a). Using current information and the EPA approach to calculating human health ambient water quality criteria the results are shown in "Table 2" below (EPA, 2015). Cyanide is regarded as non-carcinogenic and does not bioaccumulate. If a water body is designated for use as a Public Water Supply (PWS) without treatment, based on the revised human health ambient water quality criterion, the total cyanide level should be <4 ug/L, however, it is rare for a PWS to distribute untreated surface water. Other water bodies can have cyanide levels up to 400 ug/L.

"Table 2" from:
"Update of Human Health Ambient Water Quality Criteria: Cyanide" (EPA, 2015)

Table 2. Summary of EPA's Previously Recommended (2003) and Updated (2015) Human Health AWQC for Cyanide

	2003 Human Health AWQC	2015 Human Health AWQC
Water and Organism	140 µg/L	4 µg/L
Organism Only	140 µg/L	400 µg/L*

*See footnote g.

These AWQC are intended to be protective of the general adult population from noncarcinogenic effects due to chronic (up to a lifetime) exposure to cyanide from ingesting water and/or consuming fish and shellfish from inland and nearshore waters.

[g] If a water body is not designated as a drinking water supply source, a state can adopt AWQC for consumption of organisms only instead of AWQC for consumption of water and organisms. EPA recommends, however, that the state evaluate whether organism-only AWQC for non-bioaccumulative chemicals pose a risk to swimmers in those water bodies. Because cyanide has no bioaccumulation potential (BCF = 1 L/kg), EPA performed a screening analysis to determine whether the updated AWQC for organisms only is protective of incidental water ingestion from recreational uses (see section 4.1.1.3 in USEPA 2000a). EPA assumed an incidental water ingestion rate of 0.090 L/swimming event, which represents the upper (97th) percentile for children (Table 3-5 in USEPA 2011a) and a body weight of 31.8 kg, which represents the mean body weight of children ages 6 to <11 years (Table 8-1 in USEPA 2011a). No acute oral RfD was identified so EPA relied on an intermediate duration (15–364 days) MRL for cyanide of 0.05 mg CN^-/kg-d (ATSDR 2006). The resulting incidental water ingestion value (for screening purposes only) is 17,667 µg/L [(0.05 mg/kg-d × 31.8 kg × 1,000 µg/mg) / 0.090 L/d]. Therefore, the updated AWQC for consumption of organisms only of 400 µg/L for cyanide is protective of incidental water ingestion from recreational uses. Where a water body is designated as a drinking water supply source EPA recommends the AWQC for consumption of water and organisms for cyanide (4 µg/L) (USEPA 2000a).

The World Health Organization (WHO, 2003) published a document in 2003, "Cyanide in Drinking-water: Background document for development of WHO Guidelines for Drinking-water Quality". This material was originally published in a 1996 document. They concluded that a cyanide concentration of 70 ug/L was *"protective for both acute and long-term exposure."* This is based on a lowest-observed-adverse-effect level (LOAEL) in pigs, applying an uncertainty factor of 100 to reflect inter- and intra-species variation, resulted in a total daily intake (TDI) of 12 µg/kg of body weight. Twenty percent of this was allocated to drinking water, resulting in the allowable cyanide concentration of 70 ug/L. This is lower than the EPA MCL, but only by a factor of about three.

Conclusion: Cyanide's toxic effects are well-studied. It is not believed to be a carcinogen and it doesn't bioaccumulate. Based on this, and the limitations of approved analytical methods as discussed later in this report, there is little expectation that EPA will propose to lower the MCL or MCLG in the near future.

3. **Cyanide Occurrence in Drinking Water**

In early 2017 (just before January 20th), EPA published in the Federal Register (FR) its third six-year review of drinking water covering 2006 to 2011 (https://www.epa.gov/dwsixyearreview/six-year-review-3-drinking-water-standards). The FR notice is titled, "National Primary Drinking Water Regulations; Announcement of the Results of EPA's Review of Existing Drinking Water Standards and Request for Public Comment and/or Information on Related Issues" (EPA, 2017).

In addition to the FR notice itself, there are a number of supporting documents that look at the occurrence data, toxicological reports, and analytical data to see if any MCLs or MCLGs should be considered for revision. This documents included a summary report (EPA, 2016a), an examination of health effects (EPA, 2016b), an examination of quantitation limits (EPA, 2016c), and a database of the raw results. For cyanide, there were 119,659 individual results from 49 states. Of these, there were 2,144 (1.8%) detects and 80 (0.07%) were above the MCL. The highest detect was 4 mg/L in Attleboro, MA, and the lowest was 0.00005 mg/L, which is 0.05 ug/L. (NOTE: I followed up Attleboro and they claim the 4 mg/L is mistaken.)

There were a total of 1,108 detects that indicated whether the sample came from finished or raw water. It was four times more likely that a detect was from finished water than from raw water. Of these the 887 finished water samples had an average CN concentration of 44.8 ug/L and the 221 raw water samples had an average CN concentration of 30.2 ug/L. This supports our hypothesis that drinking water treatment and required cyanide sample preservation contributes to falsely elevated levels of cyanide.

In the "Summary of Six-Year Review 3 Results" (EPA, 2016a), EPA categorized cyanide as "Not Appropriate for Revision at this Time" because it has "low priority and/or no meaningful opportunity" for revision. There was a cyanide health assessment updated in 2010 (EPA, 2010a), which lowered the cyanide reference dose from 0.02 mg/kg-day to 0.0006 mg/kg-day. This corresponds to possibly lowering the MCLG from 200 ug/L to 4 ug/L.

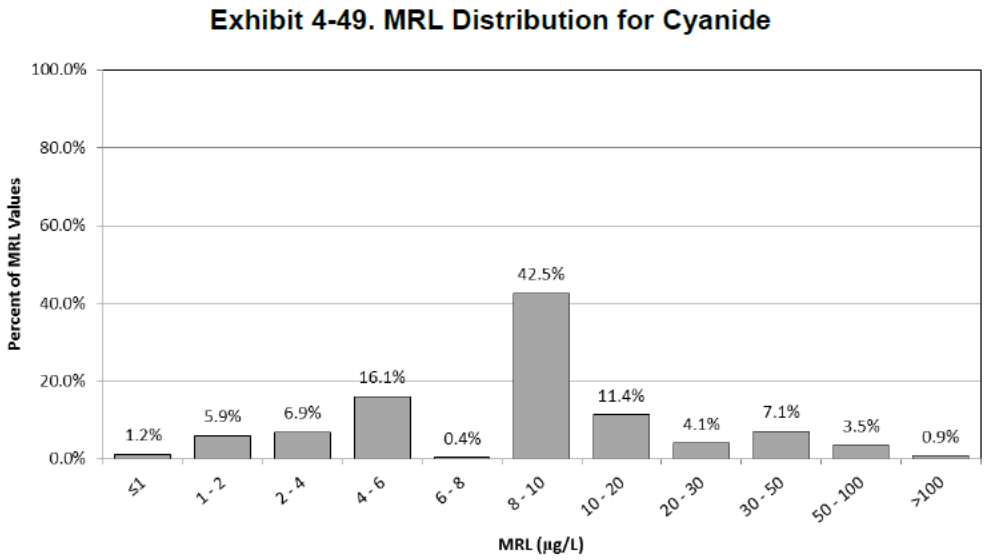
EPA's analysis of the occurrence data involves determining a reasonable Estimated Quantitation Level (EQL). Apparently, the EQL is a concentration below the established PQL that might be reasonable to use with the occurrence data to see if it might be possible to lower the MCL/MCLG (EPA, 2016c).

EPA previously concluded from Proficiency Test (PT) data that the PQL for cyanide is 100 ug/L. To pass a PT sample, results need to be within 25% of the true value. Since the PT samples are formulated at 100 ug/L or greater, and most labs pass the PT criteria, EPA decided that the PT data don't support lowering the PQL.

From the occurrence data, EPA conducted an analysis of the Minimum Reporting Levels (MRL), concluding that the modal MRL was 10 ug/L—that is, the most common

MRL was 10 ug/L. Since fewer than 80% of the MRLs were lower or equal to the modal MRL, EPA didn't base the EQL on the modal MRL.

Figure from "Development of Estimated Quantitation Levels for the Third Six-Year Review of National Primary Drinking Water Regulations (Chemical Phase Rules). (EPA. 2016c)



Next, EPA looked at Method Detection Limits (MDLs). EPA Method 335.4 has an MDL of 5.0 ug/L. Multiplying this by 10 for quantitation, gives 50 ug/L. EPA concluded that since more than 95% of the Minimum Reporting Levels (MRLs) in the occurrence dataset are less than or equal to 50 ug/L, using an Estimated Quantitation Level (EQL) of 50 ug/L for the occurrence analysis would introduce only a relatively small amount of bias from the MRL values that are above the EQL.

Based on an EQL of 50 ug/L, EPA concluded that if they were to lower the cyanide MCLG (and MCL), analytical limitations would made it difficult to determine whether the cyanide concentration in a drinking water sample was above or below the MCLG.

My Spin: There are several other EPA-approved cyanide methods for drinking water testing, and some of them are more sensitive than 335.4. However, since PT samples aren't prepared below 100 ug/L, it's not clear what precision and accuracy can be routinely achieved at lower concentrations. For all 2,144 detection, 1,378 (64%) were ≤10 ug/L, concentrations at which false positives are quite possible. Only 274 results (0.02%) were above EPA's EQL of 50 ug/L.

There are two ways of looking at this: With the MCLG at 200 ug/L, using 50 ug/L as the MRL would be reasonable. On the other hand, if the MCLG were 4 ug/L, it wouldn't be possible to show that the cyanide concentration is lower than this.

Conclusion: It appears that there isn't a strong motivation for EPA to propose lowering the cyanide MCLG.

NOTE: These EPA documents don't clearly distinguish between Total Cyanide and Free Cyanide, though it is likely that most of the occurrence data is for Total Cyanide.

4. Approved Analytical Methods

The currently approved drinking water cyanide methods, promulgated at 40 CFR 141.23 are shown in Table 1. This table has been annotated with what the methods say about treatment for oxidizers, treatment for sulfide, and preservation with NaOH.

Table 1 – Approved Drinking Water Methods for Cyanide

Methodology	Detection limit (mg/l)	Method	Treatment for Oxidizers	Treatment for Sulfide	NaOH?
Distillation, Spectrophotometric[3]	0.02	ASTM D2036-98 A	Arsenite stoic.	PbCO3	If the sample cannot be analyzed immediately, stabilize it by the addition of NaOH pellets to a pH of 12 to 12.5.
Distillation, Spectrophotometric[3]	0.02	SM 4500-CN⁻ A, C, E	Thiosulfate, arsenite, or, if necessary, ascorbic stoic.	Pb Acetate or PbCO3	Because most cyanides are very reactive and unstable, analyze samples as soon as possible. If sample cannot be analyzed immediately, add NaOH pellets or a strong NaOH solution to raise sample pH to 12 to 12.5.
Distillation, Spectrophotometric[3]	0.02	USGS I-3300-8	Sulfite stoic.	PbCO3	?
Distillation, Automated, Spectrophotometric[3]	0.005	EPA 335.4	Ascorbic slight excess. Sulfite	CdCO3	Samples must be preserved with sodium hydroxide pH ≥12 and cooled to 4°C at the time of collection.
Distillation, Amenable, Spectrophotometric[4]	0.02	ASTM D2036-98 A, B	Arsenite stoic.	PbCO3	If the sample cannot be analyzed immediately, stabilize it by the addition of NaOH pellets to a pH of 12 to 12.5.
Distillation, Amenable, Spectrophotometric[4]	0.02	SM 4500-CN⁻ A, C, G	Thiosulfate, arsenite, or, if necessary, ascorbic stoic.	Pb Acetate or PbCO3	Because most cyanides are very reactive and unstable, analyze samples as soon as possible. If sample cannot be analyzed immediately, add NaOH pellets or a strong NaOH solution to raise sample pH to 12 to 12.5.

Distillation, Selective Electrode[3 4]	0.05	SM 4500-CN− A, C, F	Thiosulfate, arsenite, or, if necessary, ascorbic stoic.	Pb Acetate or PbCO3	Because most cyanides are very reactive and unstable, analyze samples as soon as possible. If sample cannot be analyzed immediately, add NaOH pellets or a strong NaOH solution to raise sample pH to 12 to 12.5.
UV, Distillation, Spectrophotometric[9]	0.0005	Kelada-01	Arsenite or borohydride.	Dilution or PbCO3 or CdCO3	If the sample cannot be analyzed immediately, add sodium hydroxide (pellets or concentrated solution) to raise the pH to ≥ 12 for preservation.
Micro Distillation, Flow Injection, Spectrophotometric[3]	0.0006	QuikChem 10-204-00-1-X	Ascorbic or arsenite excess.	CdCO3	Samples must be preserved with sodium hydroxide at a pH ≥ 12 and cooled to 4oC at the time of collection.
Ligand Exchange with Amperometry[4]	0.0005	ASTM D6888-04	Arsenite excess.	Pb Acetate or PbCO3	The sample must be stabilized at time of collection with the addition of sodium hydroxide until a pH of 12 to 12.5 is reached.
Ligand Exchange with Amperometry[4]	0.0005	OIA-1677, DW	Ascorbic excess.	PbCO3	Immediately after collection, preserve the sample using any or all of the preservation techniques, followed by adjustment of the sample pH to >12 by addition of 1M sodium hydroxide and refrigeration at 0-4°C. Maximum holding time for samples preserved as above is 14 days. Unpreserved samples must be analyzed within 24 hours, or sooner if a change in cyanide concentration will occur.

There are also some Alternative Testing Methods for cyanide that are listed in Appendix A to Subpart C of Part 141 (Table 2), thought these methods don't have detection limits listed in the regulation. So, can a PWS/laboratory choose whatever detection limits they'd like if they use these methods?

