Analysis of 1,4-Dioxane By EPA Method 522

Analytical Methodology Recommendation Update

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1,4-Dioxane: History and Usage

- Referred to as an ‘Emergent Pollutant of Concern’ (EPOC);
- No natural occurrence reported.
- Millions of pounds produced in US annually;
- Used as a chlorinated solvent stabilizer (e.g., 1,1,1,-trichloroethane)
- Used as industrial solvent.

Environmental Fate

(ATSDR Report)

- 226,080 pounds reported to Toxics Release Inventory as released to the environment in 2003;
- Expected to volatilize from surface water and soils at moderate rate;
- Air photo-oxidation w/ half-life of 1 – 3 days;
- Resistant to biodegradation in groundwater/soils (1/2 life in years cited elsewhere)
- Binds weakly to soils - High mobility in soil;
- Water soluble - Expected to migrate with groundwater (ahead of chlorinated solvent plumes)

Regulatory & Analytical Review

- Florida Regulation 62-777 Groundwater Criteria of 3.2 ug/L
  (based on carcinogenicity).

- Method 8270 listed in the 62-777 PQL Guidance Document (needs updating).

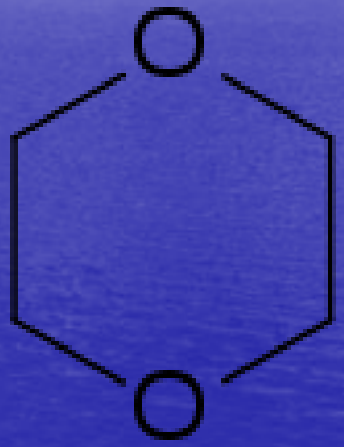
- Listed in EPA Method 8260B and 1624C, but not listed in EPA Method 8270D.

Why is 1,4-Dioxane an Issue Today

- "Invisible" Environmental Contaminate - Due to detection limits have historically analytical difficulties the been high.
- Classified as Class B2 - Probably human carcinogen.
- 1,4-Dioxane is expected to be found at a significant number of chlorinated solvent sites.

Chemical Properties

- 1,4-diethylene dioxide, p-dioxane, 1,4-dioxacyclohexane,diethylene ether.
- Flammable liquid
- MW 88.11
- Density: 1.03
- BP_{760}: 101.1 °C (121 °C for PERC)
- Vapor Pressure - 29 mm Hg @ 20 °C (14 mm Hg @ 20 °C for PERC)
- Soluble in Water



Why is Determination of 1,4-Dioxane in Water Difficult?

- Partitioning Coefficient $LogP_{O/W}$ = -0.27 (PERC = 3.4, Methanol = - 0.82)
- As LogP → 0, Equal partitioning between octanol and water

Consequences:

- Low Purge Efficiency by VOC Techniques
- Low Response in Head Space Analysis
- Poor Liquid-Liquid Extraction Efficiency

Other Analytical Complications

- Low Mass Ions (m/e 88 and 58) resulting in increased interference.
- Different labs and different method produced widely different results.

  (1–3 order of magnitude differences)

Analytical Objectives

- Reliable detection below 1 ug/L;
- Minimization of sampling and analytical losses;
- Good accuracy, precision and reproducibility among laboratories;
- Available technology;
- Cost effective.

