# Proposed Method Updates for CFR 2010

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For Training Purposes Only

# Time for ANOTHER Change!

# Updates to 40 CFR 136, Round 2

- The following are PROPOSED updates.
- The are NOT official yet.
- They should go into effect within the next three months.
- Public comment may change a few updates.
- Did I mention PROPOSED?

# Earth Shattering Changes!

# New EPA Methods and Revisions

- Method 1664B (Oil and Grease)
- Method 200.5 (Metals by ICP Axial)
- Method 525.2 (Semi-VOAs)
- Moving Many “600” methods to Table 1D
- Method 1614A (Brominated Diphenyl Ethers (flame retardants).
- Method 1668C (Chlorinated Biphenyl Congeners)

# New Methods/Revisions Continued

- Method 1622 (Cryptosporidium)
- Method 1623 (Cryptosporidium and Giardia)
- Method Revisions for 1103.1, 1106.1, 1600, 1603 and 1680 (microbiologicals)
- Method 1627 (Predicting Mine Drainage Quality)
- Method 624 (for acrolein and acrylonitrile)

# New Methods/Revisions Continued

- Addition of several Pesticide Active Ingredients method to table 1G
  - 608.1, 608.2, 614, 614.1, 615, 617, 619, 622, 622.1, 632

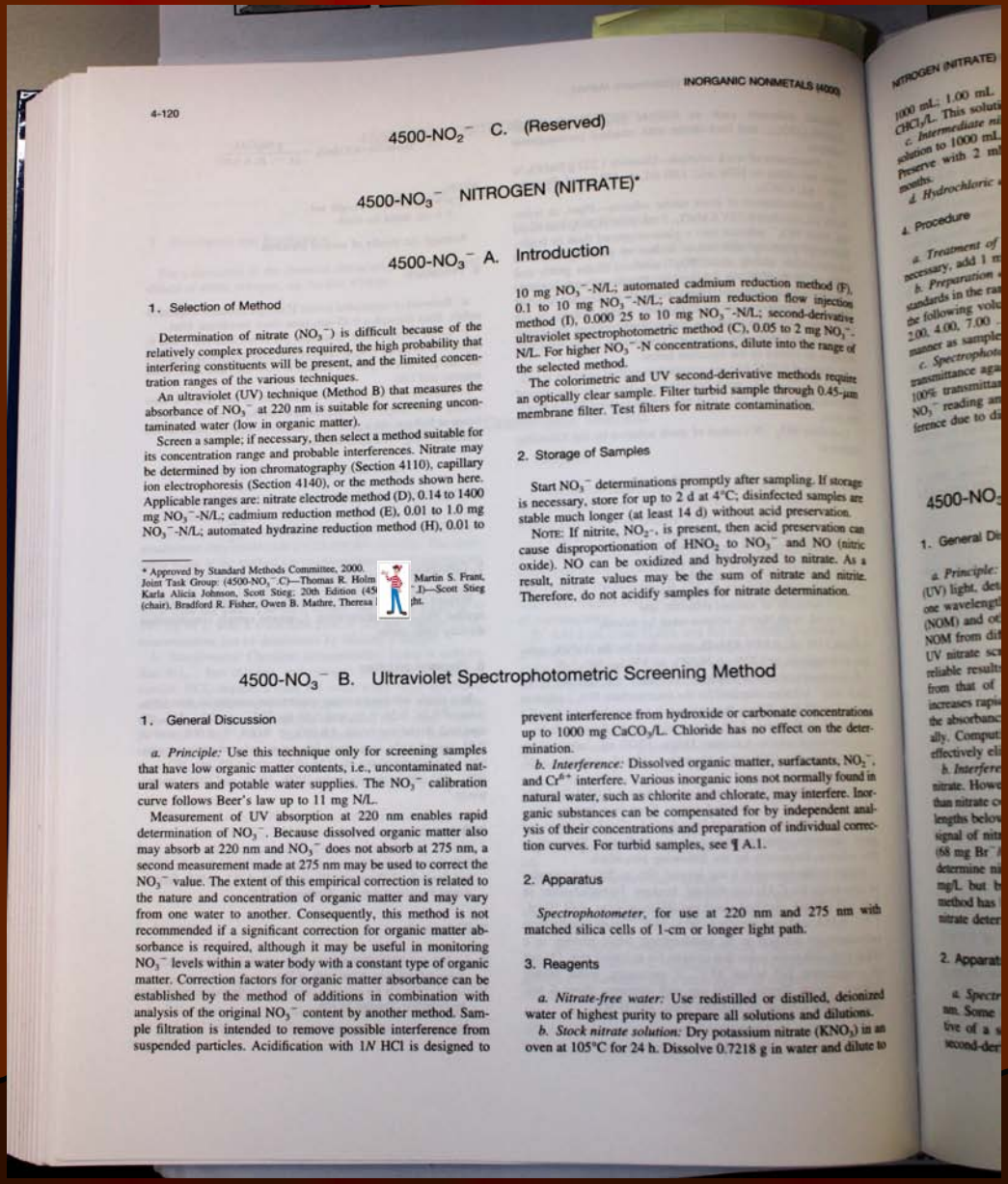
# Confused?

