



# 1,4-Dioxane in QSM 6.0

## DOECAP ASP Workshop

Wednesday, August 5, 2020, 2:20 pm

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# Housekeeping

- Presentation will not take all the time allotted
- Questions may be submitted through Q&A Tool
- Q&A will be addressed as time permits at the end



# 1,4-Dioxane-Review

- Analyte of Concern
  - Not even really “emerging” now
- Many sites across the nation
- Physical Properties confound our “normal” (GC/MS) methods
  - Requested LOQs are below “normal” method capabilities

# Status of Method Accreditation

<b>Method</b>	<b># of Labs</b>
<b>8260B, C SIM</b>	<b>12</b>
<b>8270C, D SIM</b>	<b>18</b>
<b>8270D SIM Isotope Dilution</b>	<b>1</b>
<b>EPA 522 SIM</b>	<b>1</b>
<b>TO-15 SIM</b>	<b>1</b>



# Current Status

- QSM 5.3
  - LCS Limits for EPA Method 8260
  - No Limits for other techniques
- “B-Tables” for Methods
  - B-4 “Organic Analysis by GC/MS”
  - B-22 “Organic Semi-Volatile Analysis by GC/MS in SIM Mode”



# Current Status

- No B-Table for Organic Volatile Analysis by GC/MS in SIM Mode
- No B-Table for Isotope Dilution Methods

# QSM 5.3:

## 1,4-Dioxane QC Limits as VOA

<b>1,4-Dioxane</b>	<b>8260 Solid</b>	<b>8260 Aqueous</b>	<b>TO-15</b>
<b>Avg Recovery</b>	96.4	99	96
<b>Std Dev</b>	13.7	13.4	8.6
<b>Upper Limit</b>	138	139	122
<b>Lower Limit</b>	55	59	71
<b>Data Points</b>	7968	17866	2656



# LSC QC Limits As Expected

- Average near 100%-Analytical Standards are Process Standards
- Standard Deviation somewhat wider than more well-behaved VOAs
  - Similar to alcohols/ketones
- Number of points about 60% of more common VOA Analytes





# 1,4-Dioxane is Important

- ~40% of QSM-Accredited Labs include 1,4-Dioxane Analysis
- Wide Distribution of known sites
- Regulatory Pressure, particularly on LOQs
- QSM is applicable, could be improved.



# 1,4-Dioxane is Difficult

- Physical properties make separation from water difficult
- Carryover in P&T Systems
- Doesn't work well in our “normal” (GC/MS) analytical systems



# QSM Development

## □ QSM content

- Prepared by Interagency QA Oversight Subgroup
- Considers Suggestions from Stakeholders
- Approved by EDQW



# Status of 1,4-Dioxane, QSM 6.0

- All documents in first draft
  - Have not yet been through first review by Interagency QA Oversight Subcommittee
  - Have not incorporated comments from the community
  - Have not been reviewed by EDQW



# Disclaimer

- What does this mean?
  - I'm taking my best guesses here based on information provided to me
  - The speculation in this presentation is based on discussions with EDQW representatives and consultants
  - It could be all wrong, but it's likely to be close to right.



# Probable Course of Action

- Expansion of “B-Tables” to knowingly, accommodate analytes such as 1,4-Dioxane
- Unlikely to develop additional LCS limits for other techniques at this time
- Unlikely to embrace EPA Method 522



# Why Not EPA Method 522?

- Specifically Drinking Water
  - Not a matrix of concern for QSM
  - Little demand
- SPE does not flex well to more contaminated matrices



# Additional QC Limits Unlikely

- Current development plan does not include updates to LCS QC Limits
- Adding/Updating limits is more difficult than you might expect
  - There are no easy tools in place
  - Inputs are better from more controlled systems





# B-Tables

- Routine analysis of 1,4-Dioxane using GC/MS in full-scan mode is covered under Table B-4, “Organic Analysis by GC/MS”
- Routine analysis of 1,4-Dioxane is covered to some extent under Table B-22, “Organic Semi-Volatile Analysis by GC/MS in SIM Mode”



# Routine Full-Scan

- 1,4-Dioxane can be included (and often is included) as a routine analyte in EPA 8260 analyses.
- Noted blank contamination issues are controlled by MB criteria in the table
  - No analytes detected  $> 1/2$  LOQ or  $> 1/10$ th the amount measured in any sample or  $1/10$ th the regulatory limit, whichever is greater.



# Routine Full-Scan

- 1,4-Dioxane can be included in the SVOA
  - Recoveries are routinely poor.
- Both VOAs and SVOAs are appropriately controlled by the remaining tuning, calibration and quality control criteria



# Full-Scan Tuning Criteria

- Most recent SW-846 versions of GC/MS methods have greatly reduced the required tuning frequency, e.g., 8260D, 8270E
- Consideration is being given to incorporating the reduced frequency requirements



# Calibration Criteria

- Requirements are standard for organic analyses
- Additional requirements for evaluation of error (TNI 2016 V1M4) are being considered for incorporation



# Selected-Ion Monitoring Mode

- Table B-22 for SV GC/MS SIM Analyses was added to QSM 5.1
- Primarily designed PAH analysis
  - Has utility for 1,4-Dioxane
  - Low-level pesticides, pentachlorophenol
- QSM 6.0 may expand to include VOA GC/MS SIM



# Table B-22

- Existing requirements particularly applicable to 1,4-Dioxane
  - GC/MS Tuning
  - Deuterated Monitoring Compounds (Surrogates)
  - Use of low-concentration ISTDs
  - Characteristic Ions for Confirmation



# Tuning for SIM

- Full-Scan tuning is required
  - Conundrum
- Tuning designed to show three things
  - Mass-axis calibration verification
  - “Correct” Relative Ion abundance ratios
    - Was assumed to be important for spectral matching
  - Acceptable Sensitivity





# Tuning for SIM

- Full-scan data has limited applicability to SIM data
  - Different mass spectrometer descriptors
- Discussions are planned to consider options



# Deuterated Monitoring Compounds (Surrogates)

- Original B-22 DMCs were designated to match PAH Analyses
- Low concentrations matching low concentration analysis required



# DMCs in QSM 6.0

- May change back to use of term “Surrogates”
- May add requirements for deuterated analogue of target analyte
  - *e.g.*, 1,4-Dioxane-d8



# Low-Concentration ISTDs

- B-22 requires ISTDs to be spiked at concentrations matching range of target compounds, *e.g.*, 0.40 ng/μL
- Requirement was lifted from EPA-CLP
- Allows for different ISTDs for full-scan and SIM so both can be spiked in same extract



# Characteristic Ions for Confirmation

- Each compound evaluated with three different (structural) ions, *i.e.*, not part of a cluster
- Relative intensities agree within 30% of reference spectrum
- S/N ratio  $> 3$  for each ion
  - ISTD/DMCs may use fewer ions



# QSM 6.0 B-22

- Additional option under discussion
  - Extracted Internal Standards
  - Add to sample prior to extraction
  - Monitor recovery against non-extracted IS
  - Use to provide recovery-corrected data
- Using 1,4-Dioxane-d8 would provide Isotope Dilution analysis



# Do You Have an Opinion?

- DOE-ASP has a mechanism to submit information for consideration
- Form: “QSM Issues of Concern” resides on the DOECAP Sharepoint Site under the “Resources” Tab



# Summary: 1,4-Dioxane

- Multiple analytical techniques available
- Current usage is mostly GC/MS SIM
- LOQ requirements give reasons to move to SIM and SIM with Isotope Dilution
- QSM 6.0 B-Tables are being discussed so all schemes could be included and controlled.





John says:

**THANK YOU!!!**