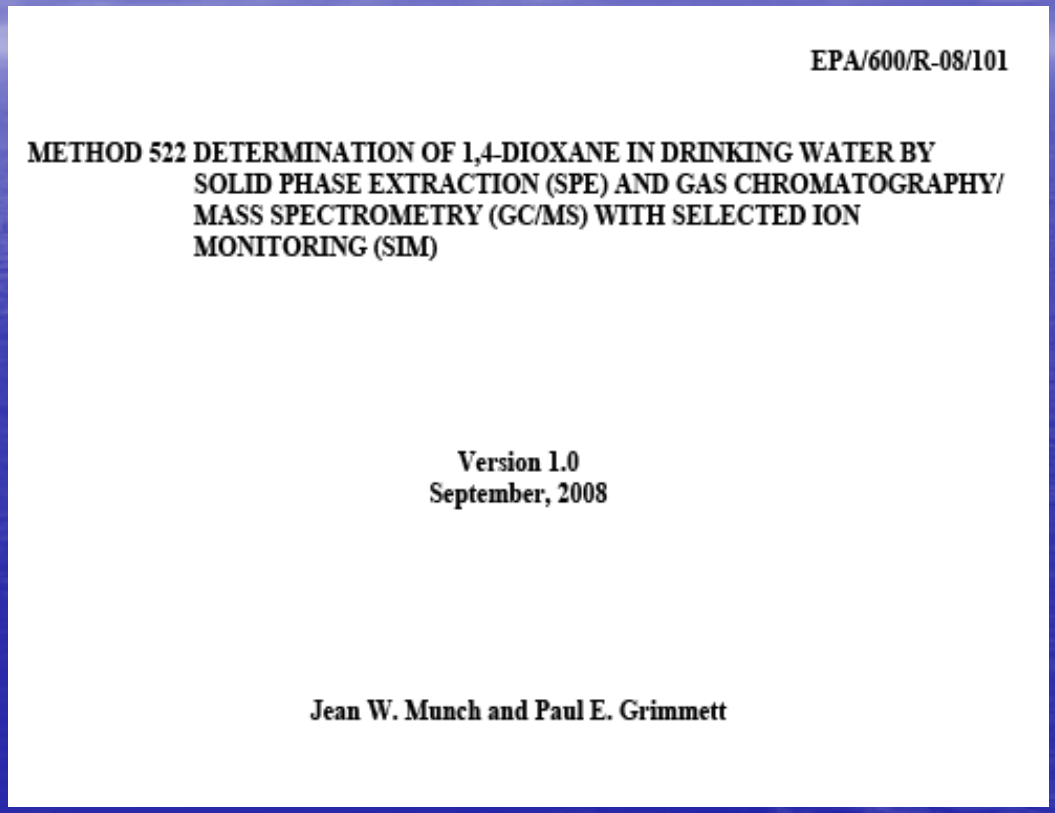
Listing of Analytical Techniques as of 2008

- Method 8260 (GC/MS Full Scan)
- Method 8260 (SIM)
- Method 8260C SIM w/ 'Isotope Dilution' and Heated Purge
- Method 1624 SIM
- Method 8261A Vacuum Distillation
- Method 8270 SIM w/Isotope Dilution

EPA Method 522

- Water Matrices
- Single Analyte Test
- Solid Phase Extraction
- 1,4-dioxane –d_8 (surrogate)
- Reporting Limits

  0.05 µg/L



EPA/600/R-08/101

METHOD 522 DETERMINATION OF 1,4-DIOXANE IN DRINKING WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)