# It Gets Worse!

# “Standard Methods” Changes

- Most recent revision of a Standard Method
- Noted in “On-Line” version
- Located at the end of the “A” version of each Standard Method in hard copy
- Many new revisions of Standard Methods added

# Where's Waldo?





## 4500-$NO_2^-$ C. (Reserved)

## 4500-$NO_3^-$ NITROGEN (NITRATE)*

### 4500-$NO_3^-$ A. Introduction

#### 1. Selection of Method

Determination of nitrate ($NO_3^-$) is difficult because of the relatively complex procedures required, the high probability that interfering constituents will be present, and the limited concentration ranges of the various techniques.

An ultraviolet (UV) technique (Method B) that measures the absorbance of $NO_3^-$ at 220 nm is suitable for screening uncontaminated water (low in organic matter).

Screen a sample; if necessary, then select a method suitable for its concentration range and probable interferences. Nitrate may be determined by ion chromatography (Section 4110), capillary ion electrophoresis (Section 4140), or the methods shown here. Applicable ranges are: nitrate electrode method (D), 0.14 to 1400 mg $NO_3^-$-N/L; cadmium reduction method (E), 0.01 to 1.0 mg $NO_3^-$-N/L; automated hydrazine reduction method (H), 0.01 to 10 mg $NO_3^-$-N/L; automated cadmium reduction method (F), 0.1 to 10 mg $NO_3^-$-N/L; cadmium reduction flow injection method (I), 0.000 25 to 10 mg $NO_3^-$-N/L; second-derivative ultraviolet spectrophotometric method (C), 0.05 to 2 mg $NO_3^-$-N/L. For higher $NO_3^-$-N concentrations, dilute into the range of the selected method.

The colorimetric and UV second-derivative methods require an optically clear sample. Filter turbid sample through 0.45-µm membrane filter. Test filters for nitrate contamination.

#### 2. Storage of Samples

Start $NO_3^-$ determinations promptly after sampling. If storage is necessary, store for up to 2 d at 4°C; disinfected samples are stable much longer (at least 14 d) without acid preservation.

NOTE: If nitrite, $NO_2^-$, is present, then acid preservation can cause disproportionation of $HNO_2$ to $NO_3^-$ and NO (nitric oxide). NO can be oxidized and hydrolyzed to nitrate. As a result, nitrate values may be the sum of nitrate and nitrite. Therefore, do not acidify samples for nitrate determination.

* Approved by Standard Methods Committee, 2000.
Joint Task Group: (4500-$NO_3^-$.C)—Thomas R. Holm (chair), Karla Alicia Johnson, Scott Stieg; 20th Edition (45 (chair), Bradford R. Fisher, Owen B. Mathre, Theresa



Martin S. Frant, J)—Scott Stieg ght.

