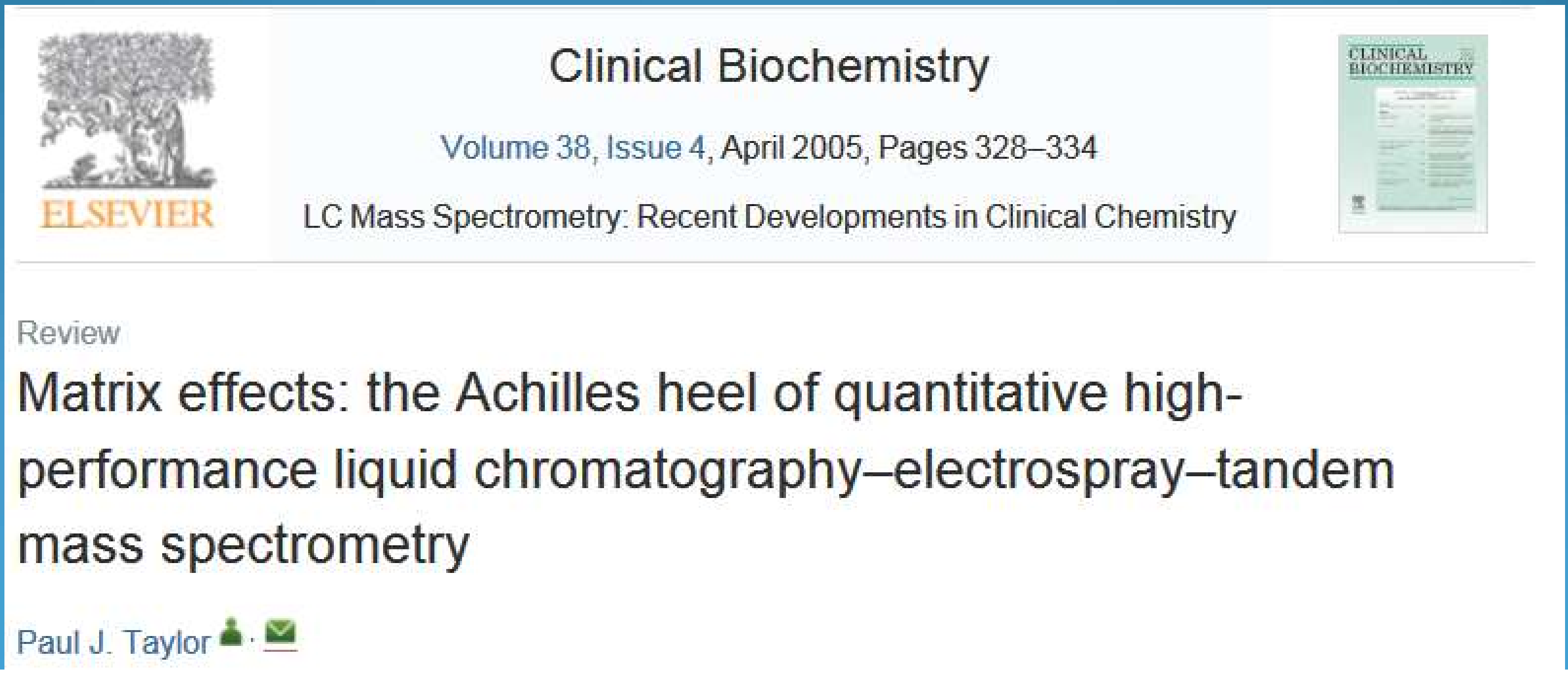
"A Look at Matrix Effects"

Mike Delaney and Chuck Blodget

Massachusetts Water Resources Authority (MWRA)



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

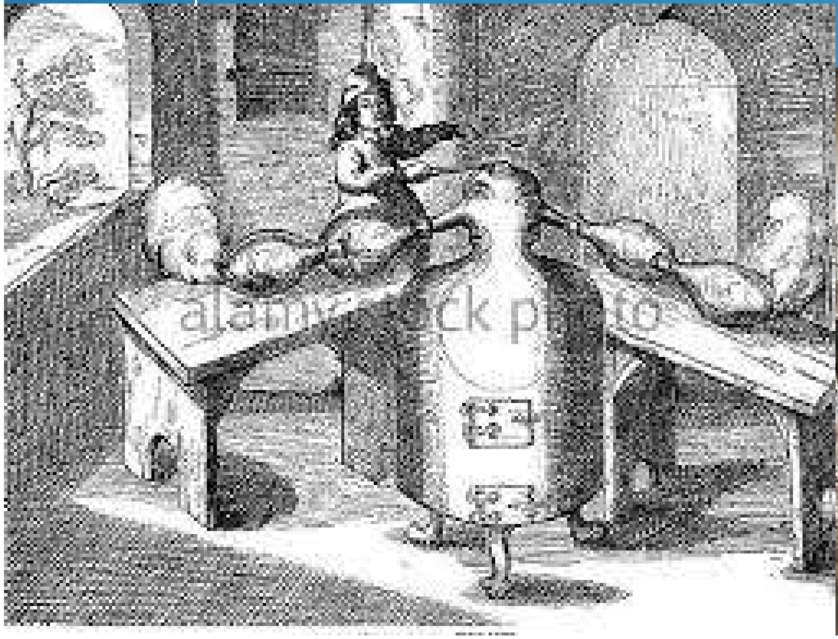
Paul J. Taylor

A Look at Matrix Effects

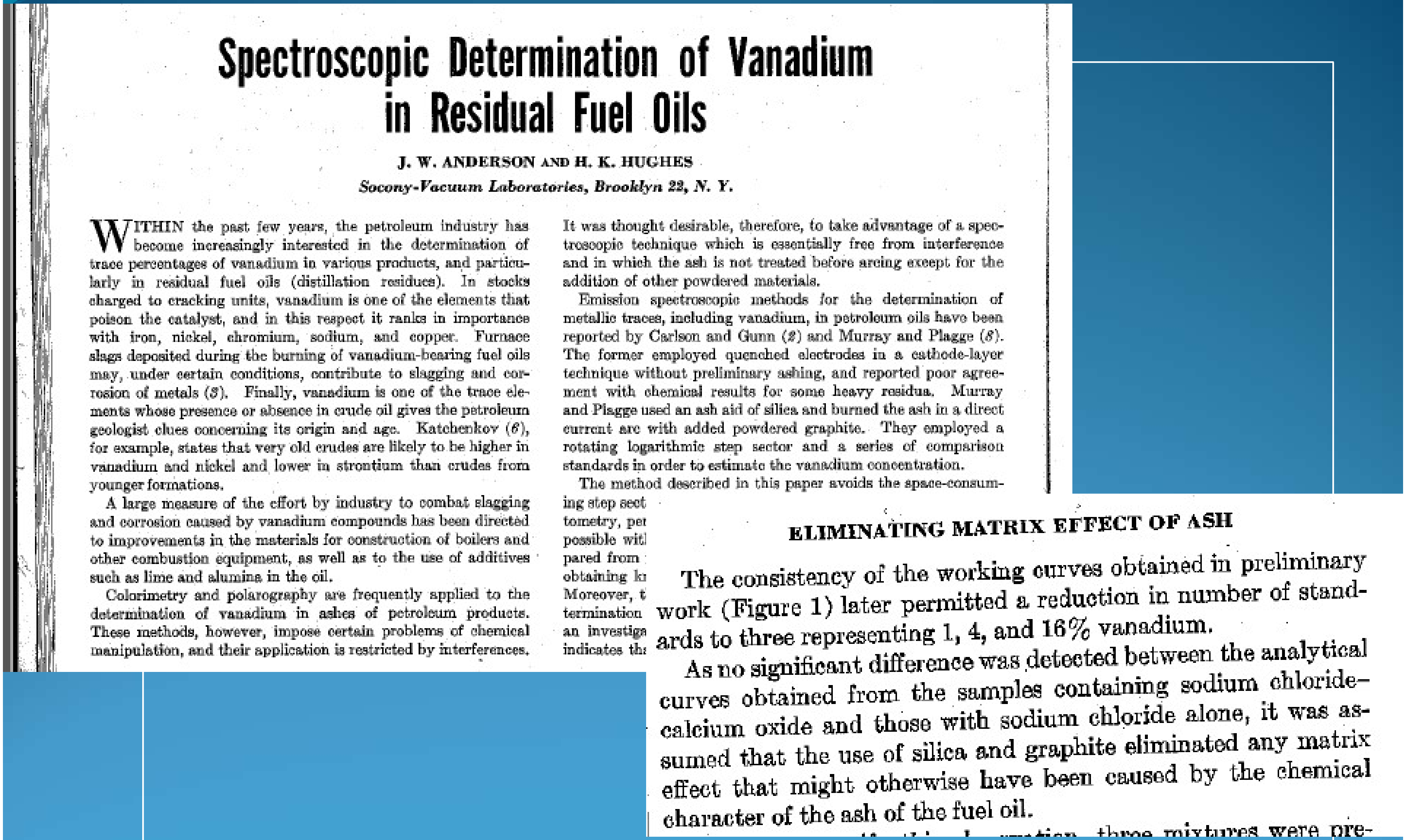
- Back in the Day – at a contract lab – Blame the sample!
- A little history.
- Newer EPA methods.
- Quantifying Matrix Effects
- Which analytes/methods are the bad actors?
- Decreasing Matrix Effects.
- Cyanide: The “baddest” actor.