Table 1 – Approved Drinking Water Methods for Cyanide

(1) Analysis for the following contaminants shall be conducted in accordance with the methods in the following table, or the alternative methods listed in appendix A to subpart C of this part, or their equivalent as determined by EPA. Criteria for analyzing arsenic, barium, beryllium, cadmium, calcium, chromium, copper, lead, nickel, selenium, sodium, and thallium with digestion or directly without digestion, and other analytical test procedures are contained in *Technical Notes on Drinking Water Methods*, EPA-600/R-94-173, October 1994. This document is available from the National Service Center for Environmental Publications (NSCEP), P.O. Box 42419, Cincinnati, OH 45242-0419 or *http://www.epa.gov/nscep/*.

Contaminant	Methodology[13]	EPA	ASTM[3]	SM[4] (18th, 19th ed.)	SM[4] (20th ed.)	SM Online[22]	Other
12. Cyanide	Manual Distillation followed by		D2036-98 A	4500-CN^- C	4500-CN^- C		
	Spectrophotometric, Amenable		D2036-98 B	4500-CN^- G	4500-CN^- G	4500-CN^- G-99	
	Spectro-photometric Manual		D2036-98 A	4500-CN^- E	4500-CN^- E	4500-CN^- E-99	I-3300-85[5]
	Spectro-photometric Semi-automated	335.4[6]					
	Selective Electrode			4500-CN^- F	4500-CN^- F	4500-CN^- F-99	
	UV, Distillation, Spectrophotometric						Kelada-01[17]
	Micro Distillation, Flow Injection, Spectrophotometric						QuikChem 10-204-00-1-X[18]
	Ligand Exchange and Amperometry[21]		D6888-04				OIA-1677, DW[20]

Table 2 – Approved Drinking Water Alternative Testing Methods for Cyanide

APPENDIX A TO SUBPART C OF PART 141—ALTERNATIVE TESTING METHODS APPROVED FOR ANALYSES UNDER THE SAFE DRINKING WATER ACT

Only the editions stated in the following table are approved.

ALTERNATIVE TESTING METHODS FOR CONTAMINANTS LISTED AT 40 CFR 141.23(k)(1)

Contaminant	Methodology	EPA method	SM 21st edition[1]	SM 22nd edition[29]	SM online[3]	ASTM[4]	Other
Cyanide	Manual Distillation followed by					D 2036-06 A	
	Spectrophotometric, Amenable		4500-CN^- G	4500-CN^- G		D 2036-06 B	
	Spectrophotometric Manual		4500-CN^- E	4500-CN^- E		D2036-06 A	
	Selective Electrode		4500-CN^- F	4500-CN^- F			
	Headspace Gas Chromatography/Mass Spectrometry						ME355.01[7]

These approved methods include the same or updated versions of the methods approved in 1992. In addition, there are methods with newer technology, including on-line distillation, micro distillation, UV digestion, and ligand exchange as an alternative to

distillation with detection by flow injection spectrophotometry or amperometry, as well as headspace GC-MS.

5. Cyanide Sample Preservation and Method Validation Studies

At the August 2016 Environmental Laboratory Advisory Board (ELAB) Face-to-Face meeting in Orange Country, CA, ELAB members requested information on validation studies that were used to approve drinking water cyanide (CN) methods. After the meeting, I requested this information from EPA's Mr. Dan Hautman (EPA/Office of Water) and also checked in with Mr. William Lipps, who has been involved with cyanide methods for some time, and the instrument vendor (OI Analytical) for the instrument that was used as the basis for the method we follow (OIA-1677).

Mr. Hautman suggested that I review the 2004 Proposed and 2007 Final Methods Update Rules (MUR) and he also provided some references that were included in the MUR file and likely integral to EPA's evaluation of these methods. He indicated that the OI method approval was *"led by Bill Telliard (long since retired) and it appears many of the same folks (U of Nevada) were involved in FIA validation (Bayer, ASTM and OI)."* Mr. Hautman provided these documents:

1. 2004 Proposed Methods Update Rule (EPA, 2004)
2. 2007 Final Methods Update Rule (EPA, 2007)
3. ASTM D6888-03 (ASTM, 2003)
4. ASTM D6888-03 Collaborative Study (ASTM, 2002)
5. "Method Comparison and Evaluation for the Analysis of Weak Acid-Dissociable Cyanide" (Sebroski & Ode, 1997).

Mr. Lipps and the current OI staff were able to provide some additional validation studies.

This section examines the available information on cyanide preservation and interference treatments method validation for wastewater and drinking water.

Wastewater Regulations.

For wastewater testing for cyanide under the Clean Water Act (CWA), detailed in 40 CFR 136, the nominal maximum cyanide holding time from collection to analysis is 14 days for wastewater samples. This maximum holding time was set by regulation, accompanied by prescribed preservation requirements, but without any supporting data to substantiate the holding time.

The Total Cyanide (TCN) holding time was proposed by EPA in 1979 and set in 1984 (EPA, 1984). The approved methods for TCN and CATC were manual distillation followed by titration or manual/automated spectrophotometry following EPA, Standard Methods, ASTM, or USGS procedures. The dechlorinating agent was proposed in 1979

as thiosulfate, but was changed to ascorbic acid in the 1984 final rule. Required preservation for TCN or CN "Amenable to Chlorination" in Table II of 40 CFR 136 (US CFR, Title 40 Part 136, 2013) was: *"Cool 4°C, NaOH to pH >12, 0.6 g ascorbic acid (only in the presence of residual chlorine)"* and the 14-day holding time had a footnote indicating that the *"maximum holding time is 24 hours if sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12."*

Data to support the TCN holding time and preservation requirements were not cited in either the 1979 proposed or 1984 final rules for 40 CFR 136.

In EPA's 2007 CWA Methods Update Rule (MUR) (USEPA, 2007) a lengthy footnote on cyanide preservation was added, but was further revised and drastically shortened in EPA's 2012 MUR, adding ASTM D7365–09a (ASTM 2009) on cyanide preservation as a reference. The 2012 MUR footnote gave laboratories a lot of leeway: *"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."*

Available cyanide was added to the list of CWA parameters in 1999 and the approved method for this was OIA-1677 (USEPA, 1999). Free cyanide (FCN) was added to the list of CWA parameters in the 2012 MUR, and the approved methods for this were listed as ASTM D7237–10 and OIA–1677–09 (USEPA, 2012). The preservation and holding time requirements are the same for total, available, and free cyanide, but the required preservation was lowered from pH>12 to pH>10 in the 2012 MUR, without discussion. Presumably this was to lessen the chance of adverse effects from high NaOH concentrations.

Drinking Water Regulations.

For drinking water regulations, the Safe Drinking Water Act was enacted in 1974 and it was amended in 1986 and 1996. Free Cyanide (FCN) was added as a regulated parameter in 1992, setting both the MCL and the MCLG at 200 µg/L. The 1992 rule allowed the use of an ion selective electrode (ISE) to measure FCN, and added several screening methods for TCN. It also defined the required cyanide preservation to be "Cool 4ºC, NaOH to pH >12", and "ascorbic acid should only be used in the presence of residual chlorine". It also defined the maximum holding time as 14 days.

This 1992 rule also included MDLs for the various cyanide methods (note these are called MDLs in the body of the regulation (p. 31798) but Detection Limit in the revised regulation itself (p. 31838). It also established a PQL for cyanide of 0.1 mg/L. This was based on data obtained from multiple laboratories from the Water Supply (WS) performance evaluation (PE) samples. The PE samples are always formulated from simple (free) cyanide at concentrations of ≥0.1 mg/L. EPA concluded that this is the

lowest concentration at which it is reasonable to expect laboratories to get results on PE samples within 25% of the true value. Because cyanide has a non-zero MCLG of 0.2 mg/L, and the analytical methods are sensitive enough, the WS data can be used to set the PQL. For other contaminants the PQL is often set at 5 to 10 times the MDL.

Note that in the regulation itself the detection limits are in the context of compositing samples and PQLs aren't mentioned at all. There is no explicit guidance reporting cyanide results.

To this day, drinking water testing for CN under 40 CFR 141 still requires that CN samples have a holding time of 14 days and are to be preserved to pH 12 with NaOH, but a footnote to the preservation/holding time table indicates: *"In all cases samples should be analyzed as soon after collection as possible. Follow additional (if any) information on preservation, containers or holding times that is specified in method."*

There does not appear to be any evaluation of holding times or preservation techniques associated with the 1992 National Primary Drinking Water Regulations.

Preservation and Treatment for Interferences.

Notwithstanding the diversity of cyanide chemistry, for drinking water testing the preservation requirement is to follow the direction of 40 CFR 141.23:

Table from 40 CFR 141.23

Contaminant	Preservative [1]	Container [2]	Time [3]
Antimony	HNO_3	P or G	6 months
Arsenic	Conc HNO_3 to pH <2.	P or G	6 months
Asbestos	4 °C	P or G	48 hours [4]
Barium	HNO_3	P or G	6 months
Beryllium	HNO_3	P or G	6 months
Cadmium	HNO_3	P or G	6 months
Chromium	HNO_3	P or G	6 months
Cyanide	4 °C, NaOH	P or G	14 days
Fluoride	None	P or G	1 month
Mercury	HNO_3	P or G	28 days
Nickel	HNO_3	P or G	6 months
Nitrate	4 °C	P or G	48 hours [5]
Nitrate-Nitrite [6]	H_2SO_4	P or G	28 days
Nitrite	4 °C	P or G	48 hours
Selenium	HNO_3	P or G	6 months
Thallium	HNO_3	P or G	6 months

[1] For cyanide determinations samples must be adjusted with sodium hydroxide to pH 12 at the time of collection. When chilling is indicated the sample must be shipped and stored at 4 °C or less. Acidification of nitrate or metals samples may be with a concentrated acid or a dilute (50% by volume) solution of the applicable concentrated acid. Acidification of samples for metals analysis is encouraged and allowed at the laboratory rather than at the time of sampling provided the shipping time and other instructions in Section 8.3 of EPA Methods 200.7 or 200.8 or 200.9 are followed.

[2] P=plastic, hard or soft; G=glass, hard or soft.

[3] In all cases samples should be analyzed as soon after collection as possible. Follow additional (if any) information on preservation, containers or holding times that is specified in method.

[4] Instructions for containers, preservation procedures and holding times as specified in Method 100.2 must be adhered to for all compliance analyses including those conducted with Method 100.1.

[5] If the sample is chlorinated, the holding time for an unacidified sample kept at 4 °C is extended to 14 days.

[6] Nitrate-Nitrite refers to a measurement of total nitrate.

Other than raising the pH to 12 and cooling the sample, the requirement is to *"Follow additional (if any) information on preservation, containers or holding times that is*

specified in method." For regulatory drinking water testing, the Public Water Supply (PWS) and their laboratory have no discretion beyond what is allowed in the method.

Moreover, an EPA representative has clearly stated that there is no latitude to alter the preservation requirements other than EPA rulemaking (Steve Wendleken, EPA OGWDW/TSC via email 4/7/16).

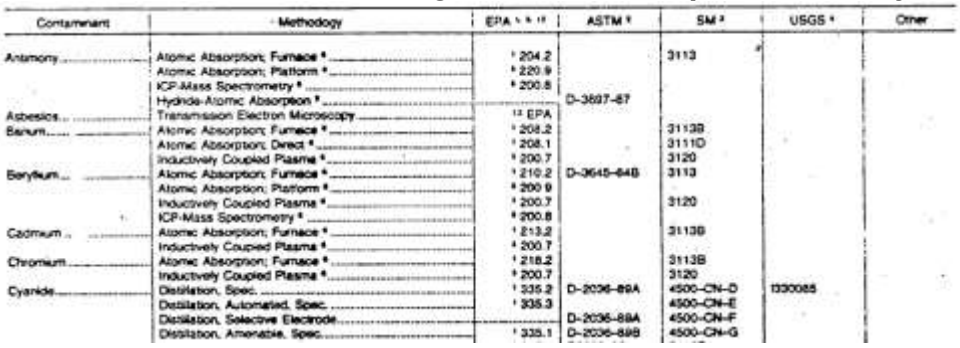
Cyanide Validation Studies.

There are some validation studies for some of the approved cyanide methods, but none were particularly focused on preservation for drinking water testing. These seem to fall into the paradigm that drinking water tends to be a cleaner matrix than wastewater and therefore should be fewer preservation and interference problems in drinking water testing. This results in few validation studies that have looked at preservation and interferences for drinking water.

1992 Drinking Water Final Rule.

When cyanide was regulated in drinking water in 1992 (EPA, 1992), the approved methods were EPA 335.2 and 335.3, ASTM D2036-89A and B, SM 4500-CN D, E, F, and G and USGS I330065. These methods were approved based on their reliability, specificity, availability, rapidity, and cost. While noting that the regulated form of cyanide is Free Cyanide, this rule approved a Cyanide Amenable to Chlorination method as a measure of Free Cyanide, and suggested testing for Total Cyanide as a cheaper alternative to screen for cyanide. Otherwise the performance or validation of the approved methods wasn't discussed.

Portion of a Table from Federal Register Final Rule published July 17, 1992



Contaminant	Methodology	EPA [1]	ASTM [2]	SM [3]	USGS [4]	Other
Antimony	Atomic Absorption; Furnace [5]	[6] 204.2		3113		
	Atomic Absorption; Platform [5]	[6] 200.9				
	ICP-Mass Spectrometry [5]	[6] 200.8				
	Hydride-Atomic Absorption [5]		D-3697-87			
Asbestos	Transmission Electron Microscopy	[12] EPA				
Barium	Atomic Absorption; Furnace [5]	[6] 208.2		3113B		
	Atomic Absorption; Direct [5]	[6] 208.1		3111D		
	Inductively Coupled Plasma [5]	[6] 200.7		3120		
Beryllium	Atomic Absorption; Furnace [5]	[6] 210.2	D-3645-84B	3113		
	Atomic Absorption; Platform [5]	[6] 200.9				
	Inductively Coupled Plasma [5]	[6] 200.7		3120		
	ICP-Mass Spectrometry [5]	[6] 200.8				
Cadmium	Atomic Absorption; Furnace [5]	[6] 213.2		3113B		
	Inductively Coupled Plasma [5]	[6] 200.7				
Chromium	Atomic Absorption; Furnace [5]	[6] 218.2		3113B		
	Inductively Coupled Plasma [5]	[6] 200.7		3120		
Cyanide	Distillation, Spec.	[6] 335.2	D-2036-89A	4500-CN-D	I330085	
	Distillation, Automated, Spec.	[6] 335.3		4500-CN-E		
	Distillation, Selective Electrode		D-2036-89A	4500-CN-F		
	Distillation, Amenable, Spec.	[6] 335.1	D-2036-89B	4500-CN-G		

2004 Proposed Methods Update Rule.

The 2004 Proposed MUR (EPA, 2004) indicated EPA's intention to approve EPA 335.4 for drinking water as being "technically equivalent" to the previous versions. Also proposed were two "Available Cyanide" methods for drinking water: ASTM D6888-03 and OIA-1677-DW.