### 4500-$NO_3^-$ B. Ultraviolet Spectrophotometric Screening Method

#### 1. General Discussion

*a. Principle:* Use this technique only for screening samples that have low organic matter contents, i.e., uncontaminated natural waters and potable water supplies. The $NO_3^-$ calibration curve follows Beer's law up to 11 mg N/L.

Measurement of UV absorption at 220 nm enables rapid determination of $NO_3^-$. Because dissolved organic matter also may absorb at 220 nm and $NO_3^-$ does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the $NO_3^-$ value. The extent of this empirical correction is related to the nature and concentration of organic matter and may vary from one water to another. Consequently, this method is not recommended if a significant correction for organic matter absorbance is required, although it may be useful in monitoring $NO_3^-$ levels within a water body with a constant type of organic matter. Correction factors for organic matter absorbance can be established by the method of additions in combination with analysis of the original $NO_3^-$ content by another method. Sample filtration is intended to remove possible interference from suspended particles. Acidification with 1*N* HCl is designed to prevent interference from hydroxide or carbonate concentrations up to 1000 mg $CaCO_3$/L. Chloride has no effect on the determination.

*b. Interference:* Dissolved organic matter, surfactants, $NO_2^-$, and $Cr^{6+}$ interfere. Various inorganic ions not normally found in natural water, such as chlorite and chlorate, may interfere. Inorganic substances can be compensated for by independent analysis of their concentrations and preparation of individual correction curves. For turbid samples, see ¶ A.1.

#### 2. Apparatus

*Spectrophotometer*, for use at 220 nm and 275 nm with matched silica cells of 1-cm or longer light path.

#### 3. Reagents

*a. Nitrate-free water:* Use redistilled or distilled, deionized water of highest purity to prepare all solutions and dilutions.

*b. Stock nitrate solution:* Dry potassium nitrate ($KNO_3$) in an oven at 105°C for 24 h. Dissolve 0.7218 g in water and dilute to

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# New ASTM Methods and Revisions

- Several for “total” and “free” Cyanide
- Luminescence-based DO
- Total and Organic Carbon
- Bisphenol A (plastic/resin biproduct) by GC/MS
- Several Nonylphenols by LC/MS/MS

# National Approval of ATPs

- Hach Method 10360 (LDO)
- In-Situ Method 1002-8-2009 (Optical DO)
- In-Situ Method 1003-8-2009 (Optical BOD)
- In-Situ Method 1004-8-2009 (Optical COD)
- Mitchell Method M5271 (Laser turbidity)
- Mitchell Method M5331 (LED turbidity)
- Orion Method AQ4500 3-09 (LED turbidity)

# National ATP approvals continued

- LLC's Systea Easy 1-Reagent Nitrate Method

# Clarifications/Corrections to 40 CFR 136.3

- Changes to o-phosphate filtration
- Listing Micro Methods for Ambient Water
- Fix typos and other errors

# TMI!

# 40 CFR 136.3 Table II Corrections

- Allow documented changes to sample preservation if method specific is different
- Define “holding time” for fecal coliforms as 8 hours max before beginning incubation
- Changes to Cyanide Preservation
- Changes to Whole Effluent Toxicity (WET) handling procedures

# Revisions to 40 CFR 136.4 & 136.5

- Easing the requirements for extreme “limited use” allowance by a Regional Coordinator
- Power to “pull” a method if deemed inappropriate nationally.