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

J. W. ANDERSON AND H. K. HUGHES

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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-consuming step sect
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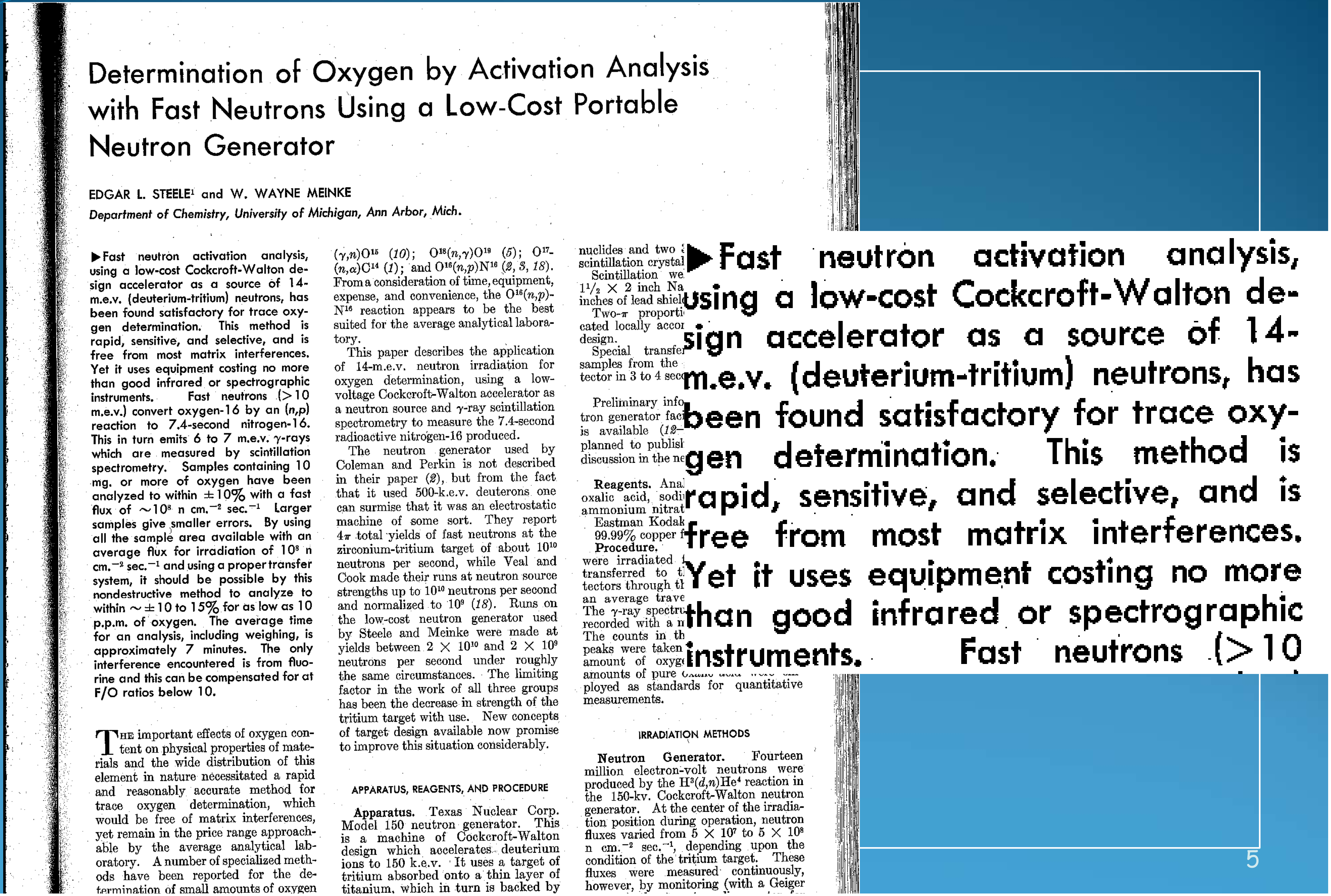
ELIMINATING MATRIX EFFECT OF ASH

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.

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
Department of Chemistry, University of Michigan, Ann Arbor, Mich.

▶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

$(\gamma,n)O^{15}$ (*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

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scintillation crystal
Scintillation we
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inches of lead shiel
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Special transfer
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amounts of pure
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%)

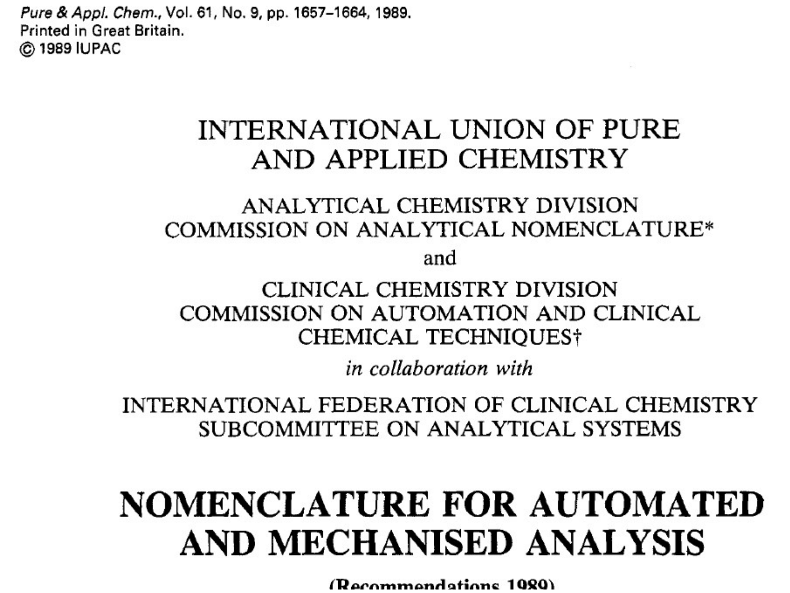
- Mentioned in the 1985 Instrumental Analysis text I used to teach undergraduates.

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."*



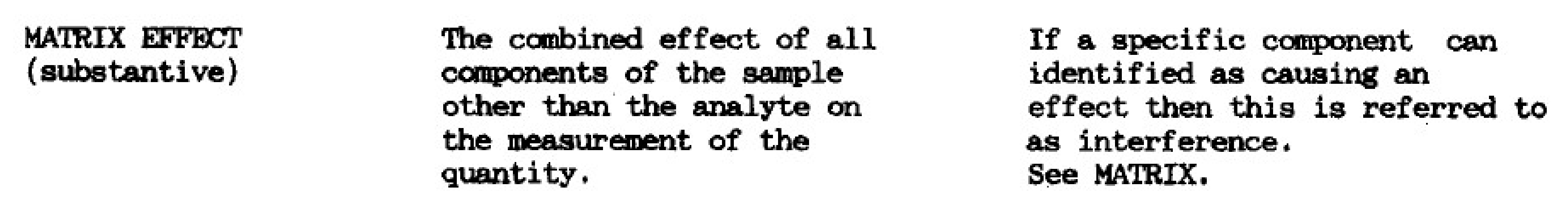
Pure & Appl. Chem., Vol. 61, No. 9, pp. 1657–1664, 1989.
Printed in Great Britain.