OIA-1677-DW was stated to be "technically equivalent" to OIA-1677, which had been approved for NPDES in 1999, and which was validated by an intra-laboratory and nine-

lab validation studies. These studies demonstrated the method's ability "to identify and overcome analytical interferences."

The justification for approving D6888-03 was that it is technologically similar to OIA-1677-DW, and was also being proposed for NPDES testing. The validation of both methods focused on wastewater.

It was noted that both methods are prone to positive interference from sulfide, but otherwise tests and treatments for interferences weren't discussed.

2007 Final Methods Update Rule,

The final 2007 MUR (EPA, 2007) approved ASTM D6888-04 and OIA-1677-DW for drinking water testing without additional discussion of validation or interferences.

Standard Methods for the Examination of Water and Wastewater

Various versions of Standard Methods cyanide methods are currently approved for drinking water testing, including methods from the 18th, 19th, 20th, 21st, and 22nd edition (Standard Methods, 2011). A Standard Methods Joint Task Group reviewed and revised this section and the revisions have been balloted. The new revision is expected to appear in the 23rd edition and presumably will be reviewed, and hopefully approved, by EPA at that time. The balloted revision includes the following statements:

Field spikes created at the time of sample collection are an effective way to demonstrate adequate preservation and treatment for interferences in both wastewater[2] and drinking water.[3]

A field dilution performed at the time of sample collection also can reduce interferences effectively. This is useful when the diluted sample's elevated reporting limit is still below the regulatory limit.[3]

2. *DELANEY, M.F. & C. BLODGET. 2015.Total cyanide field spikes for industrial wastewater samples verify successful sample integrity, preservation, pre-treatment and testing. Water Environ. Res. 87(6):559.*
3. *DELANEY, M.F. & C. BLODGET. 2016. Reliable determination of cyanide in treated water. J. Amer. Water Works Assoc. 108:E87.*

Other Cyanide Validation Studies.

Sebroski & Ode (1997) compared three methods for weak acid-dissociable cyanide (manual distillation-colorimetry, steam distillation-ion selective electrode, and ligand exchange-flow injection analysis-microdiffusion-amperometry), but this study focused on industrial wastewater and didn't particularly investigate preservation and dechlorination procedures. Also, note that the spiked environmental samples were dechlorinated, if necessary, with thiosulfate and only preserved to pH>10 (not pH>12 as required for drinking water. Two of the ten samples were raw, not treated, drinking water. No treated drinking water was included in the study.

In 2002, Sebroski conducted an ASTM interlaboratory collaborative study of the FIA Available Cyanide method using KCN samples that were tested by ten laboratories, but this study didn't investigate preservation and dechlorination procedures (ASTM, 2002).

OIA-1677 was validated in a single lab study in 1995 (I haven't been able to get a copy of this from the vendor or EPA, even though the study is reference in the method). This was followed by a multi-lab study in 1997, conducted by EPA using a variety of sample matrices. This study included nine laboratories and nine sample matrices, though it wasn't particularly focused on drinking water or treatment for interferences. However, it did lead to OIA-1677 being approved for NPDES testing in 1999 and for drinking water in 2007.

In 2009, a FCN method based on headspace GC-MS, Method 355.1, was approved by EPA as an Alternative Test Procedure (ATP) (EPA, 2009). This method was based on a CDC whole blood method. The drinking water adaptation and validation was conducted by Mr. James Eaton at the State of Maine Health and Environment Testing Laboratory. The validation of this method was designed in consultation with EPA. There was an interlaboratory validation study involving three laboratories and three samples, spiked at two concentrations. There was no evaluation of preservation or interferences and none of the samples had residual oxidants (chlorine). As written, the method can't be used for samples with residual oxidants (though I believe it is being used that way).

Delaney et al. (2007) showed that cyanide can form in the sample container when treated drinking water samples are dechlorinated, preserved with NaOH, and tested for TCR by distillation and automated spectrophotometry. These false cyanide detects were ameliorated by avoiding NaOH preservation and immediately performing the distillation on-site. This was approved by EPA in 2007, but in 2016 EPA indicated that this shouldn't have been approved.

Delaney & Blodget (2016) studied the determination of cyanide in treated drinking water and wastewater samples. In this study, the effects of holding time, preservation, and on-line digestion and distillation on cyanide results for wastewater and drinking water were examined, including the use of field dilution as a treatment for interferences and field spikes as a means to gauge whether sample integrity was maintained.

Discussion.

For drinking water testing, you have to "follow the method". You have to preserve cyanide sample for drinking to water to pH>12. You are only allowed to use the preservation and interference treatments that are explicitly written into the method you are following. Problems leading to false cyanide detections have been identified, yet validation studies of cyanide preservation and interference treatments for treated drinking water used to approve the methods are lacking.

6. Consumer Confidence Reports: How Low Must You Go?

When testing drinking water for cyanide, how low must you go? Or in other words, what are the regulatory requirements for Detection and Reporting Limits? The Federal regulations and guidance are unclear on this issue, lacking consistent and clear terminology, which is problematic.

How low you must go in testing for contaminants in drinking water is an important question for a Public Water Supply (PWS) because "detected" contaminants must be reported in the annual Consumer Confidence Report (CCR), and no PWS wants to report that there is cyanide in their drinking water—especially if cyanide isn't actually there.

Let's look at the pertinent parts of the Federal drinking water regulation. The Federal Safe Drinking Water Act. 40 CFR 141, and in particular the section on CCRs, says this:

Subpart O—Consumer Confidence Reports

§141.151 Purpose and applicability of this subpart.

(d) For the purpose of this subpart, detected means: at or above the levels prescribed by §141.23(a)(4) for inorganic contaminants, at or above the levels prescribed by §141.24(f)(7) for the contaminants listed in §141.61(a), at or above the levels prescribed by §141.24(h)(18) for the contaminants listed in §141.61(c), at or above the levels prescribed by §141.131(b)(2)(iv) for the contaminants or contaminant groups listed in §141.64, and at or above the levels prescribed by §141.25(c) for radioactive contaminants.

For cyanide, the table at §141.23(a)(4) lists "Detection Limits" for the seven approved laboratory methods, which range from 0.5 to 50 ug/L. A simple interpretation of the CCR language is that you need to report down to the detection limit for the method that you use.

The first ambiguity is the term "detection limit". What does that mean: "method detection limit" (MDL) from the method or actually achieved by the lab? Minimum reporting level (MRL)? Or something else? We will come back to that later.

Detection Limits for Inorganic Contaminants
From §141.23(a)(4)

Contaminant	MCL (mg/l)	Methodology	Detection limit (mg/l)
Cyanide	0.2	Distillation, Spectrophotometric[3]	0.02
		Distillation, Automated, Spectrophotometric[3]	0.005
		Distillation, Amenable, Spectrophotometric[4]	0.02
		Distillation, Selective Electrode[3 4]	0.05
		UV, Distillation, Spectrophotometric[9]	0.0005
		Micro Distillation, Flow Injection, Spectrophotometric[3]	0.0006
		Ligand Exchange with Amperometry[4]	0.0005

An alternate interpretation focuses on the key phrase "*at or above the levels prescribed".* Does this mean that if the lab reports a number (not a "less than"), and this number is above the detection limit listed in the table for the method, then you must regard this as a detected contaminant and report it in the CCR. This is a simply, but naïve, interpretation, implying "whatever your lab gives you is probably OK".

Either interpretation would encourage a PWS to use the least sensitive method to minimize the likelihood of getting a detected contaminant. However, this is philosophically unappealing.

Guidance Documents. There are two guidance documents for States and PWSs on implementing the CCR regulation. In guidance to States, "Revised State Implementation Guidance for the Consumer Confidence Report (CCR) Rule" (EPA, 2010b), there is no specific guidance on what a detected contaminant is, only on what information needs to go into the CCR. It is tacitly assumed that what constitutes a detected contaminant is clear. For example, *"Only the results for detected contaminants may be included in the main water quality table."*

In the guidance to PWSs, "Preparing Your Drinking Water Consumer Confidence Report: Guidance for Water Suppliers" (EPA, 2010c), the focus is on a table of federal MDLs, or perhaps more stringent State MDLs:

A detected contaminant is any "regulated" or "unregulated" (as required under 40 CFR 141.40) contaminant detected at or above its method detection limit (MDL).

See the EPA Web site at www.epa.gov/safewater/ccr/regulations.html for a list of contaminants and MDLs.

Your state may have lower MDLs that take precedence over EPA's.

If you are unsure of the MDL for a contaminant, and your laboratory reports a value greater than zero, include that in your CCR.

Unfortunately, the link to the EPA table of contaminants and MDLs is broken. I pursued this with the EPA web and CCR folks, and a document was provided that listed the cyanide "detection limits" from 40 CFR 141.23 shown above. This document has the following as a header:

U.S. EPA's Methods and Minimum Detection Limits

List taken from the 2007 version of 40 CFR 141.23 to 141.25

Note: These detection limits are for your information. They are U.S. EPA's Minimum Detection Limits, codified at 40 CFR 141.23-141.25. Your state may have different detection limits that take precedence. If you are uncertain about the inclusion of certain data, talk to your primacy agency. Some contaminants, such as lead and copper, are not listed below. If you cannot find a contaminant listed below and your lab analysis provides a detected value for that contaminants, report it in your CCR. If you are uncertain, always provide too much data rather than too little.

Here it states that these "minimum detection limits" are "for your information" and that your state may have "different detection limits that take precedence". It goes on to say that if your lab provides a detection value, then "report it in your CCR".

There is a simplistic way to interpret this:

1. There is a required MDL.
2. The lab needs to achieve the required MDL.
3. The lab needs to quantitate down to the required MDL.
4. The PWS needs to report any results above the required MDL.

This simplistic view comports with my sense of how the drinking water folks at EPA see things: your testing drinking water, that's an ideal matrix, the method should work, and if it doesn't, the lab isn't trying hard enough.

For other contaminants it is interesting to note that the pertinent section of the PWS guidance document is called: *"Item 4: Reporting Levels of Detected Contaminants".* However this guidance document doesn't provide information on reporting levels, so the PWS must go with what is in the regulation itself, which is detection limits for inorganics, metals, SOCs, and radioactive contaminants, a set "detection limit" for VOCs, and

MRLs for DBPs. The term MRL is clearly defined: *"The minimum reporting level (MRL) is the minimum concentration of each analyte that must be reported to EPA."* (Bacteria, lead and copper, cryptosporidium, and radon are handled differently and aren't discussed further here.)

Let's return to an interesting sentence in the PWS guidance document: "*If you are unsure of the MDL for a contaminant, and your laboratory reports a value greater than zero, include that in your CCR."* This is essentially the informal guidance I have received from my State DEP. It equates to…*"your lab probably knows what it's doing; whatever numbers they give you is probably fine."* I don't find this particularly reassuring because ***"I'm"*** the lab and I'm also part of the PWS.

Confusing Terminology. Labs are pretty clear on what a 40 CFR 136 Appendix B MDL is, and how to determine it. Most labs have probably taken a look at the changes to how MDLs are determined that EPA is the "pre-published" 2016 Methods Update Rule (MUR). TNI labs are probably pretty familiar with the TNI detection and quantitation requirements, and upcoming changes to these procedures. Laboratories thrive on clarity and specificity, but the terminology in 40 CFR 141 is anything but precise. What's the difference between detection limit, method detection limit, minimum detection limit, regulatory detection level, minimum reporting limit, minimum reporting level, and lowest reporting limit?

If testing drinking water is as easy as some at EPA thinks it is, perhaps they can also make the detection terminology easy for labs and PWSs to understand and utilize.

Conclusion. From a look at the federal regulations and guidance documents it is definitely unclear how low a PWS, and its lab, must go in reporting detected contaminants in their CCR.

7. Cyanide Formation During Sample Preservation and Analysis

For drinking water testing, laboratories are required to "follow the method", including how samples are preserved. This regulatory mantra is problematic for cyanide (Delaney & Blodget, 2016) and false positives from the sample preservation and testing has been demonstrated (Delaney, et al., 2007). Cyanide formation during wastewater preservation and testing has also been demonstrated (Delaney et al, 1999; Khoury et al, 2008; Stanley & Antonio, 2012). For wastewater, field dilution has been demonstrated to be useful for improved sample preservation and field spikes are useful for demonstrating sample integrity (Delaney & Blodget, 2015).

We have even demonstrated experimentally several times that detectable amounts of free cyanide can form when **deionized water** is treated like MWRA drinking water is treated and then preserved and tested using required sample preservation and approved testing methods. This is a serious problem, because the cyanide preservation and analysis are prescribed by the drinking water regulation and PWS and their laboratories are obliged to follow them.

Appendix A contains the presentation “A Look at Matrix Effects” from the 2016 National Environmental Monitoring Conference, which shows a simple experiment in which free cyanide forms when deionized water is treated as MWRA drinking water is treated and then dechlorinated with ascorbic acid, preserved with sodium hydroxide (NaOH) and tested for free cyanide. Appendix B contains a manuscript that has been submitted for publication in JAWWA on the most recent experiment. It also shows free cyanide formation when either ascorbic acid or thiosulfate were used for dechlorination.

This simple model system exemplifies the problem with cyanide’s diverse chemistry. Even when there is no sample matrix other than the drinking water treatment chemicals and the cyanide preservation, free cyanide forms, causing a false positive. It should be noted that we have shown that the false cyanide doesn’t form from the water treatment chemicals themselves—only when the cyanide preservation occurs by reducing the oxidants and raising the pH to keep HCN from escaping.