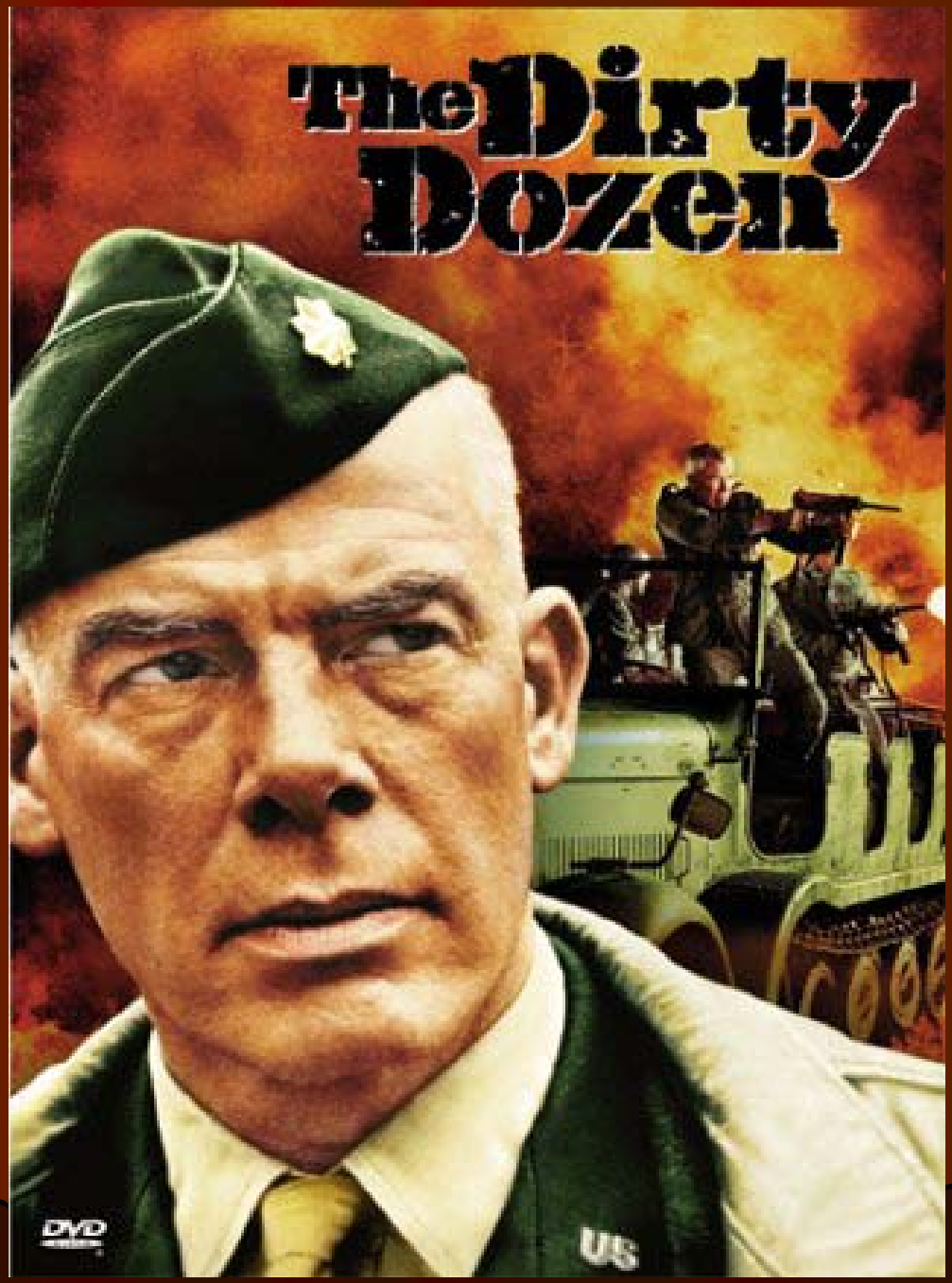
# Revisions to Method Modification 40 CFR 136.6

- Better language to define acceptable modifications to acceptable methods

# New QA/QC Language 40 CFR 136.7

- Adds minimum QA/QC requirements for all tests and analyses, where appropriate
- 12 QA/QC checks listed, so far
- Laboratory SOPs must have written rationales for inappropriate controls

Think of it as...