Version 1.0
September, 2008

Jean W. Munch and Paul E. Grimmett

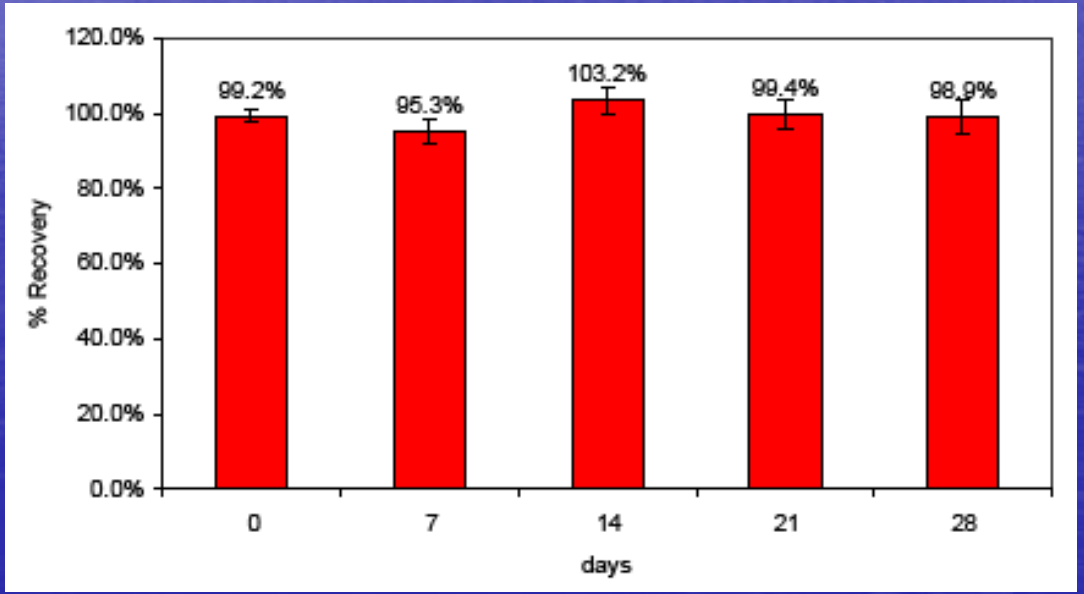
Sample Collection and Preservation

- Sodium sulfite – Dechlorination
- Sodium bisulfate – pH<4 Microbial Inhibitor
- Ship and Store – Temp. ≤ 10 °C
- Holding time – 28 days
- Extracts – 28 days @ ≤ -5 °C

1,4-Dioxane Sample Stability
(USEPA METHOD 522)

- Excellent 28 day Stability in Drink Water.
- Stability Test needs to be repeated in other water matrices.

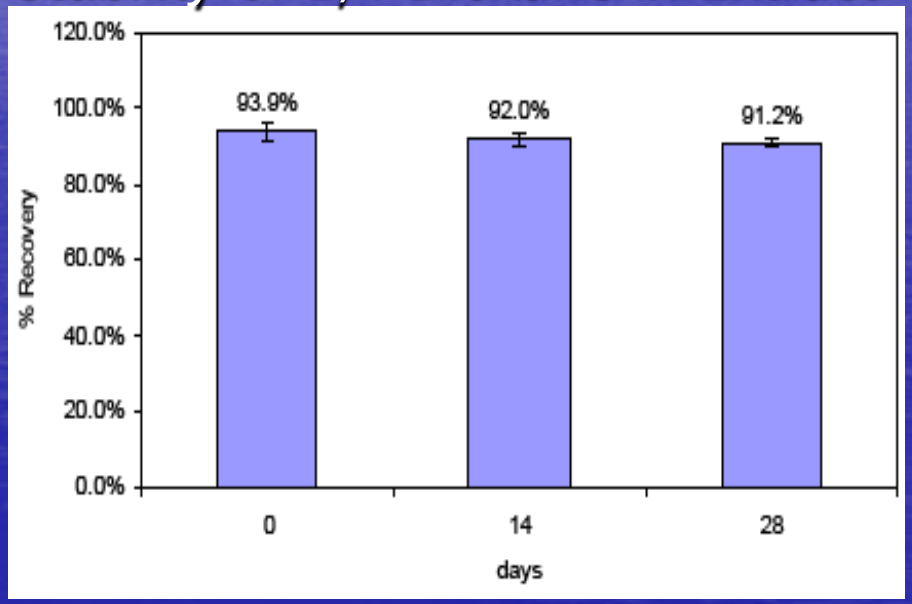
Stability of 1,4-Dioxane in Drinking Water



1,4-Dioxane Extract Stability
(USEPA METHOD 522)

- Excellent 28 day Stability in Extracts.
- Extract Stability Test should not need to be repeated for other aqueous matrices.