Prescribed drinking water testing procedures leaves PWSs, and their laboratories, without a viable alternative that would be acceptable to EPA. This must be addressed by EPA. Several alternatives are possible:

1. Immediate on-site analysis without adding NaOH,
2. Same day off-site analysis without adding NaOH, but using a field spike to show that the integrity of the sample was maintained,
3. Field dilution, with a field spike, to minimize the effect of the sample matrix, and
4. Raising the reporting limit to the PQL of 100 ug/L, to avoid detecting these false positives.

8. Recommendations

There is a problem with cyanide testing in drinking water, in that getting a false positive is a distinct possibility. When published in a CCR, this needlessly alarms the public. For example, we have demonstrated that when we treat deionized water in the same manner as our drinking water is treated and then preserve a sample of this water and test it for cyanide using the required, approved procedures, easily detectable amounts of free cyanide are formed. This “false positive” cyanide persists in the sample for days. However, the lack of flexibility in prescriptive drinking water preservation and testing for cyanide doesn’t allow this problem to be effectively avoided.

While very few cyanide detections above the current MCL (0.07%) were reported in the Third Six-Year Review, there were many detections at lower concentrations (1.8%). The reporting limits reported by laboratories for cyanide testing vary widely, from <1 ug/L to >100 ug/L, and the requirements for required minimum reporting levels are unclear and ambiguous. Clarifying guidance to States, laboratories and PWSs is needed and should not be *“If you are unsure of the MDL for a contaminant, and your laboratory reports a value greater than zero, include that in your CCR”* (EPA, 2010c).

Based on EPA's assessments in the Third Six-Year Review, there is only a *"low priority or no meaningful opportunity"* to lower the MCL or MCLG from 200 ug/L. This is primarily due to the limitation of lowering the Practical Quantitation Limit (PQL) below 100 ug/L, even though 40 CFR 141.23 lists much lower *"Detection Limits"*, though these detections limits are stated in the context of sample compositing. It should also be noted that there are no detection limits listed for the Alternative Testing Methods approved in Appendix A to Subpart C of Part 141, leading to additional confusion. This disconnect between the PQL and the listed detection limits is confusing to PWS and their laboratories. The requirements for reporting limits is unclear.

Different States have different stated or unstated requirements for drinking water cyanide testing to show compliance with the MCL, which is probably due to the ambiguity in the regulations and the lack of clear guidance from EPA. When EPA first began regulating free cyanide in drinking water in 1992, it determined that a PQL of 100 ug/L was reasonable, though the regulatory use of a PQL was unclear. When this was reexamined in the 2017 Third Six-Year Review, EPA concluded that based on Proficiency Test (PT) data a PQL lower than 100 ug/L was not justifiable. EPA then examined Method Detection Limit (MDL) data and concluded that an Estimated Quantitation Limit (EQL) of 50 ug/L was possible. However, it should be noted that MDL determinations are based on analysis of standards, which doesn't involve real sample matrices or interferences. Moreover, it should be noted that the validation studies used to support approval of regulatory drinking water cyanide methods generally did not evaluation or address preservation and treatment for interferences.

EPA should instruct States to only require cyanide reporting in drinking water down to 100 ug/L and that only detected results above 100 ug/L should be reported in CCRs. EPA should clarify in 40 CFR 141.23, as it has in 40 CFR 141.62, that free cyanide is the regulated form of cyanide. EPA should clarify that Total Cyanide and Available Cyanide are only screening tests for free cyanide. EPA should encourage States to offer certification for free cyanide in drinking water. Also, EPA should clarify that cyanide PT samples required for cyanide certification or accreditation are suitable for free, total, and available cyanide testing. EPA should encourage States to approve reduced monitoring waiver requests in 40 CFR 141.23 to allow monitoring of one sample every 9 years as long as results are consistently below the MCL and there are no industrial sources of cyanide.

Finally, EPA should clarify the requirements involving the various detection and quantitation terms: PQL, EQL, DL, MDL, MRL, LCMRL, LOD, LOQ, etc.

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10. Appendices

A. "A Look at Matrix Effects" (presented at the 2016 National Environmental Monitoring Conference, Orange County, CA).

B. "Free Cyanide Forms During Drinking Water Free Cyanide Determination" (submitted for publication in the Journal of the American Water Works Association).

Appendix A. “A Look at Matrix Effects” (presented at the 2016 National Environmental Monitoring Conference, Orange County, CA).

"A Look at Matrix Effects"

Mike Delaney and Chuck Blodget

Massachusetts Water Resources Authority (MWRA)

ELSEVIER

Clinical Biochemistry

Volume 38, Issue 4, April 2005, Pages 328–334

LC Mass Spectrometry: Recent Developments in Clinical Chemistry

Review

Matrix effects: the Achilles heel of quantitative high-performance liquid chromatography–electrospray–tandem mass spectrometry

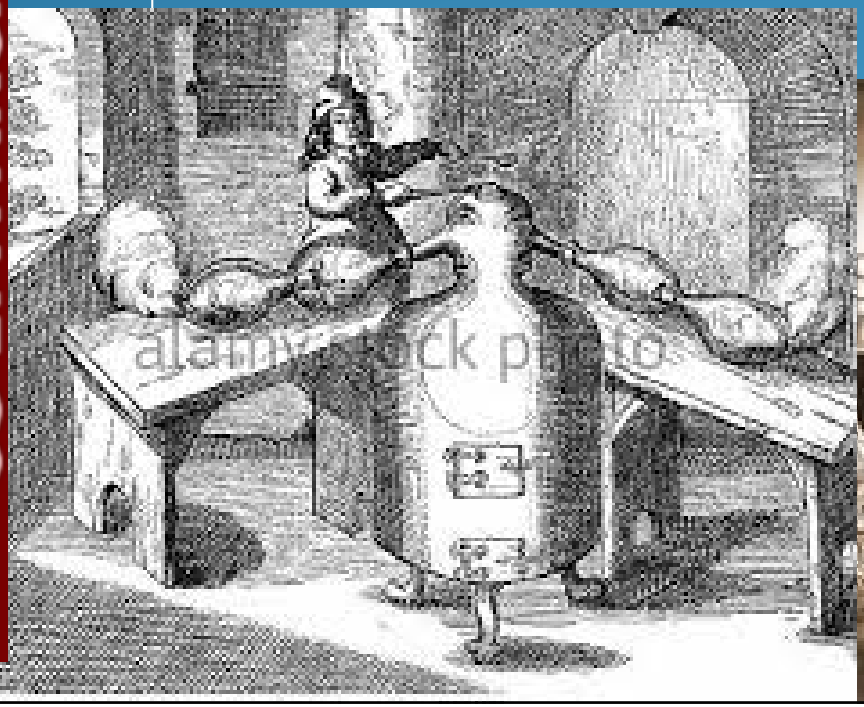
Paul J. Taylor

A Look at Matrix Effects

- Back in the Day – at a contract lab – Blame the sample!
- A little history.
- Newer EPA methods.
- Quantifying Matrix Effects
- Which analytes/methods are the bad actors?
- Decreasing Matrix Effects.
- Cyanide: The “baddest” actor.

Back in the Day

- Contract Lab – Blame the sample!
- If the LCS worked and the MS didn't (and the MSD agreed with the MS), then it's the sample's fault, and this is a matrix effect. Move on!
- PWS/POTW Lab – the sample is our product, so we have to try to get the methods to work for our sample matrix.



1951 – First use of "Matrix Effect"

Spectroscopic Determination of Vanadium in Residual Fuel Oils

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WITHIN the past few years, the petroleum industry has become increasingly interested in the determination of trace percentages of vanadium in various products, and particularly in residual fuel oils (distillation residues). In stocks charged to cracking units, vanadium is one of the elements that poison the catalyst, and in this respect it ranks in importance with iron, nickel, chromium, sodium, and copper. Furnace slags deposited during the burning of vanadium-bearing fuel oils may, under certain conditions, contribute to slagging and corrosion of metals (*3*). Finally, vanadium is one of the trace elements whose presence or absence in crude oil gives the petroleum geologist clues concerning its origin and age. Katchenkov (*6*), for example, states that very old crudes are likely to be higher in vanadium and nickel and lower in strontium than crudes from younger formations.

A large measure of the effort by industry to combat slagging and corrosion caused by vanadium compounds has been directed to improvements in the materials for construction of boilers and other combustion equipment, as well as to the use of additives such as lime and alumina in the oil.

Colorimetry and polarography are frequently applied to the determination of vanadium in ashes of petroleum products. These methods, however, impose certain problems of chemical manipulation, and their application is restricted by interferences.

It was thought desirable, therefore, to take advantage of a spectroscopic technique which is essentially free from interference and in which the ash is not treated before arcing except for the addition of other powdered materials.

Emission spectroscopic methods for the determination of metallic traces, including vanadium, in petroleum oils have been reported by Carlson and Gunn (*2*) and Murray and Plagge (*8*). The former employed quenched electrodes in a cathode-layer technique without preliminary ashing, and reported poor agreement with chemical results for some heavy residua. Murray and Plagge used an ash aid of silica and burned the ash in a direct current arc with added powdered graphite. They employed a rotating logarithmic step sector and a series of comparison standards in order to estimate the vanadium concentration.

The method described in this paper avoids the space-consum-

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indicates th

ELIMINATING MATRIX EFFECT OF ASH

The consistency of the working curves obtained in preliminary work (Figure 1) later permitted a reduction in number of standards to three representing 1, 4, and 16% vanadium.

As no significant difference was detected between the analytical curves obtained from the samples containing sodium chloride–calcium oxide and those with sodium chloride alone, it was assumed that the use of silica and graphite eliminated any matrix effect that might otherwise have been caused by the chemical character of the ash of the fuel oil.

three mixtures were pre-

1962 – First use of "Matrix Interferences"

Determination of Oxygen by Activation Analysis with Fast Neutrons Using a Low-Cost Portable Neutron Generator

EDGAR L. STEELE[1] and W. WAYNE MEINKE

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▶Fast neutron activation analysis, using a low-cost Cockcroft-Walton design accelerator as a source of 14-m.e.v. (deuterium-tritium) neutrons, has been found satisfactory for trace oxygen determination. This method is rapid, sensitive, and selective, and is free from most matrix interferences. Yet it uses equipment costing no more than good infrared or spectrographic instruments. Fast neutrons (>10 m.e.v.) convert oxygen-16 by an (n,p) reaction to 7.4-second nitrogen-16. This in turn emits 6 to 7 m.e.v. γ-rays which are measured by scintillation spectrometry. Samples containing 10 mg. or more of oxygen have been analyzed to within ±10% with a fast flux of ~10^8 n cm.$^{-2}$ sec.$^{-1}$ Larger samples give smaller errors. By using all the sample area available with an average flux for irradiation of 10^8 n cm.$^{-2}$ sec.$^{-1}$ and using a proper transfer system, it should be possible by this nondestructive method to analyze to within ~±10 to 15% for as low as 10 p.p.m. of oxygen. The average time for an analysis, including weighing, is approximately 7 minutes. The only interference encountered is from fluorine and this can be compensated for at F/O ratios below 10.

THE important effects of oxygen content on physical properties of materials and the wide distribution of this element in nature necessitated a rapid and reasonably accurate method for trace oxygen determination, which would be free of matrix interferences, yet remain in the price range approachable by the average analytical laboratory. A number of specialized methods have been reported for the determination of small amounts of oxygen (γ,n)O^{15} (*10*); $O^{18}(n,\gamma)O^{19}$ (*5*); $O^{17}(n,\alpha)C^{14}$ (*1*); and $O^{16}(n,p)N^{16}$ (*2, 3, 18*). From a consideration of time, equipment, expense, and convenience, the $O^{16}(n,p)N^{16}$ reaction appears to be the best suited for the average analytical laboratory.

This paper describes the application of 14-m.e.v. neutron irradiation for oxygen determination, using a low-voltage Cockcroft-Walton accelerator as a neutron source and γ-ray scintillation spectrometry to measure the 7.4-second radioactive nitrogen-16 produced.

The neutron generator used by Coleman and Perkin is not described in their paper (*2*), but from the fact that it used 500-k.e.v. deuterons one can surmise that it was an electrostatic machine of some sort. They report 4π total yields of fast neutrons at the zirconium-tritium target of about 10^{10} neutrons per second, while Veal and Cook made their runs at neutron source strengths up to 10^{10} neutrons per second and normalized to 10^9 (*18*). Runs on the low-cost neutron generator used by Steele and Meinke were made at yields between 2×10^{10} and 2×10^9 neutrons per second under roughly the same circumstances. The limiting factor in the work of all three groups has been the decrease in strength of the tritium target with use. New concepts of target design available now promise to improve this situation considerably.

APPARATUS, REAGENTS, AND PROCEDURE

Apparatus. Texas Nuclear Corp. Model 150 neutron generator. This is a machine of Cockcroft-Walton design which accelerates deuterium ions to 150 k.e.v. It uses a target of tritium absorbed onto a thin layer of titanium, which in turn is backed by

nuclides and two
scintillation crystal
Scintillation we
$1\frac{1}{2} \times 2$ inch Na
inches of lead shiel
Two-π proporti
cated locally accor
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Special transfer
samples from the
tector in 3 to 4 sec

Preliminary info
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is available (*12*–
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Reagents. Ana
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Eastman Kodak
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Procedure.
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recorded with a n
The counts in th
peaks were taken
amount of oxyg
amounts of pure oxalic acid were em
ployed as standards for quantitative
measurements.