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…

- **“<u>Matrix Interference</u>”** if you know what is causing the bias.
- **“<u>Matrix Effect</u>”** if you don’t know what is causing the bias.
- **“<u>Matrix Mistake</u>”** 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

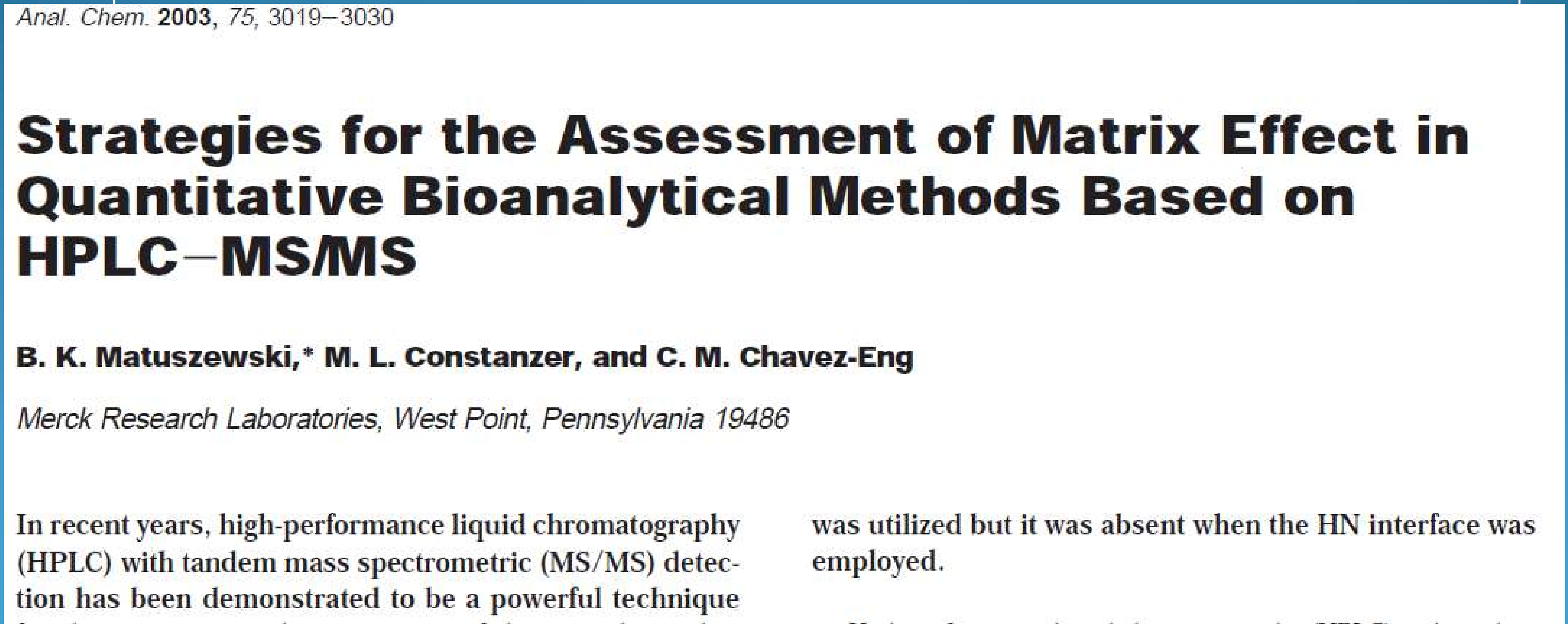
- *"8.3.3.1 If any individual P falls outside the designated range for recovery in either aliquot, or the RPD limit is exceeded, the result for the analyte in the unspiked sample is **suspect and may not be reported** or used for permitting or regulatory compliance purposes."*
- **(emphasis added)**

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

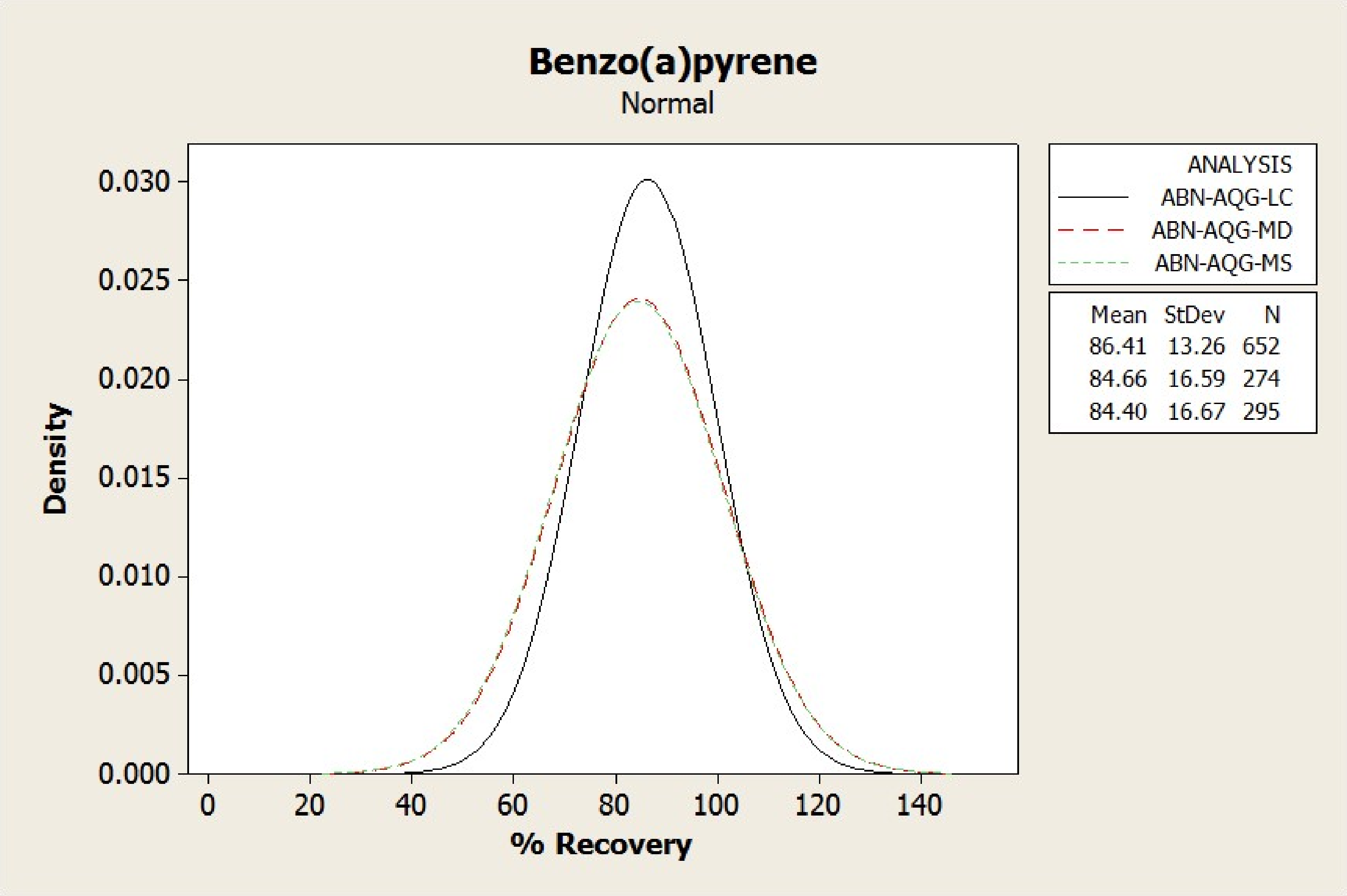
was utilized but it was absent when the HN interface was employed.