Stability of 1,4-Dioxane in Extract



Seven 10 ppb Fortified Extracts

Solid Phase Extraction (SPE) Process

Method-Specific SPE Cartridge

- Carbon molecular sieve (Supelclean Envi-Carb™ Plus)
- 0.4 gram or 2 gram cartridge

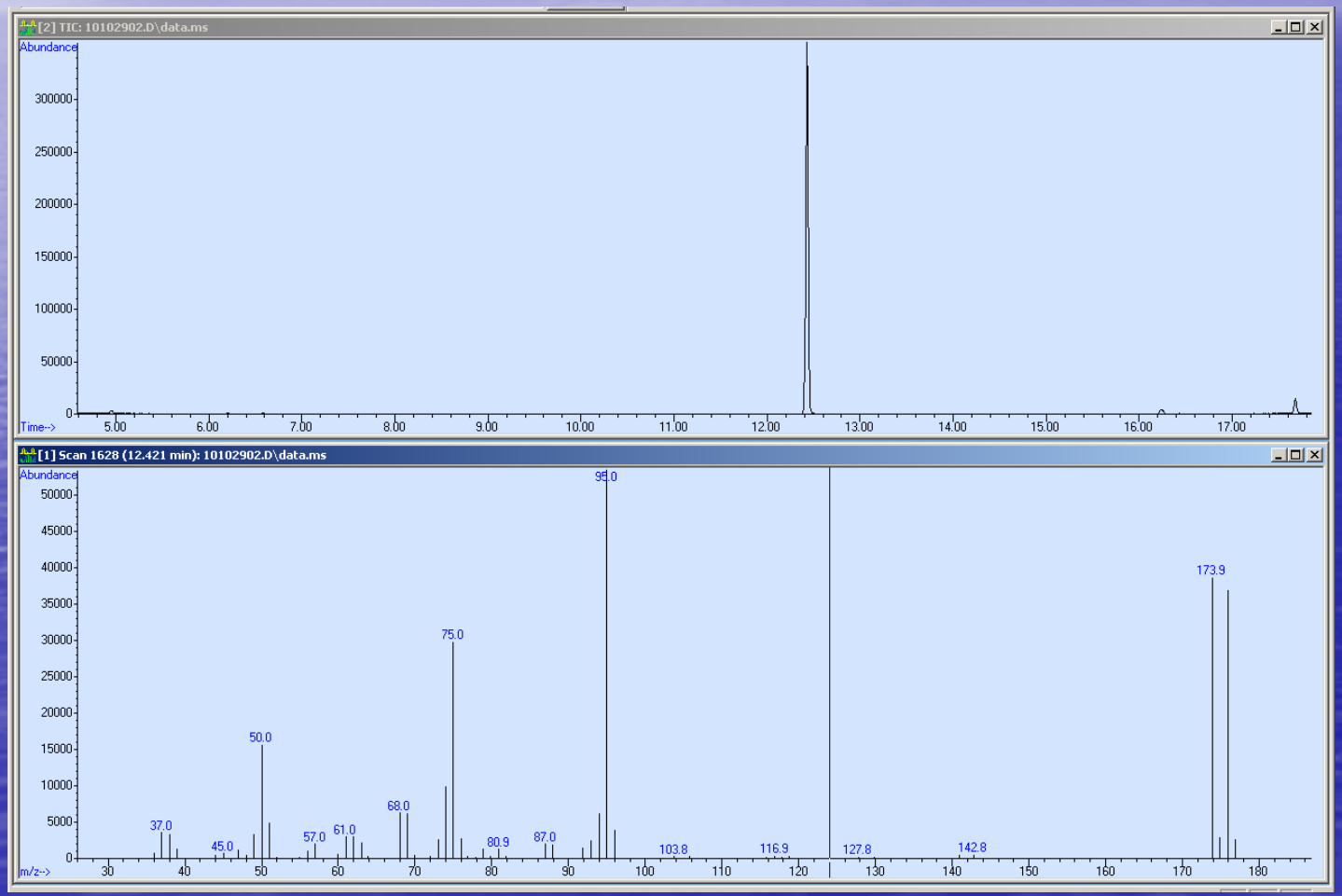
SPE Manifold

- Condition Cartridge
- Add Surrogate
- Extract Sample: 100 mL or 500 mL
- Elute Cartridge (50x Conc. Factor)
- Add THF-d_8 (Internal Standard)