IRRADIATION METHODS

Neutron Generator. Fourteen million electron-volt neutrons were produced by the $H^3(d,n)He^4$ reaction in the 150-kv. Cockcroft-Walton neutron generator. At the center of the irradiation position during operation, neutron fluxes varied from 5×10^7 to 5×10^8 n cm.$^{-2}$ sec.$^{-1}$, depending upon the condition of the tritium target. These fluxes were measured continuously, however, by monitoring (with a Geiger

▶Fast neutron activation analysis, using a low-cost Cockcroft-Walton design accelerator as a source of 14-m.e.v. (deuterium-tritium) neutrons, has been found satisfactory for trace oxygen determination. This method is rapid, sensitive, and selective, and is free from most matrix interferences. Yet it uses equipment costing no more than good infrared or spectrographic instruments. Fast neutrons (>10

A Little History

- **Matrix Effects:** Used in 792 out of 78,769 articles in "Analytical Chemistry" and "Environmental Science and Technology" journals. (1.0%)
- **Matrix Interferences:** Used in 3,189 out of 78,769 articles in "Analytical Chemistry" and "Environmental Science and Technology" journals. (4.0%)
- Mentioned in the 1985 Instrumental Analysis text I used to teach undergraduates.

What is a Matrix Effect?

- EPA Definition: *"Manifestation of non-target analytes or physical/ chemical characteristics of a sample that prevents the quantification of the target analyte (i.e., the compound or element of interest being effectively quantified by the test method) as it is routinely performed, typically adversely impacting the reliability of the determination. For example, a matrix effect can give rise to a high or low bias."* (ORD) [Forum on Environmental Measurements (FEM) Glossary]
- But "Matrix Interference" didn't retrieve a definition, and Interference wasn't defined in the context of analytical chemistry.
- Neither term is defined in the 2009 TNI standard.

IUPAC Definition

- **Matrix Effect:** *"The combined effect of all components of the sample other than the analyte on the measurement of the quantity."*
- **Interference:** *"If the specific component can be identified as causing an effect then this is referred to as an interference."*

Pure & Appl. Chem., Vol. 61, No. 9, pp. 1657–1664, 1989.
Printed in Great Britain.

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON ANALYTICAL NOMENCLATURE*
and
CLINICAL CHEMISTRY DIVISION
COMMISSION ON AUTOMATION AND CLINICAL CHEMICAL TECHNIQUES†
in collaboration with
INTERNATIONAL FEDERATION OF CLINICAL CHEMISTRY
SUBCOMMITTEE ON ANALYTICAL SYSTEMS

NOMENCLATURE FOR AUTOMATED AND MECHANISED ANALYSIS

(Recommendations 1989)

MATRIX EFFECT (substantive)	The combined effect of all components of the sample other than the analyte on the measurement of the quantity.	If a specific component can identified as causing an effect then this is referred to as interference. See MATRIX.

It's all about Accuracy and Bias

- *"Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency."* - 2009 TNI Standard
- *"In chemical analysis, matrix refers to the components of a sample other than the analyte of interest. The matrix can have a considerable effect on the way the analysis is conducted and the quality of the results obtained; such effects are called matrix effects."* - Wikipedia.
- *"A matrix effect can give rise to a high or low bias."* (EPA ORD)

To Summarize…

- **"Matrix Interference"** if you know what is causing the bias.
- **"Matrix Effect"** if you don't know what is causing the bias.
- **"Matrix Mistake"** if there is something wrong with the method itself and it is affecting the target analyte. (I made that up.)

Newer EPA Methods –Draft 625.1

- *"8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is* ***suspect and may not be reported*** *or used for permitting or regulatory compliance purposes."*
- **(emphasis added)**

Newer EPA Methods –Draft 625.1

- Although, there is an out for problematic analytes:
  - *"8.1.7 The large number of analytes tested in performance tests in this method present a substantial probability that one or more will fail acceptance criteria when many analytes are tested simultaneously, and a re-test is allowed if this situation should occur. If, however, continued re-testing results in further repeated failures, the laboratory should document the failures (e.g., as qualifiers on results) and either avoid reporting results for analytes that failed or* ***report the problem and failures with the data.*** *..."* **(emphasis added)**

Quantifying Matrix Effects

- HPLC-MS/MS/MS...a good technique, but not a "great" technique. A lot of the work on Matrix Effects is in the LC-MS literature.
- Matrix Effect:
  - ME (%) = MS Recovery / LCS Recovery * 100

Anal. Chem. **2003,** *75,* 3019−3030

Strategies for the Assessment of Matrix Effect in Quantitative Bioanalytical Methods Based on HPLC−MS/MS

B. K. Matuszewski,* M. L. Constanzer, and C. M. Chavez-Eng

Merck Research Laboratories, West Point, Pennsylvania 19486

In recent years, high-performance liquid chromatography (HPLC) with tandem mass spectrometric (MS/MS) detection has been demonstrated to be a powerful technique

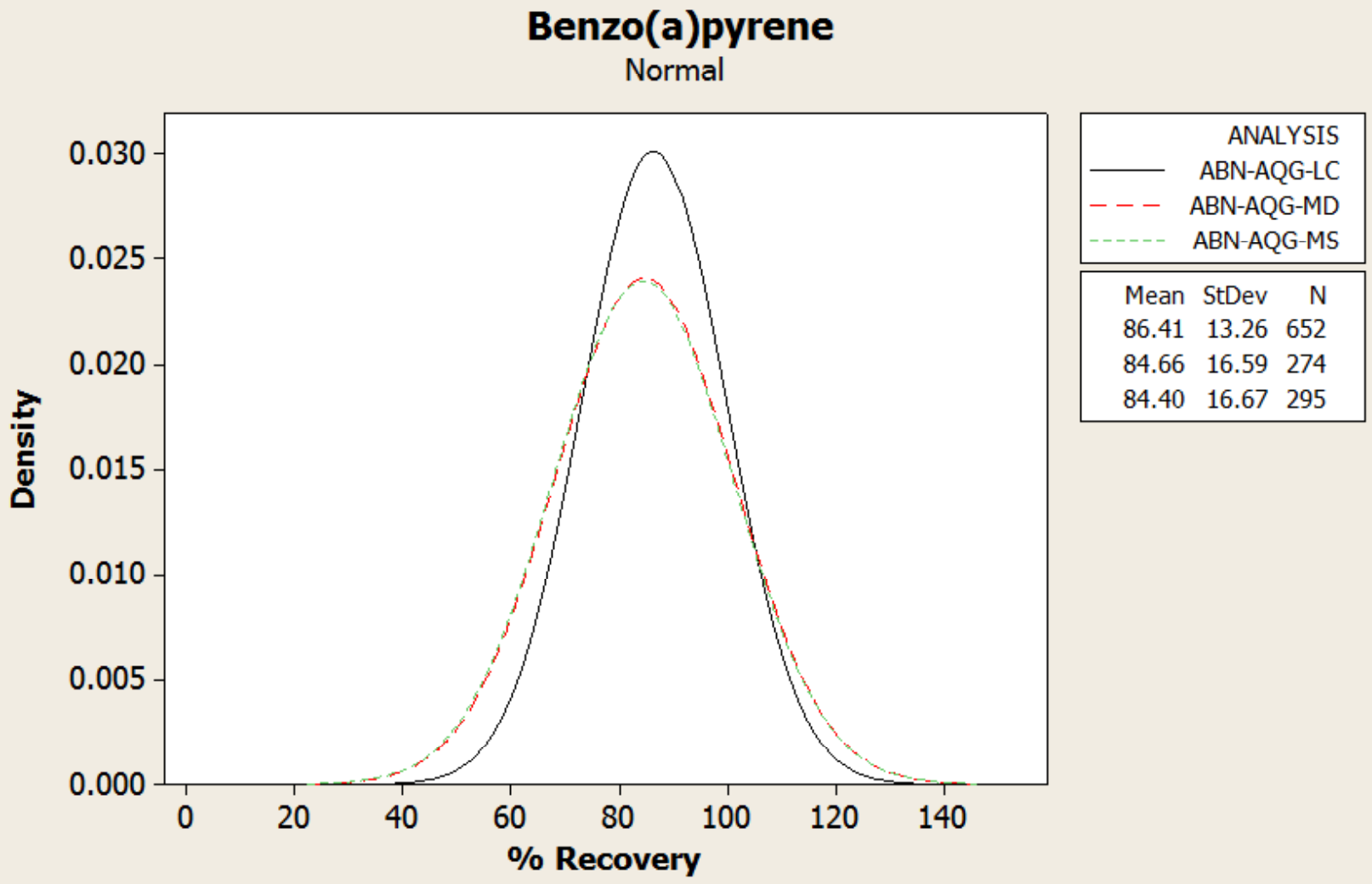
was utilized but it was absent when the HN interface was employed.

Quantifying Matrix Effects

- Matrix Effect: Recovery with and without matrix...
  - ME (%) = MS Recovery / LCS Recovery * 100
- If the MS and LCS give the same recovery, then
  - ME = 100%,
  - meaning no matrix effect is evident.
- ME >100 % means signal enhancement.
- ME < 100% means signal suppression.
- My lab has a lot of MS/MSD and LCS recovery data; I could use this in bulk to go looking for significant matrix effects.

Benzo(a)pyrene by Method 624

- Slight but significant Matrix Effect
- F = 1.571 vs. F* = 1.143



Quantifying Matrix Effects

- Bulk search for Matrix Effects:
  - Take a set of LCS and MS/MSD recoveries.
  - Calculate the standard deviation of the recoveries.
  - Calculate the F-statistic:

$$F = s^2_{MS/MSD} / s^2_{LCS}$$

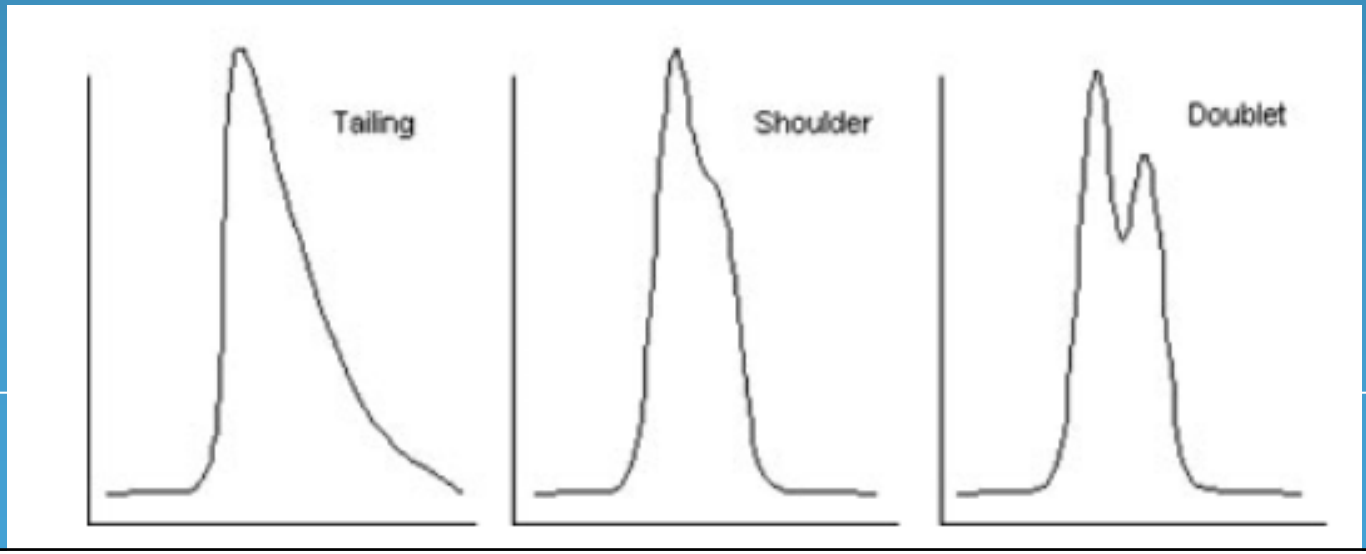
  - Compare F to the critical value. If is significant, there appears to be a significant Matrix Effect.
- For example: Benzene by Method 624 purge-and-trap GC/MS:

	N	s (%)	F	F*	Conclusion
LCS	1141	7.660	1.039	1.124	Not significant
MS/MSD	584	7.810			

alyte	Method	N (LC)	N (MS/MD)	S (LC)	S (MS/MD)	Fcalc	Fcrit 0.05	Significant at 95%?
nzene	624	1141	584	7.66	7.81	1.040	1.124	N.S.
a)P	624	652	569	13.26	16.62	1.571	1.143	S
nzoid Acid	624	652	567	9.93	147.77	221.672	1.143	way S
rylonitrile	624	1725	1141	14.48	14.67	1.025	1.093	N.S.
rolein	624	584	1141	28.54	43.40	2.312	1.124	S
rolein	603	25	50	12.08	27.02	5.001	1.727	S
3	AAN	150	232	3.83	5.90	2.377	1.274	S
4	AAN	107	118	3.98	6.53	2.690	1.368	S
2 (by diff)	AAN	180	212	2.60	11.29	18.842	1.266	S
3/NO2	AAN	178	211	3.57	5.39	2.276	1.268	S
	Titration	308	584	8.18	7.90	0.932	1.176	N.S.
	UV/VIS	325	800	6.60	7.58	1.317	1.163	S
3	ISE	320	277	7.21	10.90	2.286	1.212	S
Total	AAN	267	701	5.87	20.89	12.665	1.179	S
Total	FIA	79	219	3.86	10.00	6.719	1.346	S

Decreasing a Simple Matrix Interference

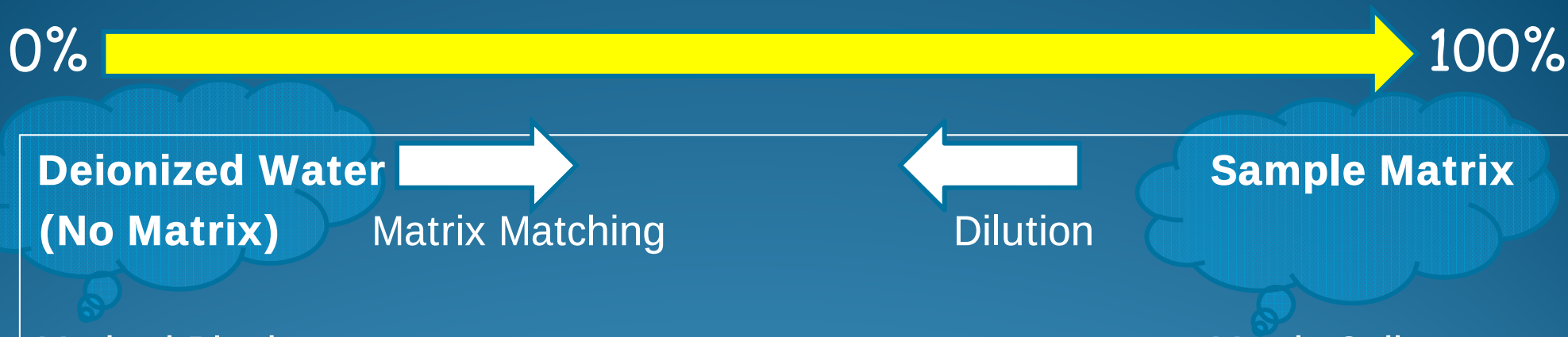
- **Simple Example:** A non-target compound co-elutes with a target analyte.
- The matrix interference can be decreased by:
  - Better cleanup. Remove the interference.
  - Better chromatography. Separate the interference from the target analyte.
  - Better detector – more selective. Detect the target analyte but not the interference.