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



Mean	StDev	N
86.41	13.26	652
84.66	16.59	274
84.40	16.67	295

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:

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

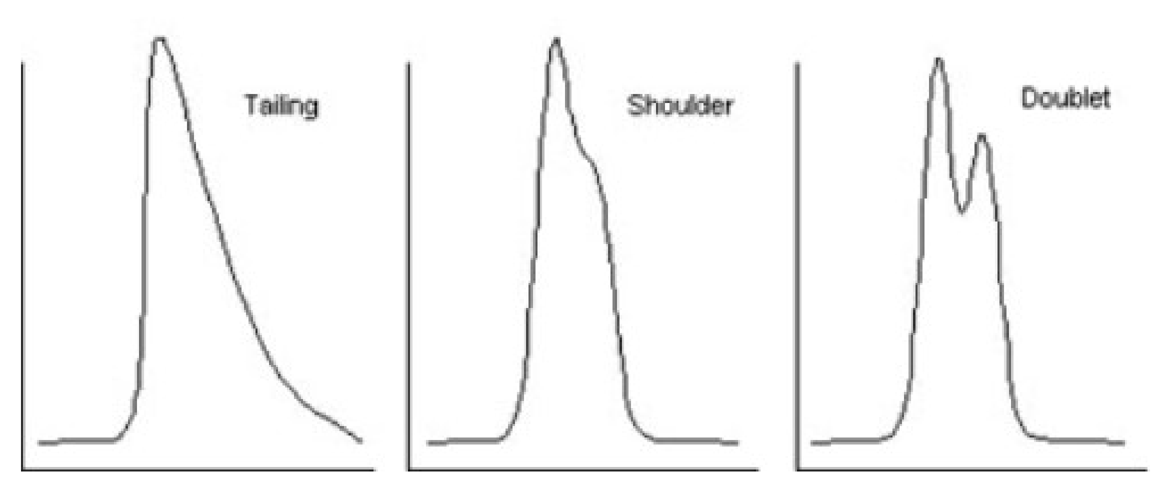
  - Compare F to the critical value. If is significant, there appears to be a significant Matrix Effect.
- For example: Benzene by Method 624 purge-and-trap GC/MS:

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

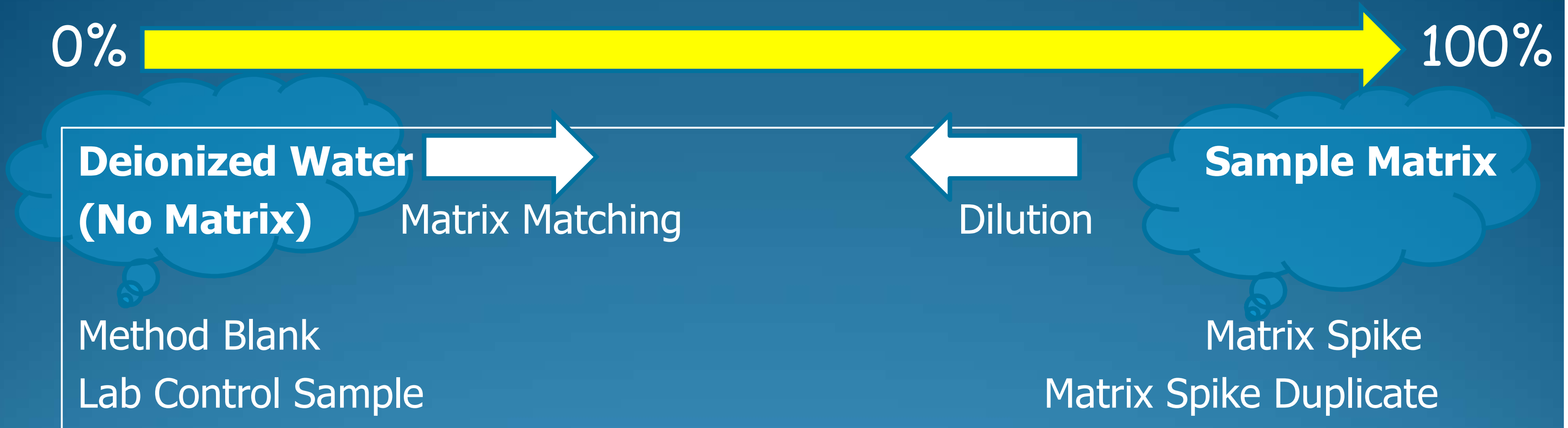
Analyte	Method	N (LC)	N (MS/MD)	S (LC)	S (MS/MD)	Fcalc	Fcrit 0.05	Significant at 95%?
Benzene	624	1141	584	7.66	7.81	1.040	1.124	N.S.
B(a)P	624	652	569	13.26	16.62	1.571	1.143	S
Benzoid Acid	624	652	567	9.93	147.77	221.672	1.143	way S
Acrylonitrile	624	1725	1141	14.48	14.67	1.025	1.093	N.S.
Acrolein	624	584	1141	28.54	43.40	2.312	1.124	S
Acrolein	603	25	50	12.08	27.02	5.001	1.727	S
NH3	AAN	150	232	3.83	5.90	2.377	1.274	S
PO4	AAN	107	118	3.98	6.53	2.690	1.368	S
NO2 (by diff)	AAN	180	212	2.60	11.29	18.842	1.266	S
NO3/NO2	AAN	178	211	3.57	5.39	2.276	1.268	S
S--	Titration	308	584	8.18	7.90	0.932	1.176	N.S.
S--	UV/VIS	325	800	6.60	7.58	1.317	1.163	S
NH3	ISE	320	277	7.21	10.90	2.286	1.212	S
CN Total	AAN	267	701	5.87	20.89	12.665	1.179	S
CN 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



0%

100%

Deionized Water
(No Matrix)

Matrix Matching

Dilution

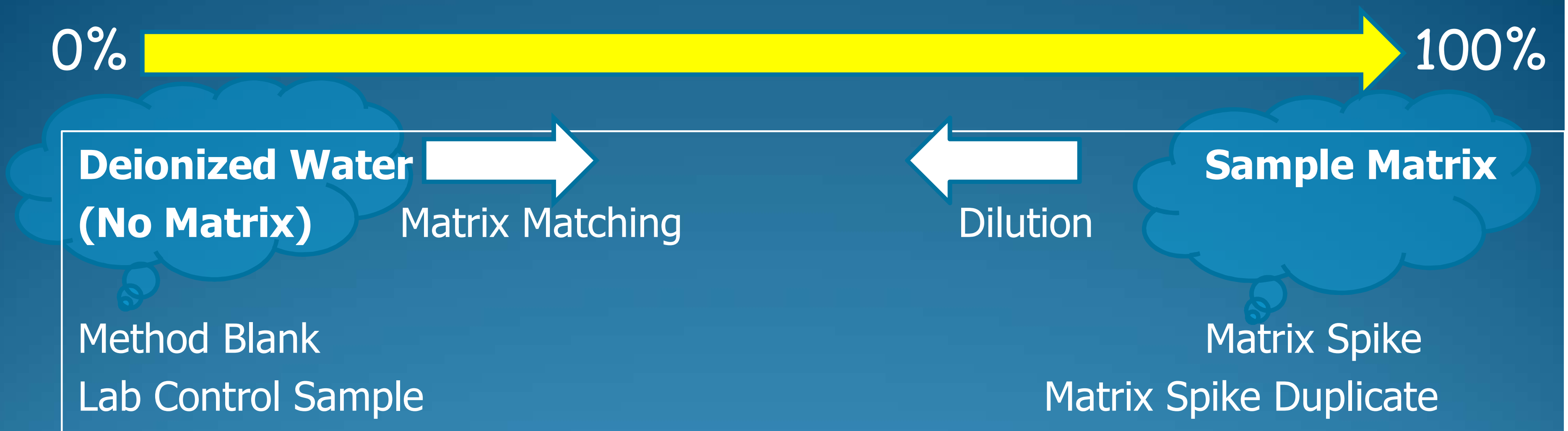
Sample Matrix

Method Blank
Lab Control Sample

Matrix Spike
Matrix Spike Duplicate

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

Decreasing Subtle Matrix Effects



0% 100%

Deionized Water (No Matrix)