Instrumentation for Analysis

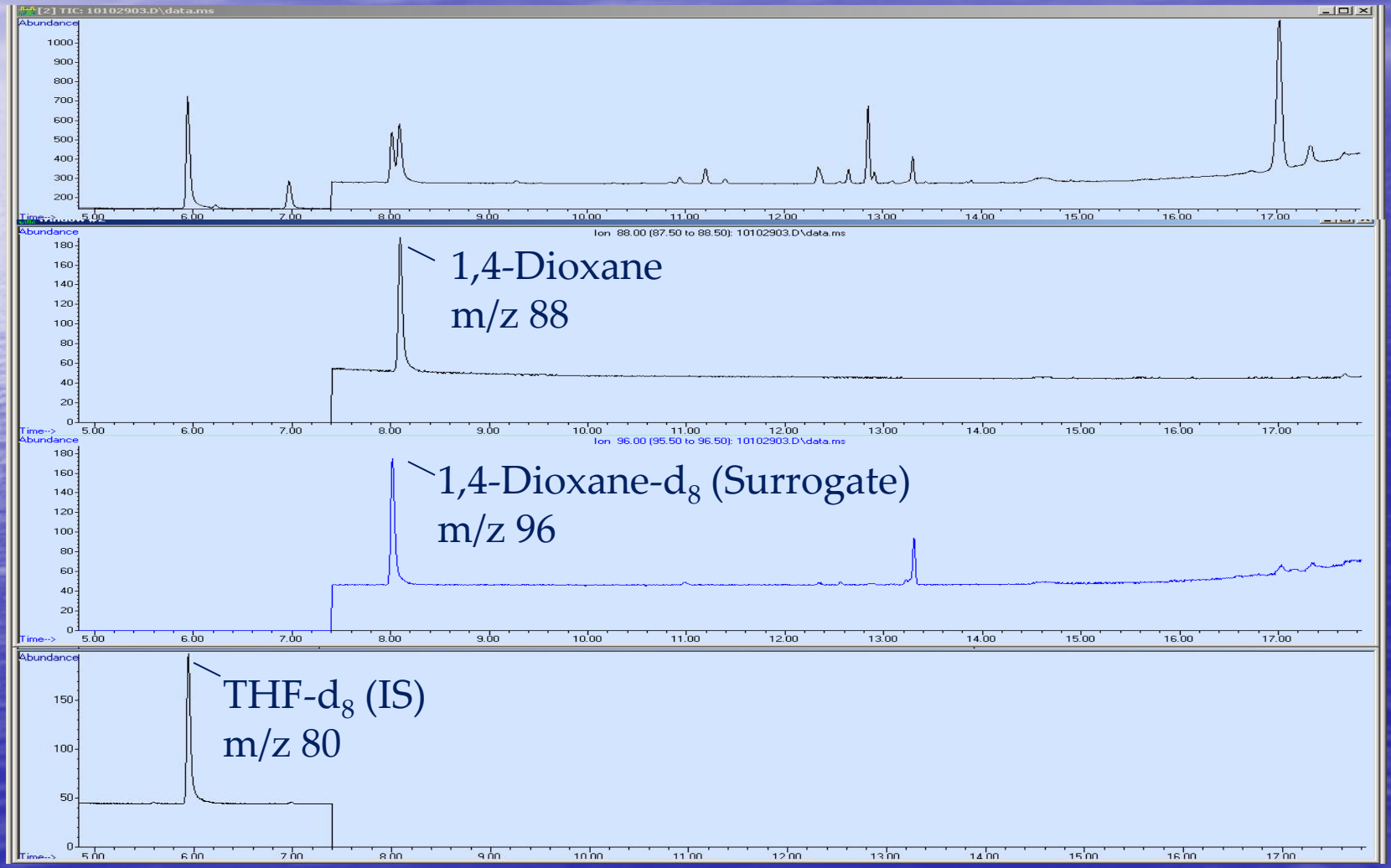
- Agilent 5973 or 5975 GC/MS
- DB-624 or DB-VRX Column (30m x 0.25 mm x 1.4 µm)
- 1µL Injection volume
- Run time < 18 minutes
- BFB Tune Check