Decreasing Subtle Matrix Effects

- Consider these:
  - Matrix Matching/Matrix Modifier
  - Internal Standards
  - Dilution (“Matrix Minimization”)
  - Standard Addition (MSA, MOSA)

Decreasing Subtle Matrix Effects



- Or this:
  - Field Dilutions (with Field Spikes)

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]

Decreasing Subtle Matrix Effects

0% → 100%

Deionized Water (No Matrix) → Matrix Matching | Dilution ← **Sample Matrix**

Method Blank
Lab Control Sample

Matrix Spike
Matrix Spike Duplicate

- Or even this: Standard Dilution Analysis

analytical chemistry

Article

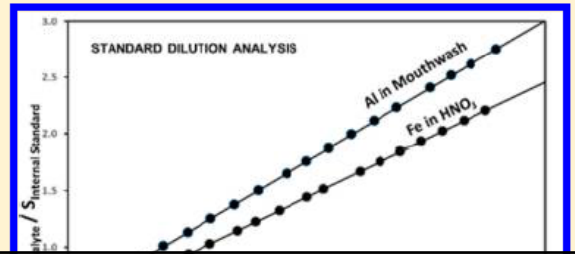
pubs.acs.org/ac

Standard Dilution Analysis

Willis B. Jones,[†] George L. Donati,*[,†] Clifton P. Calloway, Jr.,[‡] and Bradley T. Jones[†]

[†]Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 21709, United States
[‡]Department of Chemistry, Physics and Geology, Winthrop University, Rock Hill, South Carolina 29733, United States

ABSTRACT: Standard dilution analysis (SDA) is a novel calibration method that may be applied to most instrumental techniques that will accept liquid samples and are capable of monitoring two wavelengths simultaneously. It combines the traditional methods of standard additions and internal standards. Therefore, it simultaneously corrects for matrix effects and for fluctuations due to changes in sample size, orientation, or instrumental parameters. SDA requires only 200 s per sample with inductively coupled



Dilution is a Solution

- When you have sensitivity to spare, dilution reduces matrix effects (e.g. LC-MS):

analytical chemistry

Article

pubs.acs.org/ac

Reduction of Matrix Effects in Liquid Chromatography–Electrospray Ionization–Mass Spectrometry by Dilution of the Sample Extracts: How Much Dilution is Needed?

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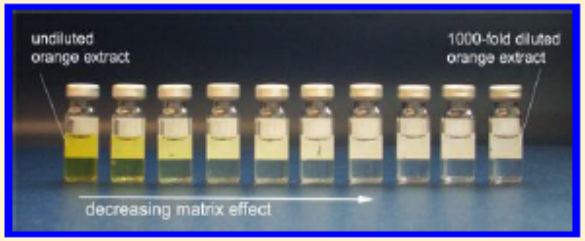
Supporting Information

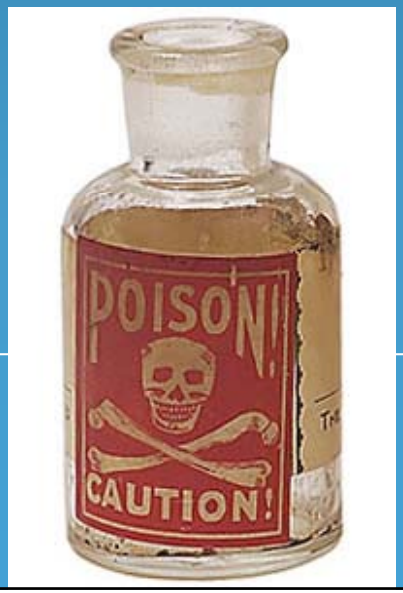
ABSTRACT: In this study, the relationship between matrix concentration and suppression of electrospray ionization (matrix effects) was investigated. Ion suppression of pesticides present in QuEChERS extracts was used as an example. Residue-free extracts of four different commodities, avocado, black tea, orange, and rocket (arugula), were fortified with 39 pesticides each. For many of the resulting 156 pesticide/matrix combinations, considerable matrix effects were observed if the coextracted matrix of 8 mg of equivalent sample (in the case of tea: 1.6 mg) was injected with the undiluted extracts. The reduction of these matrix effects was measured at 10 levels of dilution up to 1000-fold. The results obtained indicate a linear correlation between matrix effects and the logarithm of matrix concentration (or dilution factor) until the zero-effect level of further dilution was reached. Using the logarithmic equations, it could be shown that a dilution of extracts by a factor of 25–40 reduces ion suppression to less than 20% if the initial suppression is ≤80%. For stronger matrix effects or complete elimination of suppression, higher dilution factors were needed. The observed correlation was independent from the two instrument platforms used, but the degree of matrix effects differed slightly between the two mass spectrometers in this study.



Tremendous developments in mass spectrometry have causes for enhancement are very rarely proposed, but there are

Cyanide: The "Baddest" Bad Actor

- Cyanide is a particular issue.
- There is a fair bit of literature on the "bad behavior" of cyanide in wastewater and drinking water testing.
- Cyanide can be formed or destroyed, and this can happen during sampling, preservation, storage, and testing.



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.

Environ. Sci. Technol. **2007,** *41,* 8383–8387

False Cyanide Formation during Drinking Water Sample Preservation and Storage

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Received June 07, 2007. Revised manuscript received September 19, 2007. Accepted September 27, 2007.

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

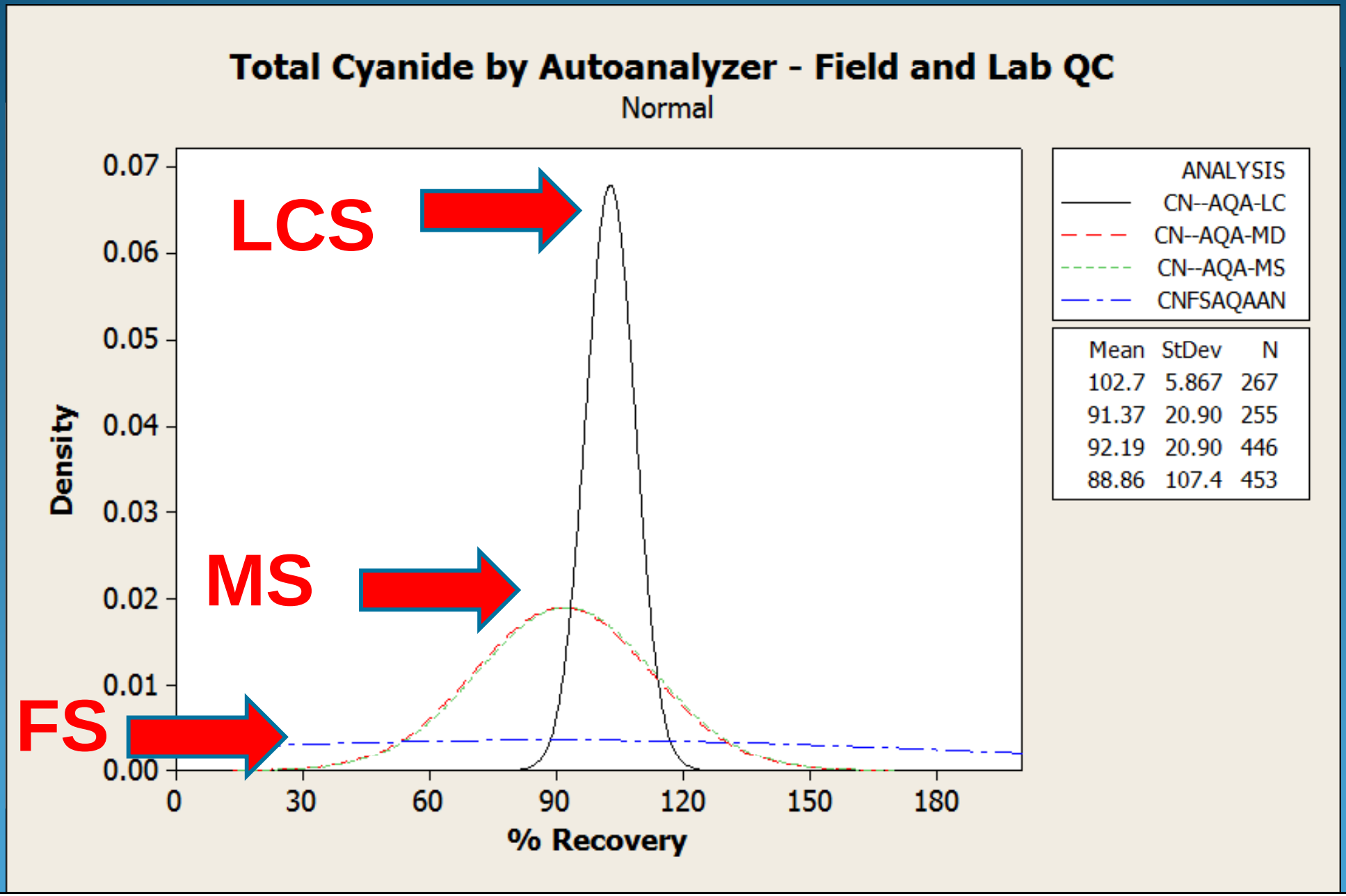
Potential Interferences for Cyanide

- From ASTM D7365-09a:
  - Aldehydes, Color, Dissolved Solids, Fatty Acids, Mercury, Metal Anions, Metal Cations, Nitrate, Nitrite, Oxidants, Photodecomposition, Sugars, Sulfides, Turbidity, Sulfur Compounds, Thiocyanate...and *"Unknowns that cause negative results."*

Designation: D7365 – 09a (Reapproved 2015)

Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide[1]

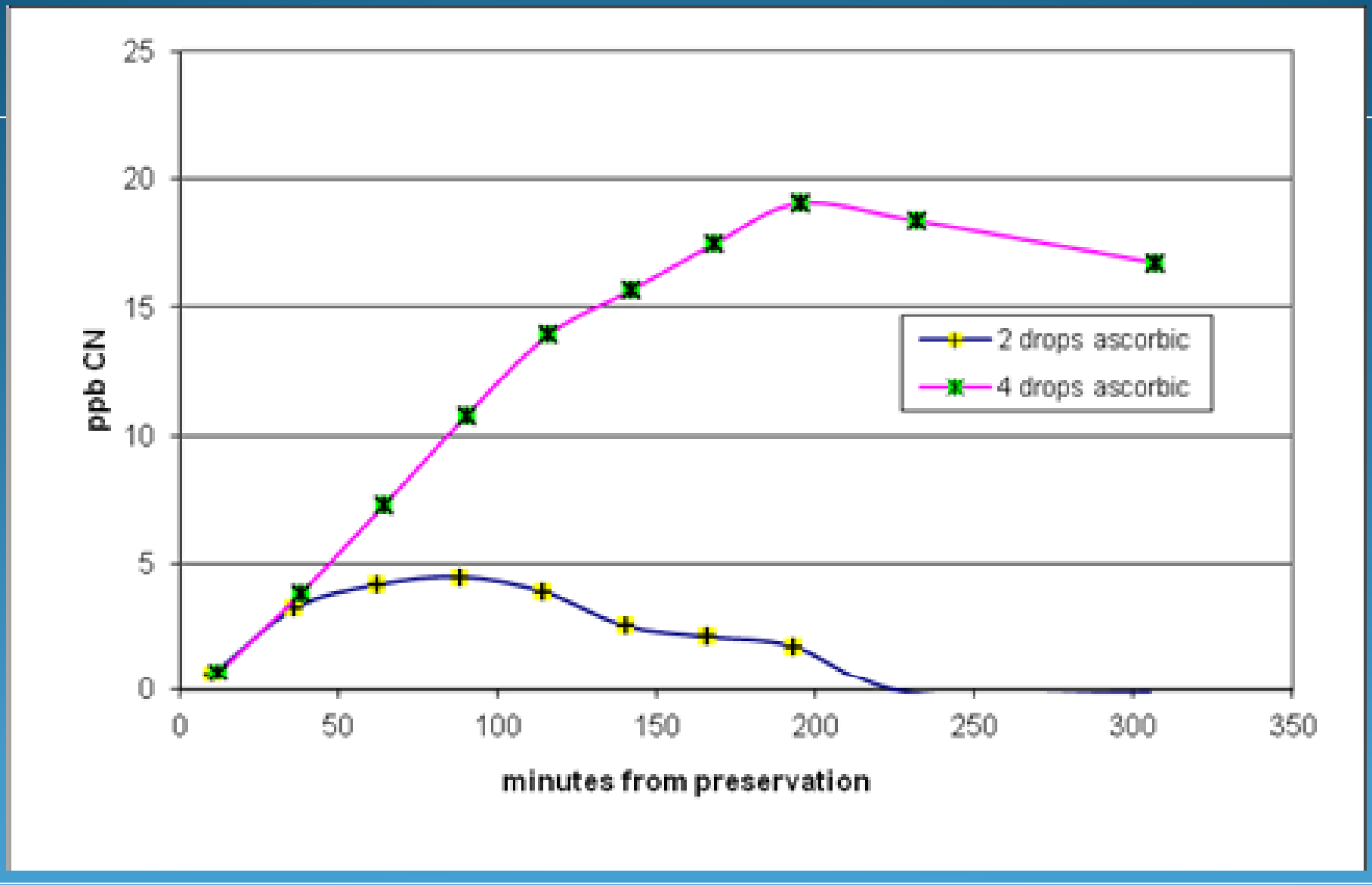
Cyanide: The Baddest Bad Actor



Simple Illuminating Experiment

- **Routine Drinking Water Treatment:**
  - Deionized Water.
  - Raise pH to 9 and 25 mg/L Alkalinity (for corrosion control).
  - Add 1.4 mg/L hypochlorite (disinfection).
  - Add ammonia to 0.5 mg/L NH3-N as NH_4OH (to form chloramine residual disinfectant).
- **Routine Cyanide Sampling:**
  - Dechlorinate with ascorbic acid. (9-50 minutes)
  - Preserve with NaOH to pH >12.
- **Tests positive for Free CN by FIA/Amperometry :**
  - This is a problem: Drinking water treatment and the approved cyanide sampling and testing procedure gets a hit for cyanide when no cyanide was present.
- **Or in other words…If it happens in deionized water, why shouldn't it happen in drinking water?**

Simple Illuminating Experiment



Tale of Two Public Water Supplies

- MWRA's PWS: Ozone and Chloramines:
  - In 2007 got Total Cyanide hits that were demonstrated to be forming in the sample container. Approved by MassDEP and EPA to use on-site distillation and avoid NaOH. (ES&T Publication)
  - In 2015 switched to Free Cyanide. Demonstrated that field dilution, avoiding NaOH, and same day analysis supported by field spikes could get substantiated results without cyanide its. (JAWWA Publication)
- Another PWS: Filtration and Hypochlorite: Free cyanide was detected up to 47 ug/L in the treated water but not in the source water. The Free Cyanide level seemed to depend on how carefully the hypochlorite was neutralized with ascorbic acid (stoichiometric).