Matrix Matching

Dilution

Sample Matrix

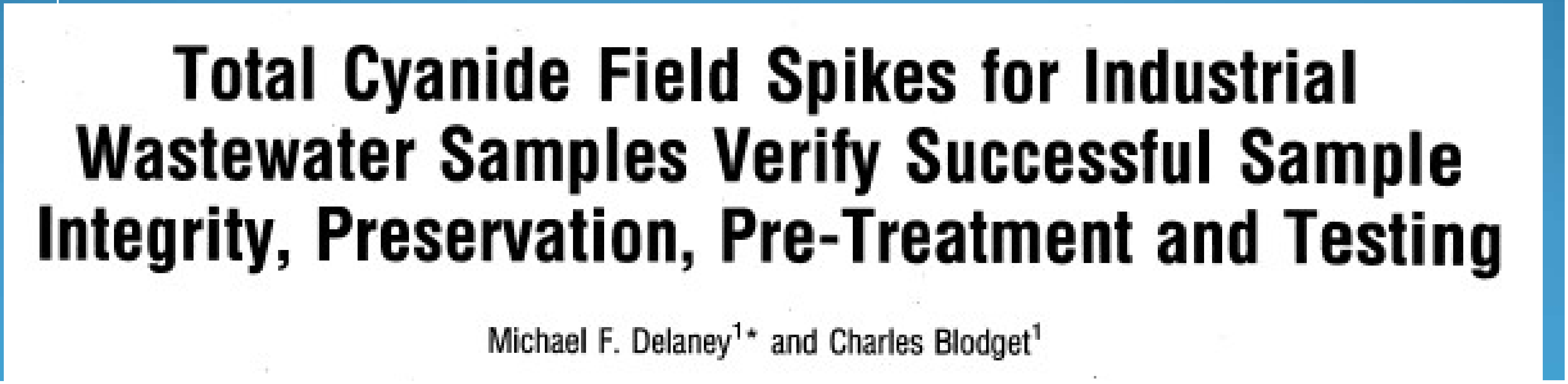
Method Blank

Lab Control Sample

Matrix Spike

Matrix Spike Duplicate

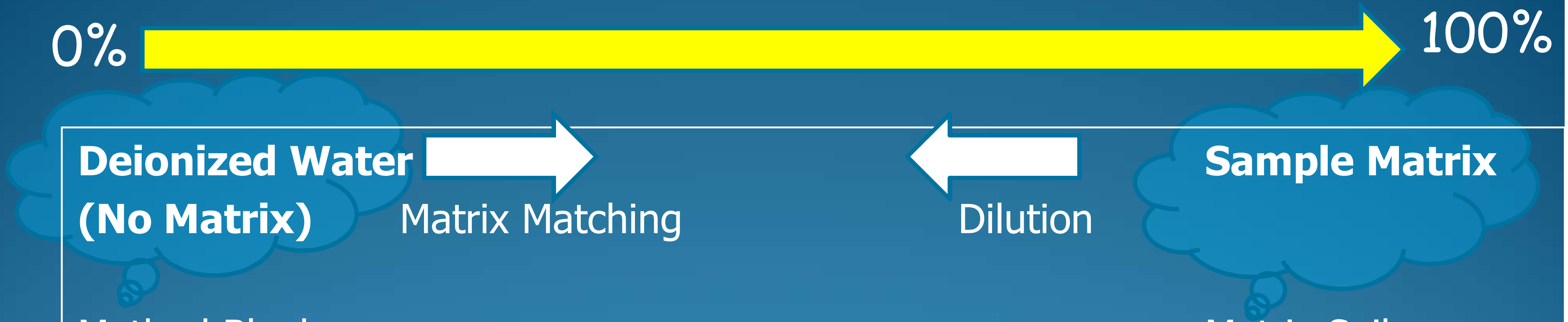
- Or this:
  - Field Dilutions (with Field Spikes)



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**

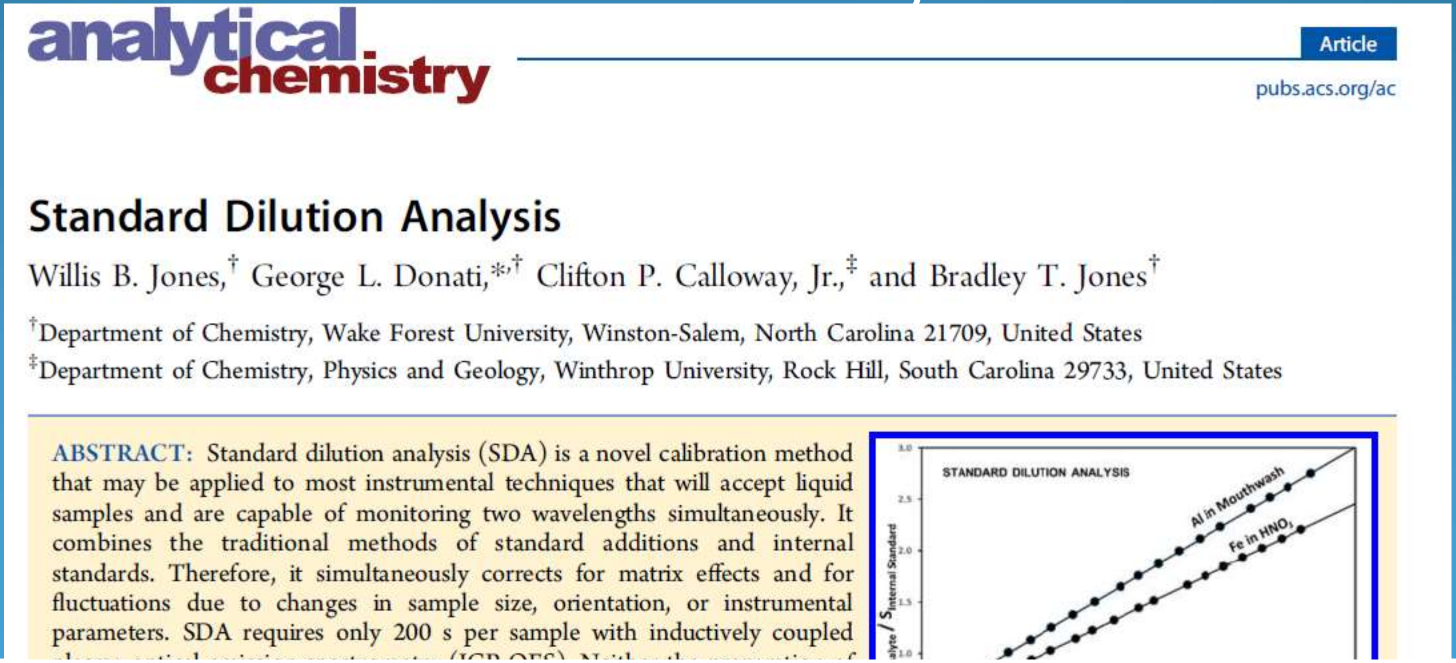
Method Blank

Lab Control Sample

Matrix Spike

Matrix Spike Duplicate

- Or even this: Standard Dilution Analysis



analytical chemistry

Article

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Standard Dilution Analysis

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

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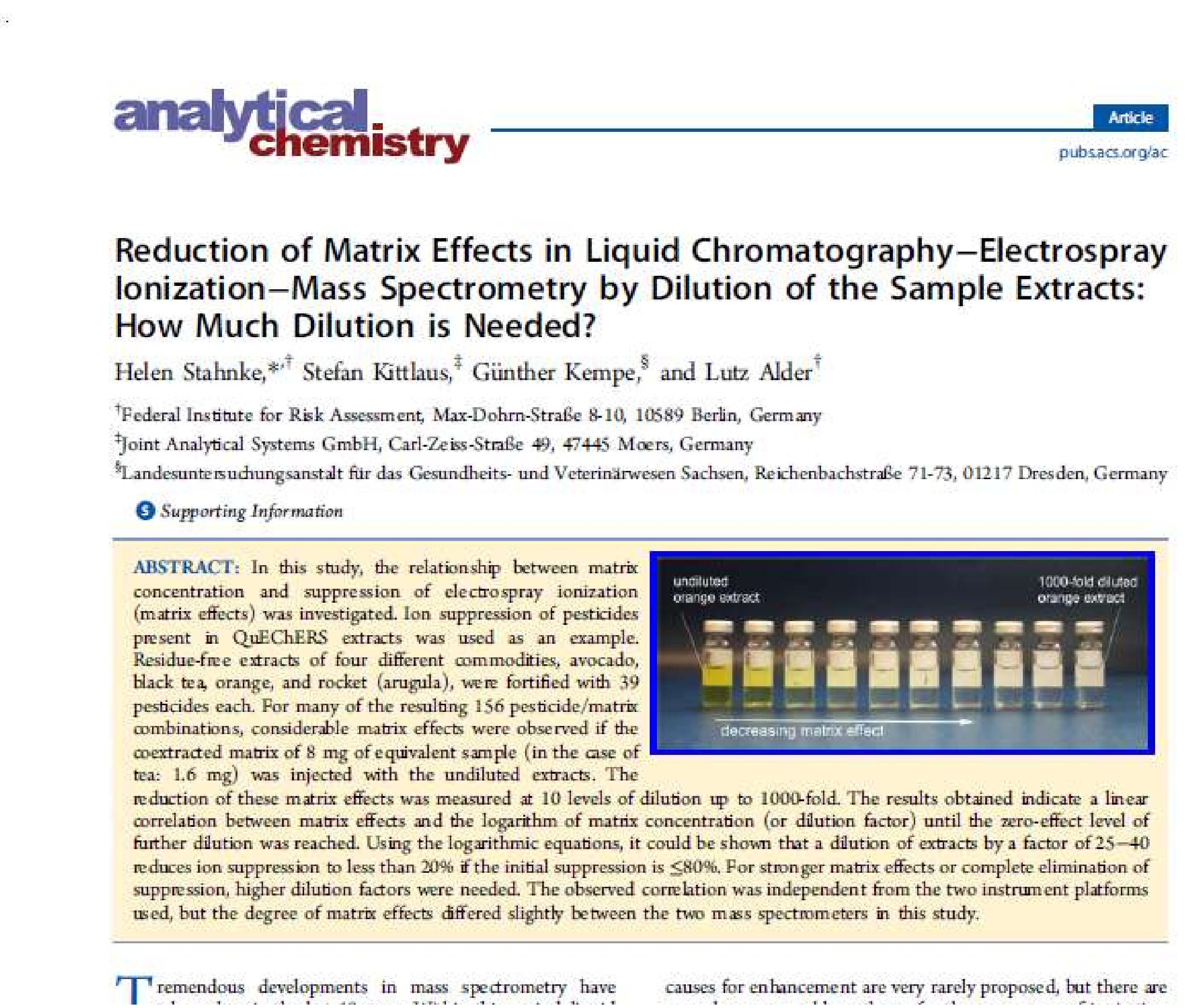
ABSTRACT: Standard dilution analysis (SDA) is a novel calibration method that may be applied to most instrumental techniques that will accept liquid samples and are capable of monitoring two wavelengths simultaneously. It combines the traditional methods of standard additions and internal standards. 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