BFB Tune Chromatogram



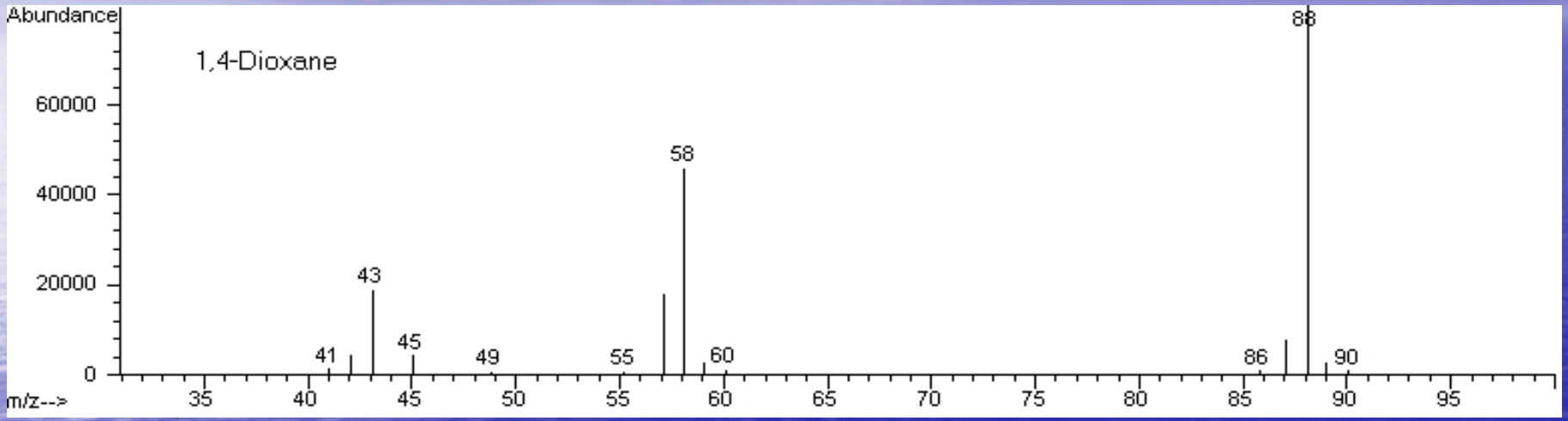
1,4-Dioxane Analysis Mass Chromatogram

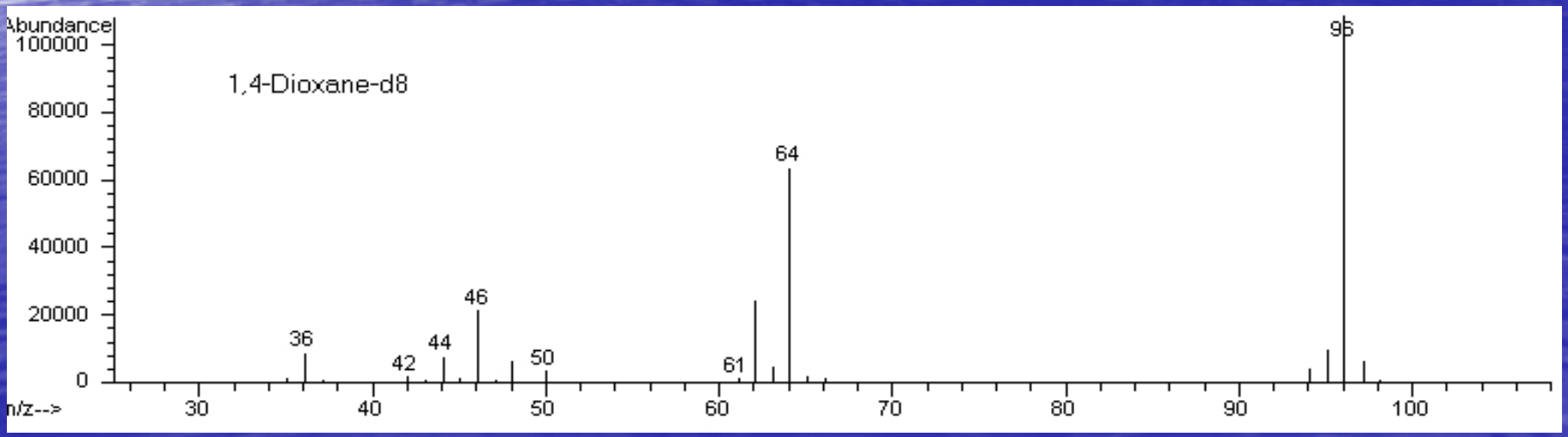
Selected Ion Monitoring



1,4-Dioxane/1,4-Dioxane-d_8

Mass Ion Spectra