For Drinking Water:
"Follow the Method"

(1) Analysis for the following contaminants shall be conducted in accordance with the methods in the following table, or the alternative methods listed in appendix A to subpart C of this part, or their equivalent as determined by EPA. Criteria for analyzing arsenic, barium, beryllium, cadmium, calcium, chromium, copper, lead, nickel, selenium, sodium, and thallium with digestion or directly without digestion, and other analytical test procedures are contained in *Technical Notes on Drinking Water Methods*, EPA–600/R–94–173, October 1994. This document is available from the National Service Center for Environmental Publications (NSCEP), P.O. Box 42419, Cincinnati, OH 45242–0419 or *http://www.epa.gov/nscep/*.

LABORATORY CERTIFICATION

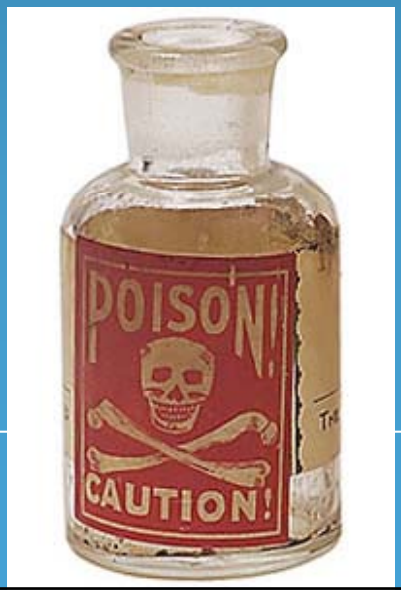
When using an approved method to obtain certification or to conduct compliance monitoring, EPA strongly encourages users of methods that are published in an EPA manual to follow instructions contained in the introductions to these manuals, unless the instructions conflict with statements in this document, or in the drinking water regulations. Although "must" can be argued to be a stronger word than "should" in requiring adherence to method procedures, some approved methods use these terms interchangeably. Analytical methods for drinking water are written to be prescriptive enough to provide uniformity of data quality, and flexible enough to allow analysts to exercise judgment, skill and initiative to improve the overall quality and efficiency of compliance monitoring. The Agency does not believe that semantical differences between "must" or "should" limits the authority of certification officials to enforce provisions of the methods.

Consumer Confidence Report

- Follow the method, take your hits, and explain them in your CCR.
- Required CCR Language:
  - Major sources in drinking water: *"Discharge from steel/metal factories; Discharge from plastic and fertilizer factories."*
  - Health effects language: *"Some people who drink water containing cyanide well in excess of the MCL over many years could experience nerve damage or problems with their thyroid."*

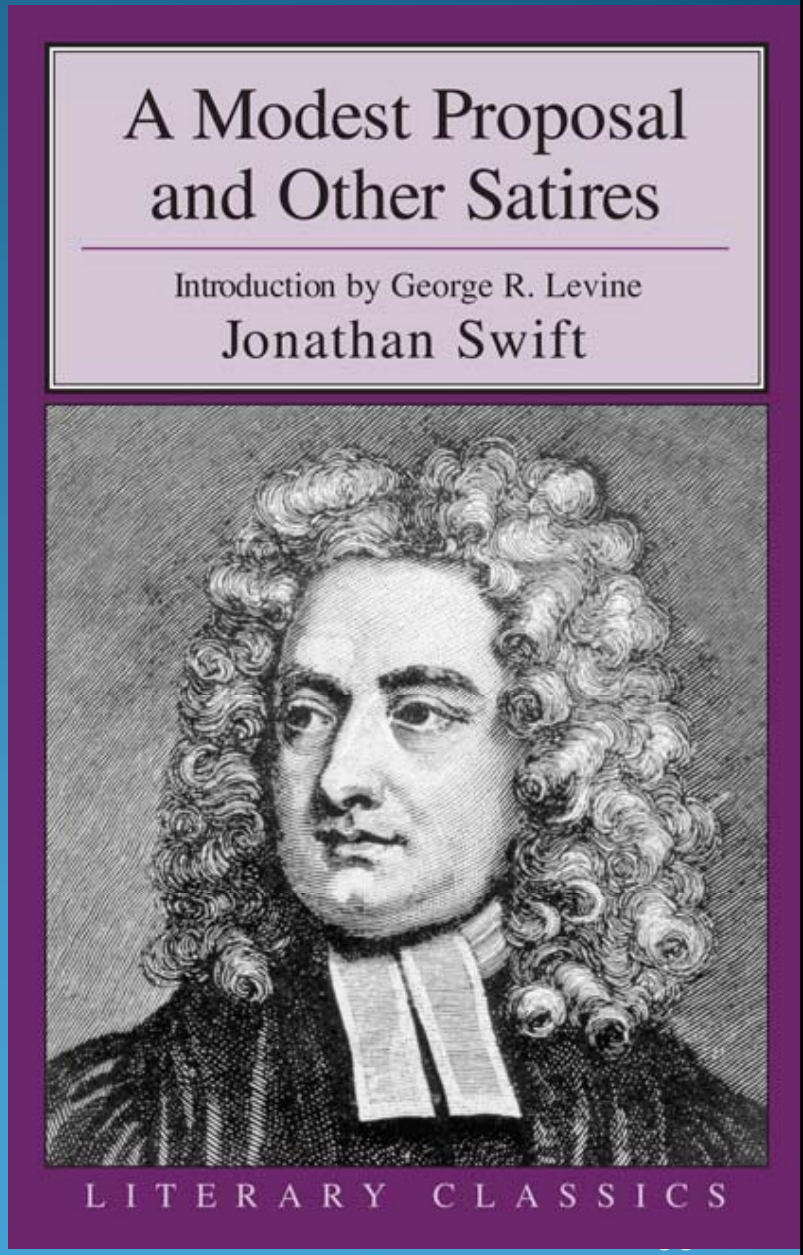
Drinking Water Alternatives?

- Follow the method, take your hits, and explain them in your CCR. ("There's cyanide in your drinking water!")
- Use a less sensitive method. (Dumb down the test.)
- Improve the method. (Difficult to get approval.)
- Develop a better method. (However, drinking water alternate test procedures (ATPs) must be national.)



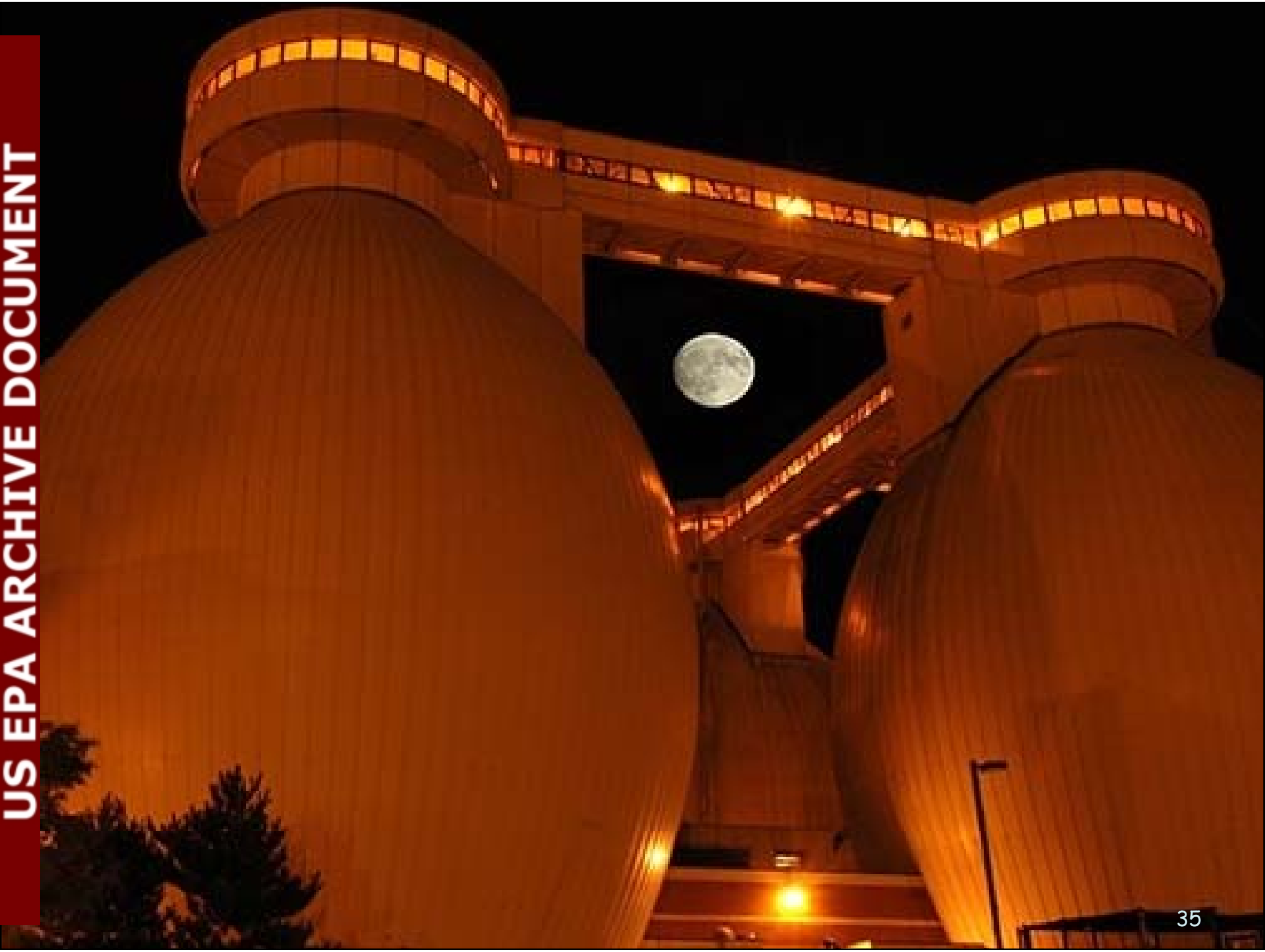
Conclusions: A Modest Proposal

- Matrix Effects and Matrix Interferences are common.
- You may not be able to avoid the issue by “blaming the sample”.
- There are alternatives to lessening or avoiding matrix effects and matrix interferences.
- Field dilution and field spikes are worthy of consideration.
- Cyanide is the “baddest” actor.



Thank you!

- Thank you to the MWRA Laboratory Services employees for their efforts over the course of this project.



Appendix B: "Free Cyanide Forms During Drinking Water Free Cyanide Determination" (submitted for publication in the Journal of the American Water Works Association).

Free Cyanide Forms During Drinking Water Free Cyanide Determination

Michael F. Delaney and Charles Blodget*

Department of Laboratory Services, Massachusetts Water Resources Authority (MWRA), 190 Tafts Avenue, Winthrop, Massachusetts 02152 USA

KEYWORDS

Cyanide, Cyanide Monitoring, Drinking Water, Free Cyanide

ABSTRACT

Easily detectable amounts of free cyanide (FCN) were formed when deionized water was treated like drinking water and preserved and tested for FCN. This occurred when either ascorbic acid or thiosulfate were used to dechlorinate, though higher FCN concentrations were observed with ascorbic acid. The amount of FCN observed was up to 50 – 60 ug/L, but strongly depended on the amount of ascorbic acid used. The amount of FCN observed was less dependent on the amount of thiosulfate used. The FCN was observed immediately after the samples were preserved, tended to increase, primarily during the first 24 hours, and persisted for at least five days. This demonstrates the potential to get false positive FCN results on drinking water samples that a United States Public Water Supply (PWS) would need to report in its Consumer

Confidence Report (CCR). Since drinking water sampling, preservation, and testing is prescriptive, there are few available ways to avoid these false positives.

INTRODUCTION

In the United States, Public Water Supplies (PWS) must test their final treated drinking water (DW) for a variety of potential contaminants, including cyanide (CN), to comply with State or Federal regulations. Such regulatory testing must follow approved test methods, including how samples are collected and preserved. While the regulated form is free cyanide (FCN), it is common to screen samples using a total cyanide (TCN) test.