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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

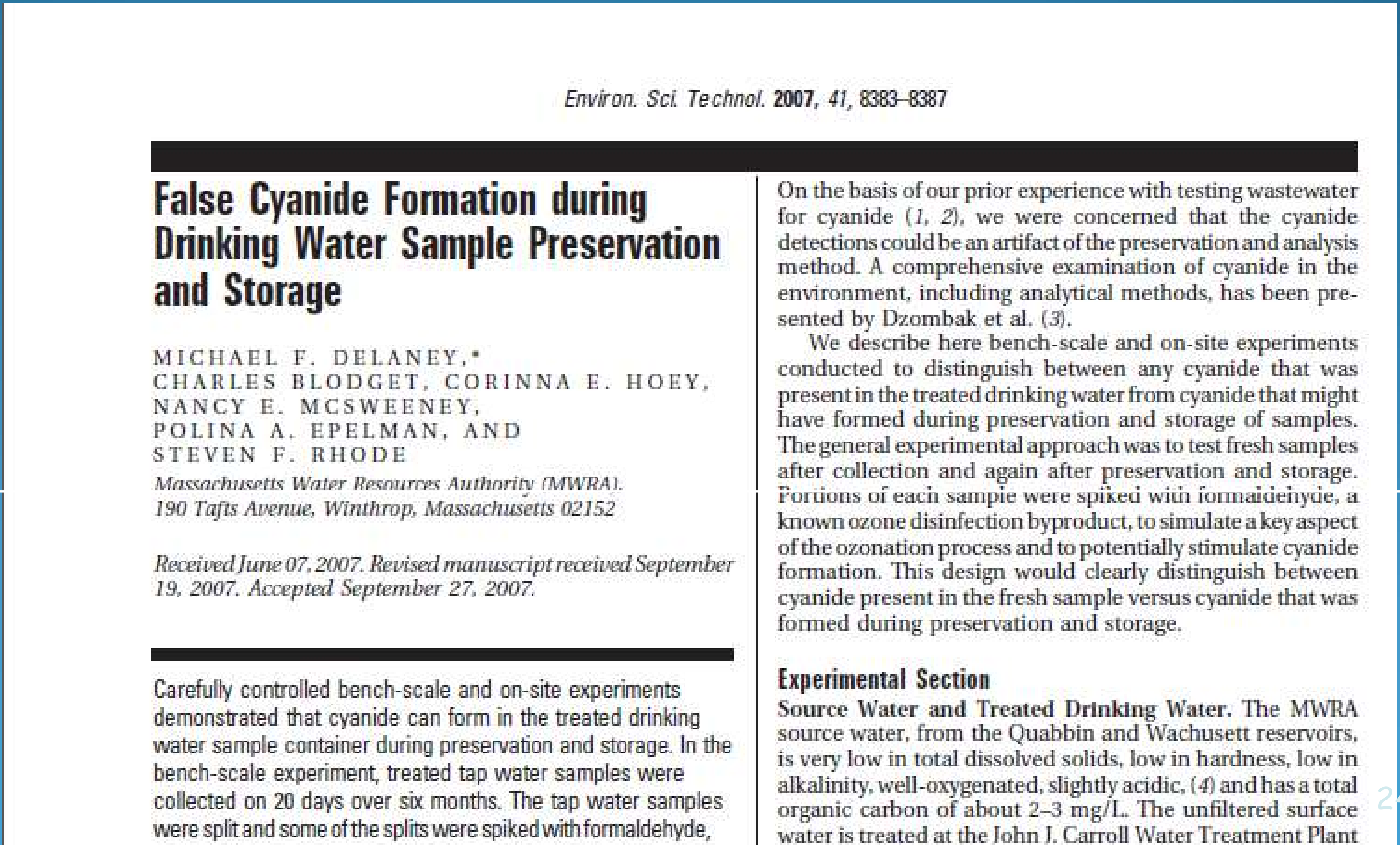
causes for enhancement are very rarely proposed, but there are

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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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*).

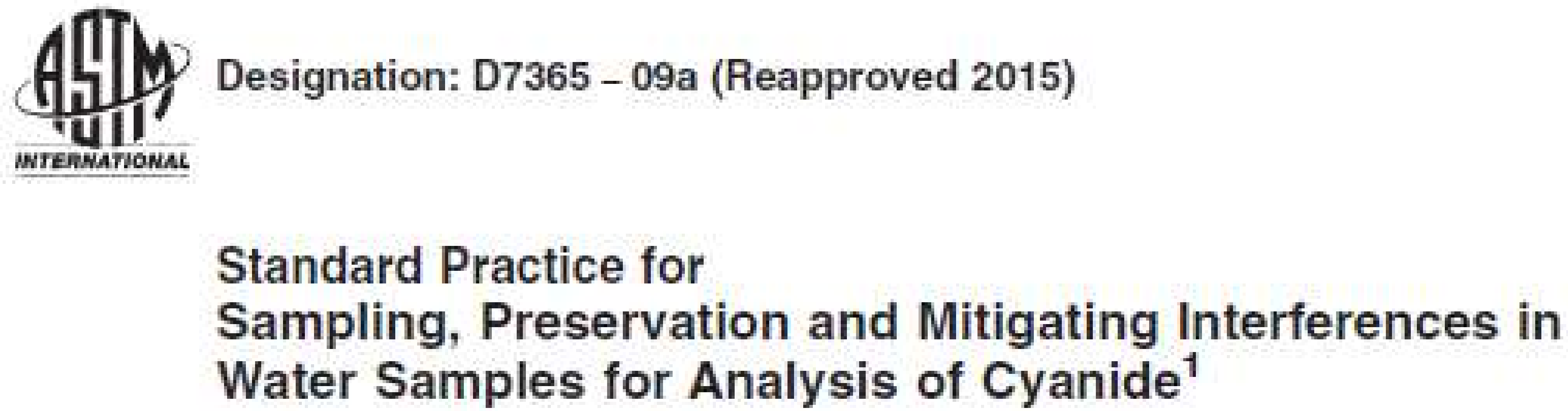
We describe here bench-scale and on-site experiments conducted to distinguish between any cyanide that was present in the treated drinking water from cyanide that might have formed during preservation and storage of samples. The general experimental approach was to test fresh samples after collection 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