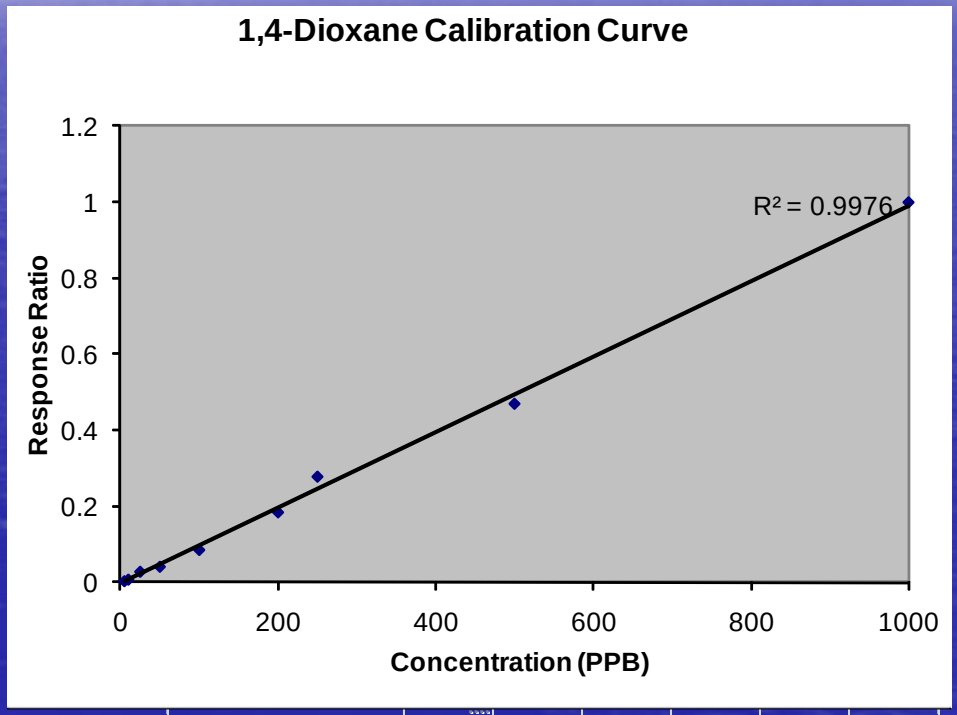




Instrument Calibration

(FDEP SOP SV-015)

- Sample Calibration Range: 0.20 to 20 µg/L
- 10.0 to 1000 µg/L on Instrument (due to 50x CF)
- 7 Calibration Levels
- IS/Surrogate @ 100 µg/L

