The Devil is in the Details: Little Known Details about Selected Methods

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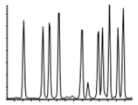
Shepherd Technical Services, LLC

2018 TCEQ Environmental Trade Fair



Shepherd
Technical
Services, LLC

Acknowledgment

This presentation represents a compilation of the experience of all of

Shepherd Technical Services'

Assessors

from all of the programs STS supports.

About this talk…

- We hope the information is “old news”
  - Our experience is that it isn’t…

Requirements in the Standard

- **NELAC 5.5.9.2 Essential Quality Control Procedures**

- "The laboratory shall ensure that the essential standards outlined in Appendix D or mandated methods or regulations (whichever are more stringent) are incorporated into their method manuals."

Requirements in the Standard

- TNI V1M4 1.2 Scope

- "Additional quality control requirements that are either specified by method, regulation or project shall be met by laboratories."

BOD SM 5210 B (2001)

- NOT the same as EPA 405.1

- pH: Section 4.*b*: *Sample preparation and pretreatment:*

  "All samples—Check pH; if it is not between 6.0 and 8.0, adjust sample temperature to 20 ± 3°C, then adjust pH to 7.0 to 7.2"

- Time: Section 5.*g*:

  "After preparing dilution, measure initial DO within 30 min."

HEM EPA 1664A/B

- Balance checks: Section 9.5 and Section 10

9.5 Calibration verification—Verify calibration of the balance per Section 10 before and after each analytical batch. If calibration is not verified after measurement of the analytical batch, recalibrate the balance and reweigh the batch.

10.1 Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights.

HEM EPA 1664A/B

- Reagent Specifications: Section 7.0

7.3 *n*-Hexane—85% minimum purity, 99.0% min. saturated C_6 isomers

7.7 Silica gel—Anhydrous, 75 - 150 micrometers

7.8 Hexadecane—98% minimum purity.

7.9 Stearic acid—98% minimum purity.

PRACTICAL or LABORATORY GRADE IS NOT SUFFICIENT!

Mercury EPA 245.1

- 7.3 Nitric Acid (HNO_3), concentrated (sp.gr. 1.41), assayed mercury level is not to exceed 1 µg/L.
- 7.4 Sulfuric Acid (H_2SO_4), concentrated (sp.gr. 1.84), assayed mercury level is not to exceed 1 µg/L

- **5.6.4.2 Documentation and Labeling of Standards, Reagents, and Reference Materials**

- a) The laboratory shall retain records for all standards, reagents, reference materials, and media, including the manufacturer/vendor, the manufacturer's *Certificate of Analysis or purity (if available*),

ThermoFisher SCIENTIFIC

Certificate of Analysis

1 Reagent Lane
Fair Lawn, NJ 07410
201.796.7100 tel
201.796.1329 fax

ThermoFisher Scientific's Quality System has been found to conform to Quality Management System Standard ISO9001:2008 standard by SAI Global Certificate Number CERT - 0090918

This is to certify that units of the lot number below were tested and found to comply with the specifications of the grade listed. Certain data have been supplied by third parties. ThermoFisher Scientific expressly disclaims all warranties, expressed or implied, including the implied warranties of merchantability and fitness for a particular purpose. Certain products (USP/FCC/NF/EP/BP/JP grades) are sold for use in food, drug, or medical device manufacturing.ThermoFisher does not maintain DMF's with the FDA. The following are the actual analytical results obtained:

Catalog Number	A200	Quality Test / Release Date	03/26/2018
Lot Number	179020		
Description	NITRIC ACID, CERTIFIED ACS		
Country of Origin	USA	Suggested Retest Date	Mar/2023
Chemical Origin	Inorganic-non animal		
BSE/TSE Comment	No animal products are used as starting raw material ingredients, or used in processing, including lubricants, processing aids, or any other material that might migrate to the finished product.		
Chemical Comment			

Result Name	Units	Specifications	Test Value
APPEARANCE		REPORT	Clear, colorless free from suspended matter
ALUMINUM	ppm	<= 0.2	<0.1
IRON (Fe)	ppm	<= 0.2	<0.2
LEAD (Pb)	ppm	<= 0.1	<0.05
MAGNESIUM (Mg)	ppm	<= 0.3	<0.05
NICKEL (Ni)	ppm	<= 0.05	<0.05
PHOSPHATE (PO4)	ppm	<= 0.2	<0.2

Hg?

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Catalog Number	A300	Quality Test / Release Date	03/29/2018
Lot Number	181458		
Description	SULFURIC ACID, CERTIFIED ACS		
Country of Origin	United States	Suggested Retest Date	Mar/2023
Chemical Origin	Inorganic-non animal		
BSE/TSE Comment	No animal products are used as starting raw material ingredients, or used in processing, including lubricants, processing aids, or any other material that might migrate to the finished product.		
Chemical Comment			

MANGANESE (Mn)	ppm	<= 0.2	<0.1
MERCURY (Hg)	ppb	<= 5	<5
NICKEL (Ni)	ppm	<= 0.1	<0.1

Mercury EPA 245.1

- 11.2.2 Prepare calibration standards by transferring 0.5, 1.0, 2.0, 5.0, and 10 mL aliquots …. Dilute the standard aliquots to 100 mL with reagent water (Section 7.2) and process as described in Sections 11.1.2, 11.1.3 (without heating), and 11.1.5.