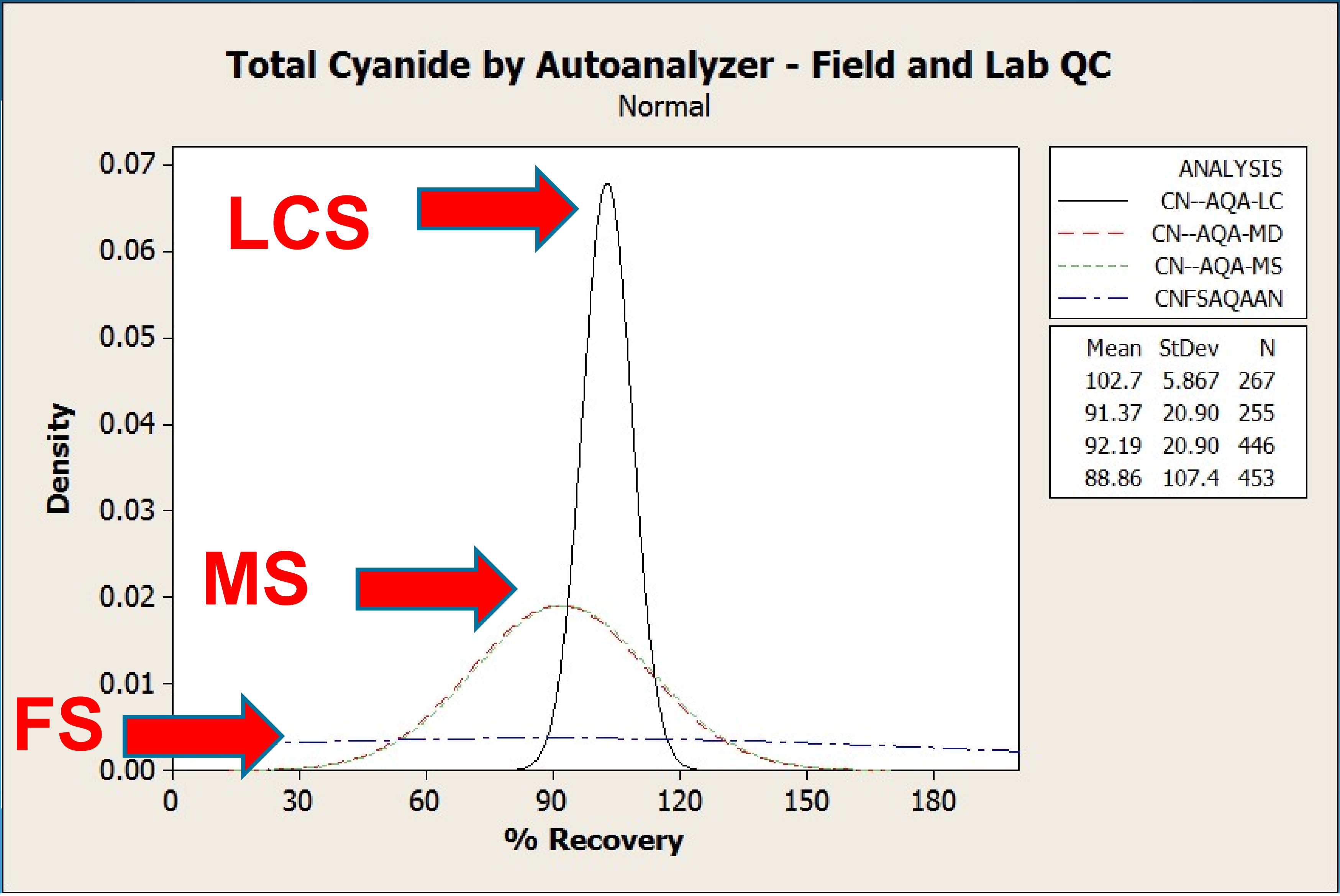
- From ASTM D7365-09a:
  - Aldehydes, Color, Dissolved Solids, Fatty Acids, Mercury, Metal Anions, Metal Cations, Nitrate, Nitrite, Oxidants, Photodecomposition, Sugars, Sulfides, Turbidity, Sulfur Compounds, Thiocyanate…and *"Unknowns that cause negative results."*