The FCN Maximum Contaminant Level Goal (MCLG) in drinking water, set by the United States Environmental Protection Agency (EPA) is 200 ug/L (EPA, 2017). Drinking water with FCN concentrations less than this are considered to be "safe". The approved CN methods have regulatory detection limits from 0.5 to 50 ug/L, and accredited/certified DW laboratories often report CN concentrations down to these levels. PWS are required to report detected contaminants in their annual Consumer Confidence Reports (CCR), but the EPA regulations are unclear about detection and quantitation, so there is a lot of uncertainty within the PWS community regarding CCR requirements.

Cyanide has the additional level of complexity in that it can be formed or destroyed by a variety of chemical reactions. Previous studies demonstrated that cyanide can form in the preserved sample container (Delaney, et al, 2007) or during the sample preservation and analysis (Delaney & Blodget, 2016). This experiment was conducted to verify previous observations regarding FCN formation during drinking water treatment and cyanide testing. It is a more

thorough and controlled study similar to previously described results (Delaney & Blodget, 2016a).

MATERIALS AND METHODS

Using deionized water, drinking water treatment mimicked what is used by the Massachusetts Water Resources Authority (MWRA) at its John J. Carroll Water Treatment Plant in Marlborough, MA, where corrosion control is achieved by raising the pH and alkalinity with carbonate, disinfection with hypochlorite, and residual disinfection by forming chloramines using ammonia. On Day 0, deionized water was used to prepare 1 mM bicarbonate buffer, which was adjusted to pH 9.08 with 1M NaOH (sample "1 buffer"). The buffer was dosed with hypochlorite (7 mL of 0.05% available chlorine hypochlorite solution added to 1-L), resulting in a total chlorine residual (TCR) of 3.2 mg/L. The chlorinated buffer was then treated with 0.6 mg/L NH3-N ammonia (6 mL of 100 mg/L NH3-N added to 1-L) to form chloramines (sample "2 untreated").

This 1-L chloramine solution was split into eight 100-mL portions, to which varying amounts of ascorbic acid or sodium thiosulfate were added for dechlorination, as shown in Table 1. Each of the dosing levels was apparently enough to completely neutralize the chlorine, demonstrated by TCR analysis. Then the samples were adjusted to pH>12 with NaOH. Each sample was tested for FCN several times up to 5-6 hours post-preparation on Day 0 and then again several times on Days 1, 4, and 5. All samples were refrigerated at <6 C when not on the instrument, so this is mimicking what would happen to a regular cyanide sample.

On Day 4, a second deionized water sample was prepared as described above except the hypochlorite dosed was lower by about half. After hypochlorite and ammonia dosing, this sample had a TCR of 1.7 mg/L. This sample was tested that day and the next day.

Analytical method. All FCN analyses were performed by flow injection analysis (FIA) with gas diffusion through a membrane to isolate the HCN followed by amperometric detection with a silver electrode following OIA-1677-DW (OI Analytical, 2004) (1). Routine calibration and calibration verification procedures for this method were followed, with calibration from 2 to 200 ug/L and a reporting limit of 2 ug/L. All FCN analyses were accompanied by successful batch quality control tests including a laboratory reagent blank (method blank) below the 2 ug/L reporting limit (lowest calibration standard) and a FCN laboratory fortified blank within control limits.

RESULTS AND DISCUSSION

The description of each sample treatment is shown in Table 1. The FCN results for ascorbic acid dechlorinated samples are shown in Figure 1 and for thiosulfate dechlorinated samples in Figure 2. All carbonate buffer samples (Sample "1 buffer") and chloraminated, but not dechlorinated, samples (Sample "2 untreated") had FCN <2 ug/L over the course of the study, showing that FCN wasn't formed until the samples was dechlorinated and basified. An unexplained artifact was observed in which the FCN concentrations generally increased slightly over the course of several hours while the samples were at room temperature being retested each day. It is not known if this was due to the samples warming up, instrument drift, or another cause.

The consequences of this experiment are significant—free cyanide forms when water is treated as drinking water is treated and then preserved and tested for free cyanide. Easily detectable false positives were observed whether ascorbic acid or thiosulfate were used for dechlorination. These are false positives because they are formed during the required sample preservation and testing. While the exact reaction mechanism is unknown, it is possibly similar to the base catalyzed formation of cyanogen chloride from monochloramine studied by Pedersen *et al.* (1999).

For drinking water testing, laboratories are required to "follow the method", including how samples are preserved. This regulatory mantra is problematic for cyanide (Delaney & Blodget, 2016) and similar false positives from the sample preservation and testing has been demonstrated (Delaney, et al, 2007). Cyanide formation during wastewater preservation and testing has also been demonstrated (Delaney et al, 1999; Khoury et al, 2008; Stanley & Antonio, 2012). For wastewater, field dilution has been demonstrated to be useful for improved sample preservation and field spikes are useful for demonstrating sample integrity (Delaney & Blodget, 2015).

For drinking water cyanide testing under EPA's Safe Drinking Water Act for inorganics, 40 CFR 141.23 (EPA, 2014), the required cyanide preservation is that the sample be *"adjusted with sodium hydroxide to pH 12 at the time of collection" and cooled to "4 °C or less".* Also, the requirement is to *"follow additional (if any) information on preservation, containers or holding times that is specified in method."* So, as written, the regulation requires that information on dechlorination comes from the method itself.

While the requirement is to follow the preservation requirements in the regulation and the method, in practice field preservation likely has a wide range of variation. Even so, the method requirements vary. Method OIA-1677-DW says, *"Treat with 0.6 g of ascorbic acid per liter of sample."* EPA Method 335.4 (EPA, 1993) says, *"Add ascorbic acid, a few crystals at a time,*

until a drop of sample produces no color on the indicator paper; then add an additional 0.06 g of ascorbic acid for each liter of sample volume." Standard Methods 4500-CN-11 B (Standard Methods, 2012) says, *"Add small portions of sodium thiosulfate solution (0.02 g/L) with constant re-testing until the oxidizers are neutralized. Avoid any excess thiosulfate solution."* In this experiment, the sample treatments correspond to preservation requirements of the methods as follows:

Method OIA-1677-DW: sample a3

Method EPA 335.4: sample a1

Method SM 4500-CN-11 B: sample t1

In the regulations at 40 CFR 141.23, detection limits are listed for each approved method, ranging from 0.5 ug/L to 50 ug/L, though it isn't clear what the required minimum reporting limits are, and different states have interpreted this differently. These detection limits are listed in regards to requirements for compositing samples to reduce laboratory costs. For Method OIA-1677-DW, the listed detection limit in the regulation is 0.5 ug/L, though the method lists the minimum level as 2 ug/L. The detection limits listed for EPA 335.4 and SM 4500-CN-11 are both 20 ug/L. However, it is unclear what any given certified laboratory in any given state would use as its reporting limit. Virtually any of the detected free cyanide results in this study could be regarded as "detects" that would need to be reported in the PWS' Consumer Confidence Report.

In recognition that in practice it may not be possible to reliably report results down to the method's detection limit, EPA uses the Practical Quantitation Limit (PQL), defined as *''the lowest achievable level of analytical quantitation during routine laboratory operating conditions within specified limits of precision and accuracy''* (USEPA, 1985). When EPA first regulated FCN in drinking water (EPA, 1992) it stated that the Practical Quantitation Limit (PQL) was 100

ug/L. This PQL was recently reiterated by EPA (EPA, 2017) as still being appropriate. California uses a required reporting limit, termed a Detection Limit for Purposes of Reporting (DLR) for cyanide in drinking water of 50 ug/L (California EPA, 2017). From this study it is clear that FCN detected results on drinking water samples below 100 ug/L should be regarded as suspect and possibly false positives.

While we cannot unequivocally state that FCN is being detected in this study, previous investigations using the automated spectrophotometric total cyanide and ion selective electrode free cyanide analyses lend credence that FCN is being detected. It is possible that these results are due to an unexpected interference, but even if it were an interference, the situation is still "false detection" because there is no detectable cyanide in the samples at the start, and the preservation and testing is according to method requirements.

Sulfide is a potential interference, but there isn't a significant amount of sulfur in the ascorbic acid samples and these samples developed higher cyanide concentrations than the thiosulfate experiments. Also, Method OIA-1677-DW indicates that sulfide is potentially both a positive and a negative interference: *"Sulfide is a positive interferent in this method (References 15.3 and 15.4), because an acidified sample containing sulfide liberates hydrogen sulfide that is passed through the membrane and produces a signal at the silver electrode. In addition, sulfide ion reacts with cyanide ion in solution to reduce its concentration over time."*

It should be noted that this experiment was conducted at pH 9 with added alkalinity because that is the pH and alkalinity at which MWRA adjusts its water for corrosion control. Other pH, alkalinity levels, or corrosion control approaches, such as phosphate-based, have not been studied.

Thiosulfate was observed to give lower FCN concentrations than ascorbic acid. This is consistent with guidance in Standard Methods: *"Ascorbic acid is no longer being recommended for preservation of samples for cyanide analysis. Ascorbic acid functions as a carbon donor in the presence of nitrite or nitrate, and generates cyanide during the distillation. Sodium thiosulfate is an adequate dechlorinating agent as long as it is not used in excess. Sodium arsenite also may be used, but it is a hazardous material. If ascorbic acid must be used, add sulfamic acid (2 g/500 mL sample) before adding ascorbic acid and sodium hydroxide."*

A previous study indicated some FCN formation when dechlorinated drinking water with arsenite (Delaney & Blodget, 2016). Also the use of sulfamic acid hasn't been studied because it isn't included as an option in Method OIA-1677-DW.

CONCLUSION

This study demonstrates a fundamental flaw in the required preservation and approved methods for cyanide. It is unknown to what extent this flaw is adversely affecting routine drinking water testing for cyanide, but it could be pervasive, especially if laboratories report results down to the detection limits published in 40 CFR 141.23. EPA should provide clarification to States, PWS, and their laboratories that drinking water cyanide results only need to be reported down to the PQL of 100 ug/L and any detected results below 100 ug/L need not be reported in a PWS' Consumer Confidence Report. To go any lower than that would require deviating from the regulation and approved methods. For example, field dilution to reduce the matrix interference, elimination of NaOH preservation, same day analysis, and the use of a field spike to demonstrate sample integrity has been demonstrated to be a successful approach (Delaney & Blodget, 2016).

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FOOTNOTES

1. CNSolution™ Cyanide Analyzer, OI Analytical, College Station, TX.

Table 1. Sample Preparation

Sample	NH3-N mg/L	TCR Before Dechlorination	Ascorbic Acid g/L	Sodium Thiosulfate g/L	Final pH
1 buffer	0	--	--	--	9.08
2 untreated	0.6	--	--	--	~9
a1	0.6	3.2	0.03	--	12.03
a2	0.6	3.2	0.075	--	12.03
a3	0.6	3.2	0.6	--	12.14
a4	0.6	3.2	1.8	--	12.17
t1	0.6	3.2	--	0.015	12.05
t2	0.6	3.2	--	0.02	12.05
t3	0.6	3.2	--	0.04	12.05
t4	0.6	3.2	--	0.06	12.05
2b untreated	0.6	--	--	--	9.16
a2b	0.6	1.7	0.075	--	12.17

Figure 1. Free cyanide formation over time in samples dechlorinated with ascorbic acid for sample treatments described in Table 1.

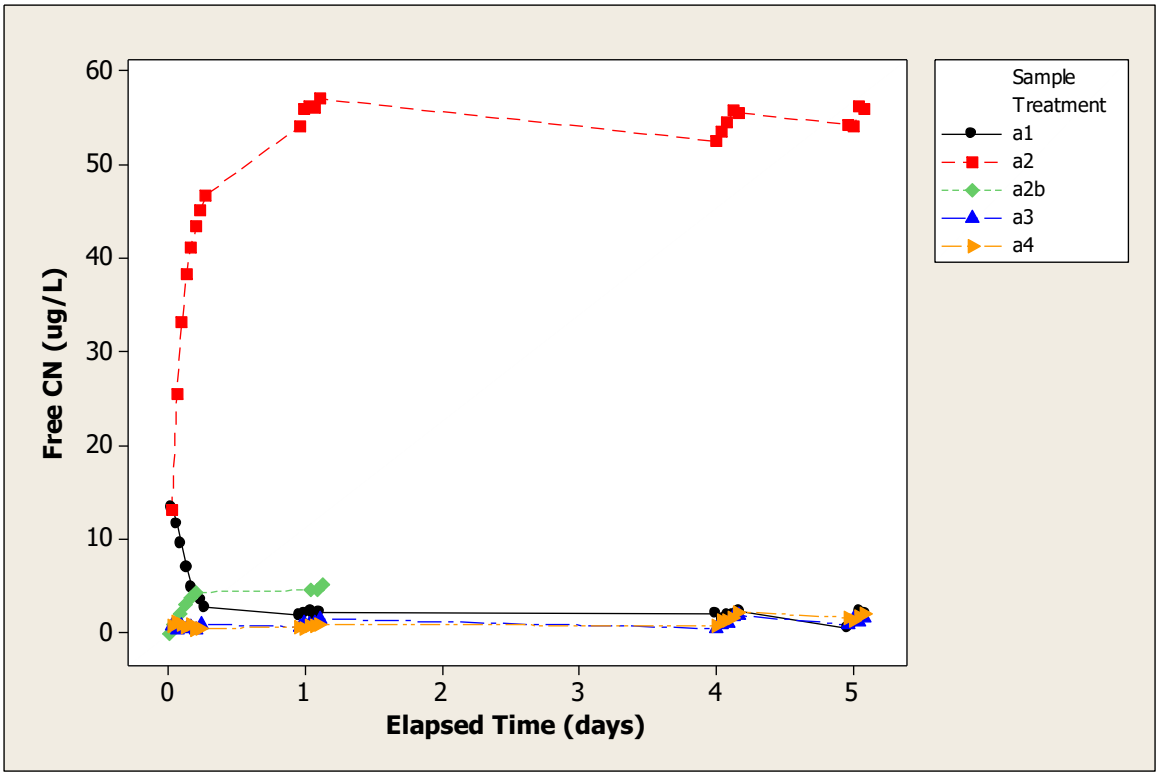

Figure 2. Free cyanide formation over time in samples dechlorinated with thiosulfate for sample treatments described in Table 1.