- Drinking Water: MUST NOT CHANGE THE PROCEDURE

EPA Method 8270

- Resolution check:
- 7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. (8270C)

EPA Method 8270

- Resolution check:
- 11.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 50% of the average of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. (8270D)

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Quant Time: Oct 18 14:04:46 2017
Quant Method : C:\msdchem\1\methods\8270d_101217.m
Quant Title  : SW846 8270D OR EPA 625
QLast Update : Fri Oct 13 11:55:47 2017
Response via : Initial Calibration
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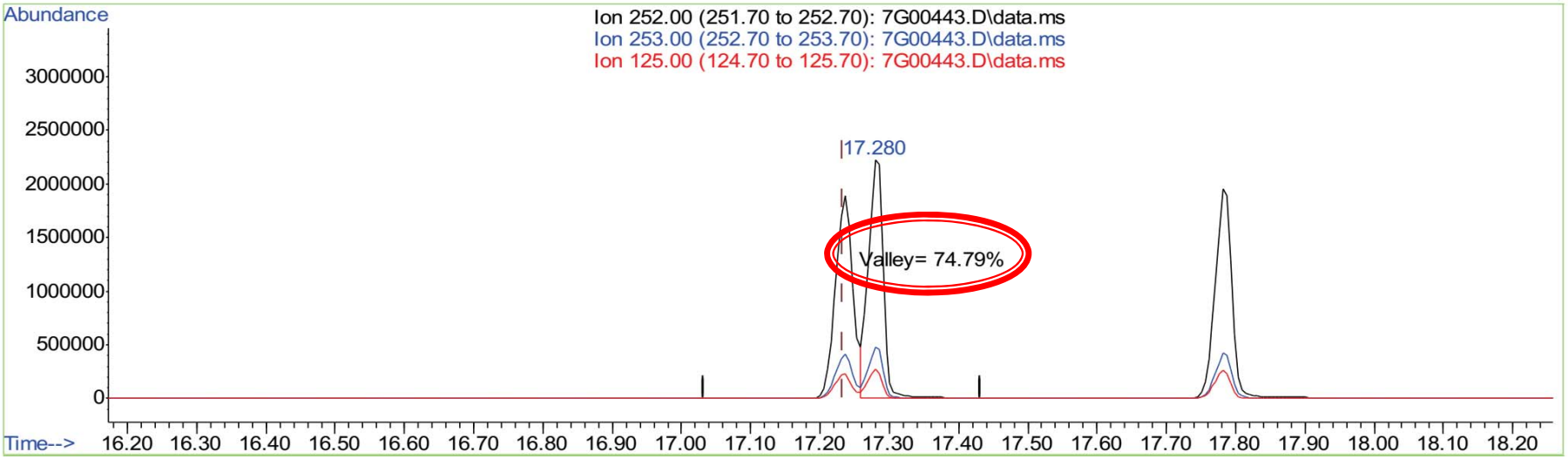

By the way…also in EPA 625.1

Units of Measure

- SM 2510 B Conductivity

  Section 5:

  Report temperature-compensated conductivities as "µmho/cm @ 25.0 °C."

- EPA 9045 pH in Soils

  7.2.5 Report the results as "soil pH measured in water at °C" where " °C " is the temperature at which the test was conducted.

- SM 5540 C. Anionic Surfactants as MBAS

  Section 5:

  Report as "MBAS, calculated as LAS, mol wt _____ ."

Conductivity Calibration

SM 2510 B:

SM 2020 B: 2. Ongoing Quality Control
a. Calibration/standardization: Calibrate the method or standardize titration reagents using the directions in the procedure.

Conductivity Calibration

SM 2510:

2. Measurement

a. Instrumental measurements: In the laboratory, conductance, G_s, (or resistance) of a standard KCl solution is measured and from the corresponding conductivity, k_s, (Table 2510:I) a cell constant, C, cm^{-1}, is calculated:

$$C = \frac{k_s}{G_s}$$

Conductivity Calibration

SM 2510:

Most conductivity meters do not display the actual solution conductance, G, or resistance, R; rather, they generally have a dial that permits the user to adjust the internal cell constant to match the conductivity, k_s, of a standard. Once the cell constant has been determined, or set, the conductivity of an unknown solution,

$$k_u = CG_u$$

will be displayed by the meter.

Conductivity Calibration

SM 2510 B:

4. Procedure

a. Determination of cell constant: Rinse conductivity cell with at least three portions of 0.01*M* KCl solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. If a conductivity meter displays resistance, *R*, ohms, measure resistance of this portion and note temperature. Compute cell constant, *C:*

$$C,\ \text{cm}^{-1} = (0.001412)(R_{KCl})[1 + 0.0191(t - 25)]$$

where:

R_{KCl} = measured resistance, ohms, and
t = observed temperature, °C.