The Dirty Dozen
DVD
US

# The Twelve QA/QC Essentials

1. Demonstration of Capability (DOC)
2. Method Detection Limit (MDL)
3. Laboratory Reagent (method) Blank (LRB)
4. Laboratory Fortified Blank (LFB), also referred to as a spiked blank or laboratory control sample (LCS)

# The 12 continued

5. Matrix spike (MS), matrix spike duplicate (MSD) or laboratory fortified blank duplicate (LFBD) for suspected difficult matrices
6. Internal standards, surrogate standards (for organic analysis) or tracers (for radiochemistry)

# More of the “Dirty Dozen”

7. Calibration (initial and continuing), initial and continuing performance (ICP) solutions also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV)
8. Control Charts (or other trend analyses of quality control results)

# Still more of “the twelve…”

9. Corrective Actions (root cause analyses)
10. QC acceptance criteria
11. Definitions of a batch (preparation and analytical
12. Specify a minimum frequency for conducting the QC checks.

# And the “closing requirement”

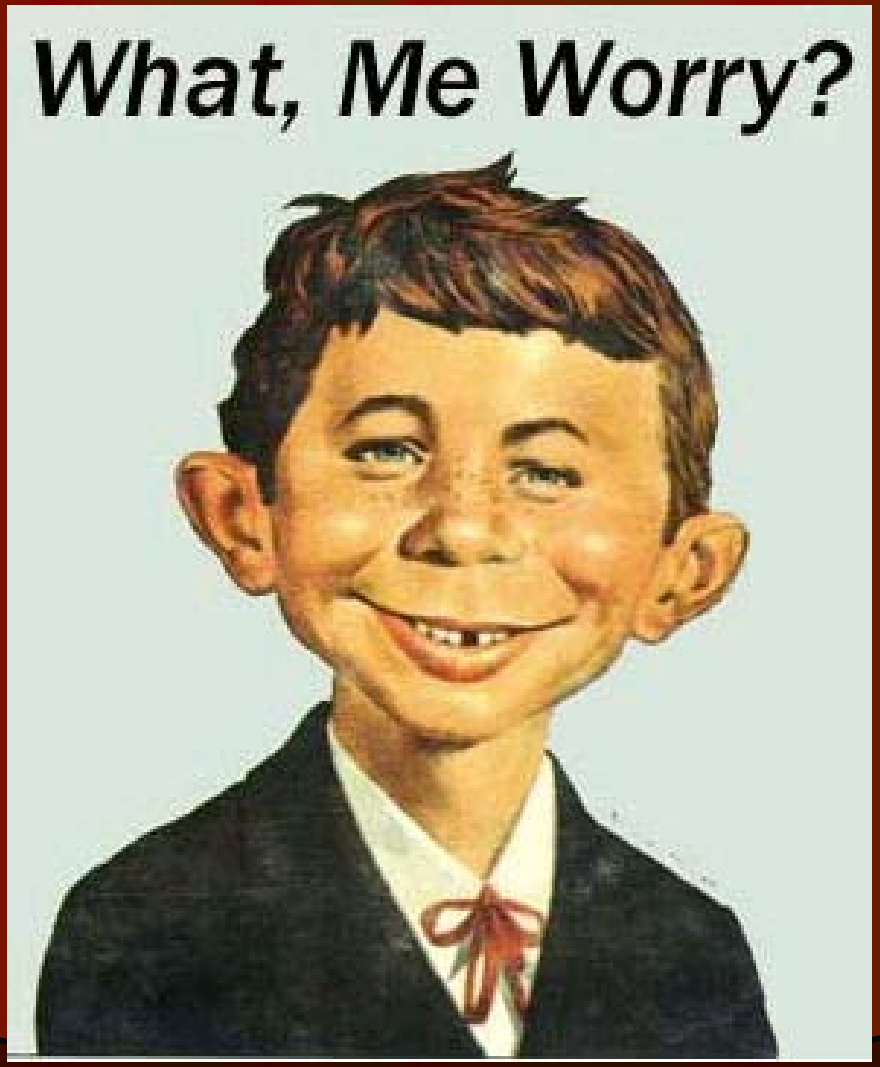
- These twelve quality control checks must

# Withdrawal of Appendices for 40 CFR 136

- Removal of Appendices A, C and most of D.

# Whew!

# Any Questions?



# Thank You, Thank You VERY Much!

# Contacts

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