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

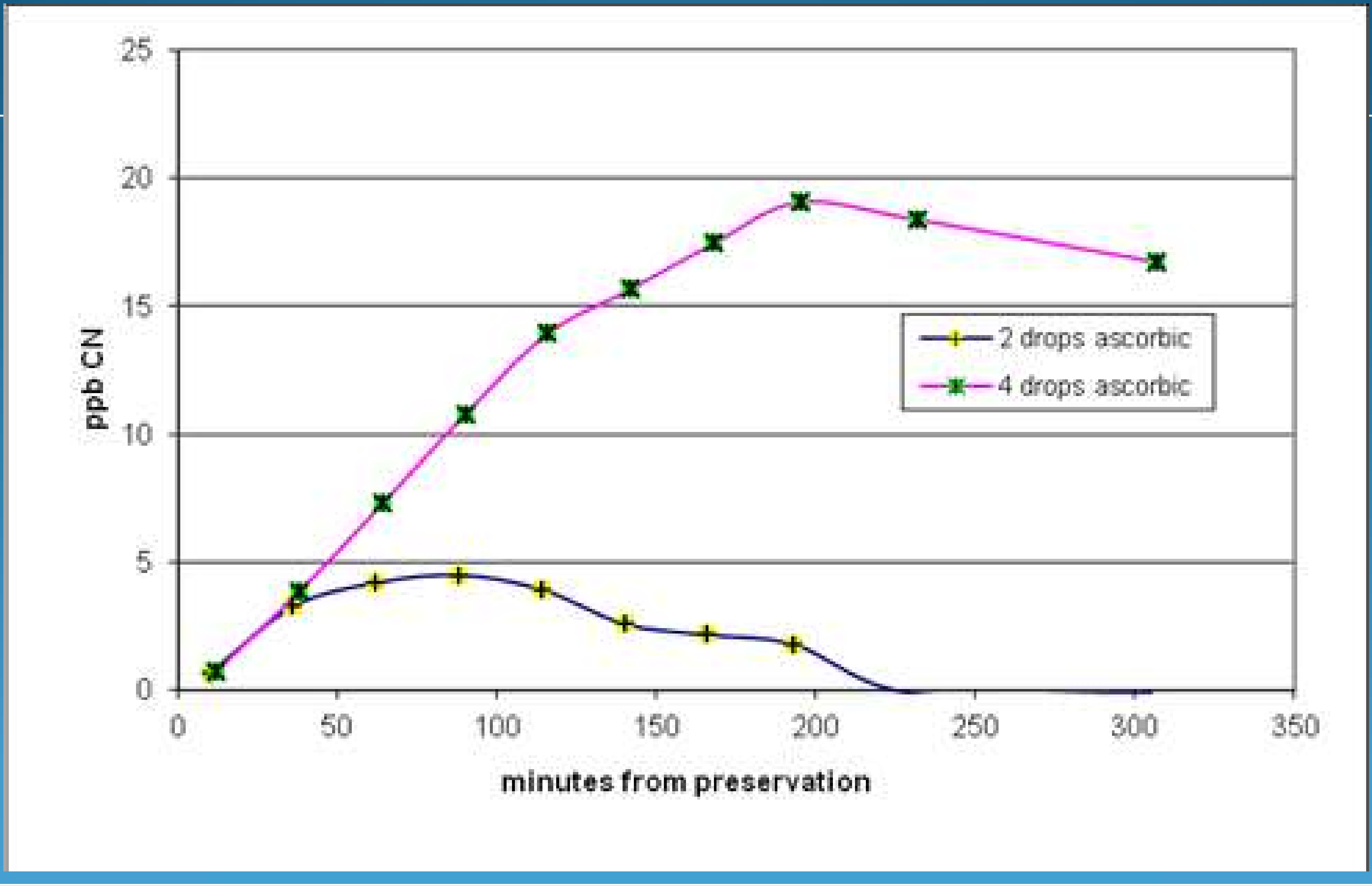


Simple Illuminating Experiment

- **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?**

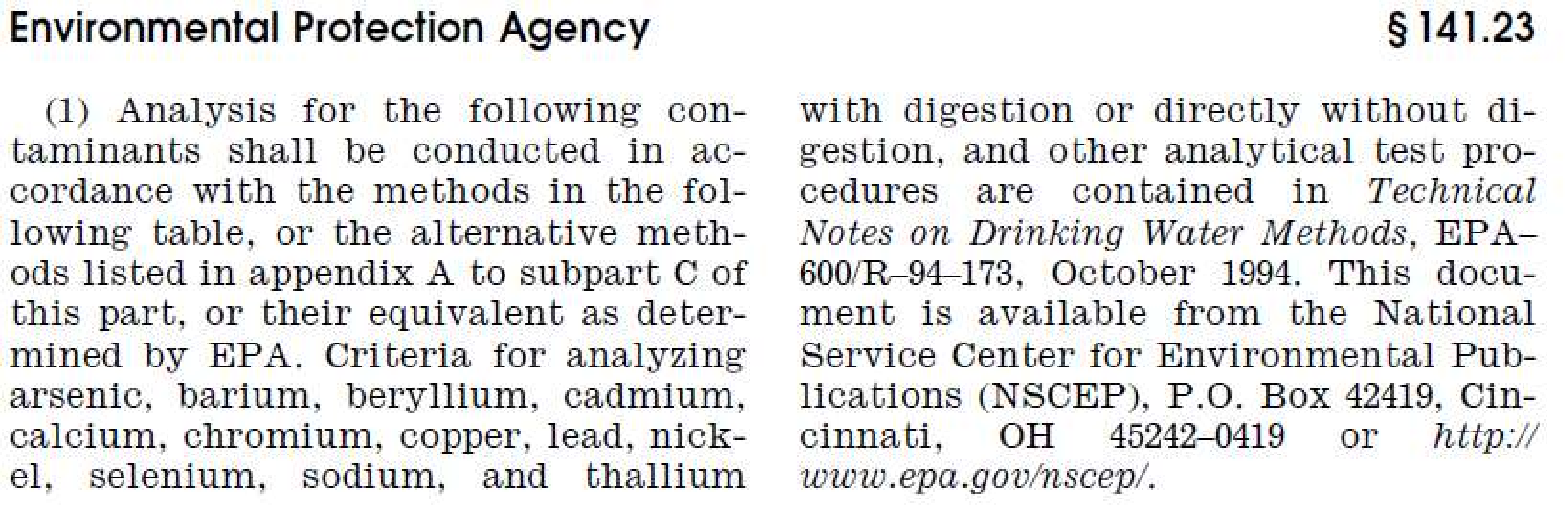
Simple Illuminating Experiment



Tale of Two Public Water Supplies

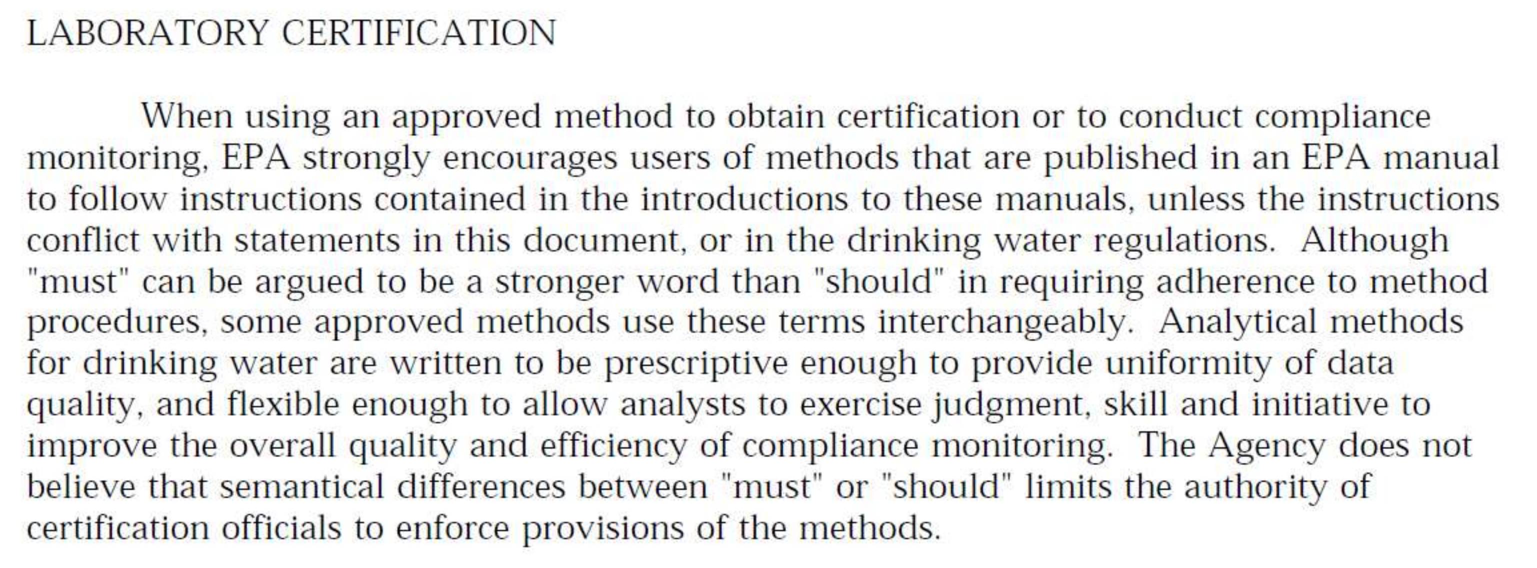
- MWRA's PWS: Ozone and Chloramines:
  - In 2007 got Total Cyanide hits that were demonstrated to be forming in the sample container. Approved by MassDEP and EPA to use on-site distillation and avoid NaOH. (ES&T Publication)
  - In 2015 switched to Free Cyanide. Demonstrated that field dilution, avoiding 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"



Environmental Protection Agency **§ 141.23**

(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

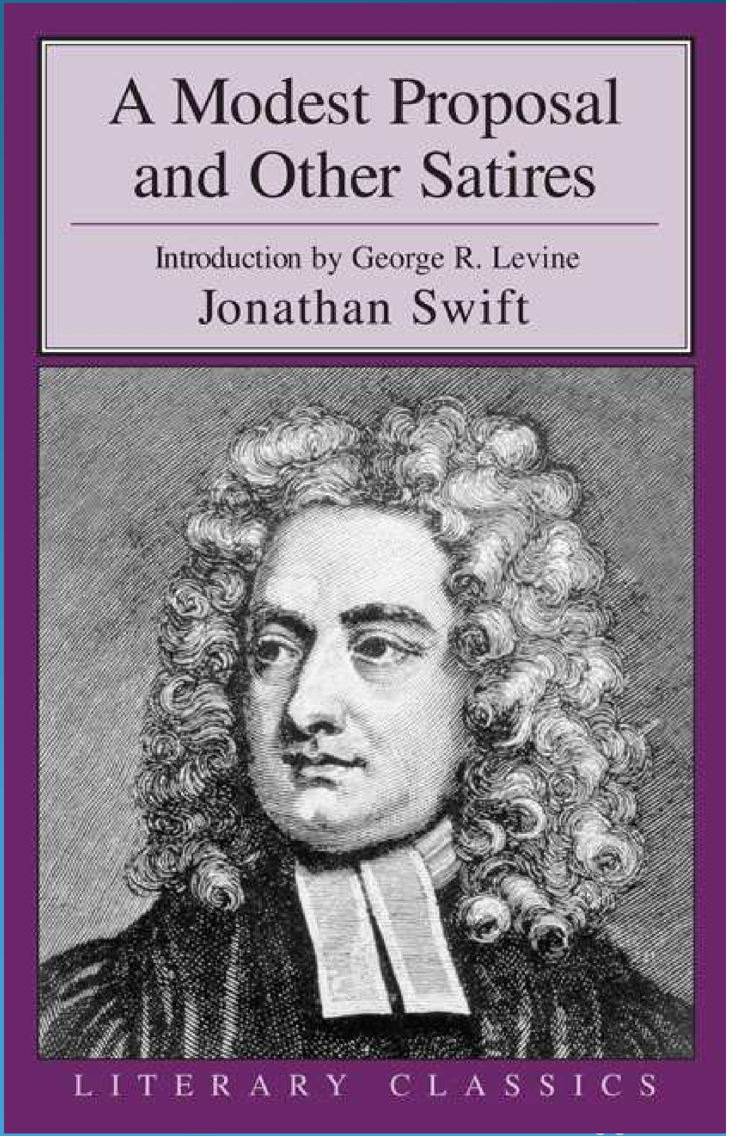
- Follow the method, take your hits, and explain them in your CCR.
- Required CCR Language:
  - Major sources in drinking water: *"Discharge from steel/metal factories; Discharge from plastic and fertilizer factories."*
  - Health effects language: *"Some people who drink water containing cyanide well 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.