Conductivity meters often indicate conductivity directly. Commercial probes commonly contain a temperature sensor. With such instruments, rinse probe three times with 0.0100*M* KCl, as above. Adjust temperature compensation dial to 0.0191 C^{-1}. With probe in standard KCl solution, adjust meter to read 1412 μmho/cm. This procedure automatically adjusts cell constant internal to the meter.

Quanti-Tray® wells

- Problem with empty wells
  - MPN based upon number of positive wells out total number of wells on the tray (97 total wells for Quanti-Tray®/2000).

- Empty wells acceptable if <2 wells per tray
  - (IDEXX Memo)

SM 9020 B Sample Receipt

- Section 12.*c* :
  - Actual laboratory reports may be kept, or data may be transferred to tabular summaries, provided that the following information is included: date, place, and time of sampling; name of sample collector; identification of sample; date and time of sample receipt; condition and ***temperature of received sample…***

Microbiology Media pH

- NELAC App. D 3.6.d)
  - Documentation for media purchased pre-prepared, ready-to-use shall include manufacturer, lot number, type and amount of media received, date of receipt, expiration date of the media, and ***pH of the media.***

- Similar language in TNI V1M5 1.7.3.5.d

EPA Method 524.2

- Preparation of Calibration Standards
  - Section 7.8.2

    "To prepare a calibration standard, add an appropriate volume of a primary dilution standard containing all analytes of concern to an aliquot of acidified (pH 2) reagent water in a volumetric flask."
- 4 minute Desorb Time

TCLP …<groan>

- 18 hour temperatures-min/max

- Matrix spikes for metals:
  - 8.2.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

TCLP …<groan vol. 2>

- Standard Additions:
  - 8.4 The use of internal calibration quantitation methods shall be employed for a metallic contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.
  - 8.4.1. The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

SM 4500-NO_3^- E or F/EPA 353.2

- Method E

3. Reagents

b. Copper-cadmium granules: Wash 25 g new or used 20- to 100-mesh Cd granules† with 6N HCl and rinse with water. Swirl Cd with 100 mL 2% CuSO4 solution for 5 min or until blue color partially fades. Decant and repeat with fresh CuSO4 until a brown colloidal precipitate begins to develop. Gently flush with water to remove all precipitated Cu.

SM 4500-NO_3^- E or F/EPA 353.2

- Method F

3. Reagents

d. Copper-cadmium granules: See 4500-NO_3^- E.3*b*

SM 4500-NO_3^- E or F/EPA 353.2

- EPA 353.2

7.0 REAGENTS AND STANDARDS

7.1 Granulated cadmium: 40-60 mesh (CASRN 7440-43-9). Other mesh sizes may be used.

7.2 Copper-cadmium: The cadmium granules (new or used) are cleaned with dilute HCl (Section 7.6) and copperized with 2% solution of copper sulfate (Section 7.7) in the following manner: …

SM 4500-NO_3^- E or F/EPA 353.2

- TNI V1M4 4.13.3 Additional Requirements

  f/xi): standard and reagent origin, receipt, preparation, and use;

- NELAC 2003 5.4.12.2.5.3 Analytical Records

  The essential information to be associated with analysis, such as strip charts, tabular printouts, computer data files, analytical notebooks, and run logs, shall include:

  i) standard and reagent origin, receipt, preparation, and use;

SM 2020/3020/4020/5020 Tables

- The “Section XX20” portions of Standard Methods provide the Quality Assurance and Quality Control requirements for the relevant methods

- Aside from specific requirements there are Tables listing required QC elements (e.g. MS, LCS, etc.) for each method

SM 2020/3020/4020/5020

- **2012 Method Update Rule**

- **Federal Register** / Vol. 77, No. 97 / Friday, May 18, 2012

- "Consequently, today's rule clarifies that an analyst using these consensus standard body methods for reporting under the CWA must also comply with the quality assurance and quality control requirements listed in the appropriate sections in that consensus standard body compendium."

SM 2020/3020/4020/5020

- **Particular requirements:**
- 3020/4020:

  Section 2.a

  "Repeat initial calibration daily or when starting a new batch of samples, unless the method permits calibration verification between batches."

SM 2020/3020/4020/5020

- **Particular requirements:**
- 2020:

  2. Ongoing Quality Control
  a. Calibration/standardization: Calibrate the method or standardize titration reagents using the directions in the procedure. Methods in Part 2000 that require calibration or titration reagent standardization are indicated in Table 2020.II.

SM 2020/3020/4020/5020

- **Particular requirements:**
- 2020:

  2. Ongoing Quality Control

  a. Calibration/standardization verification: Verify standardized titration reagents by periodically re-standardizing .... *Re-standardize reagents once a month* or when improper storage occurs. If the titration reagent's normality (titer value) has changed, then use the measured value, adjust the normality (titer value) as the procedure describes, or prepare and standardize fresh titration reagent as needed.

Summary

- Many methods have complex details that require careful attention to these details
- Some methods are Method Defined Parameters and must be followed exactly
- Some methods have QC detailed in another document (e.g., SM 4020)
- There is no substitute for reading the methods and developing intimate familiarity with the DETAILS of each method in your lab.

Conclusion

Know your Reference Methods!

Thank You

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