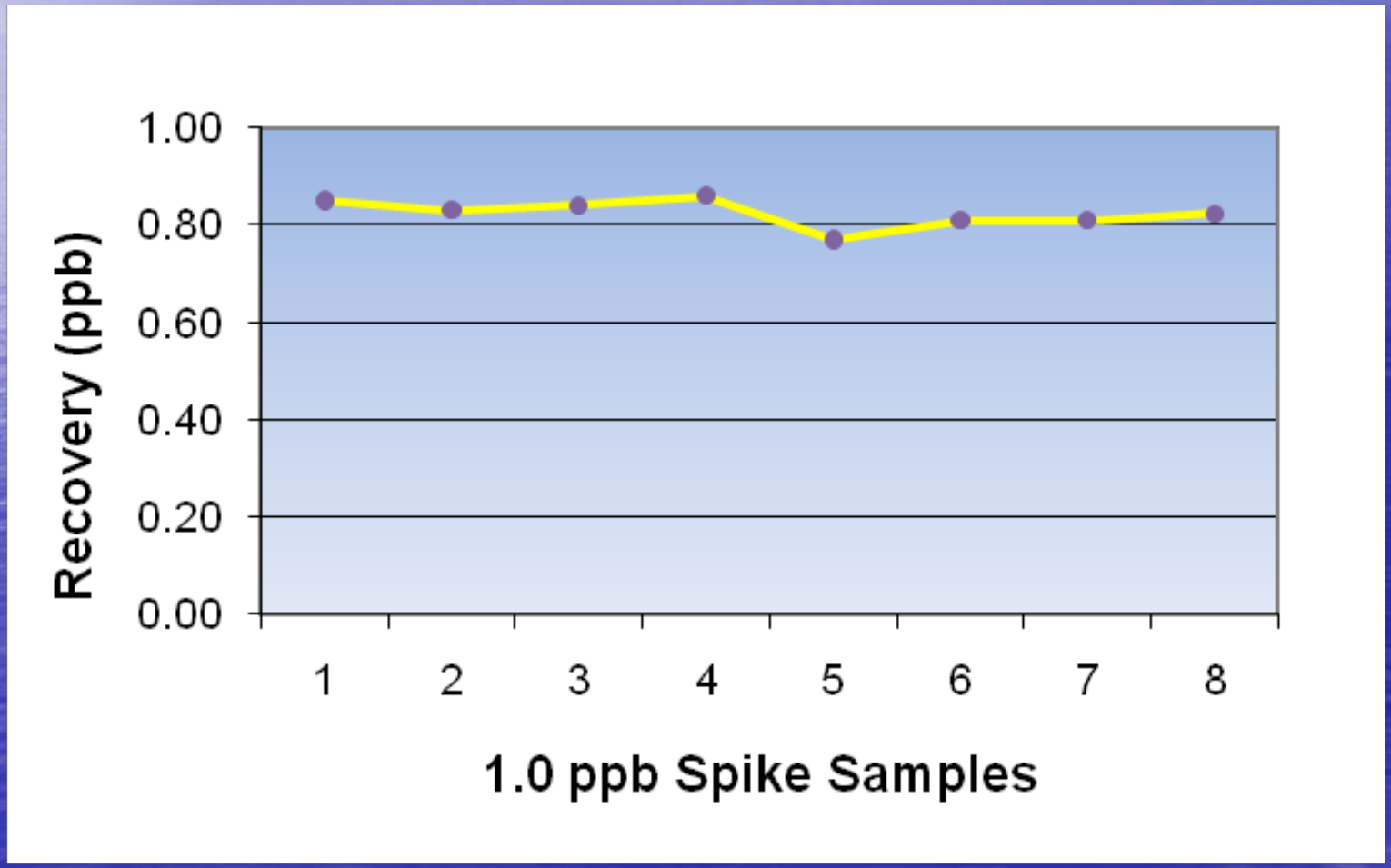


EPA Method 522 QA/QC

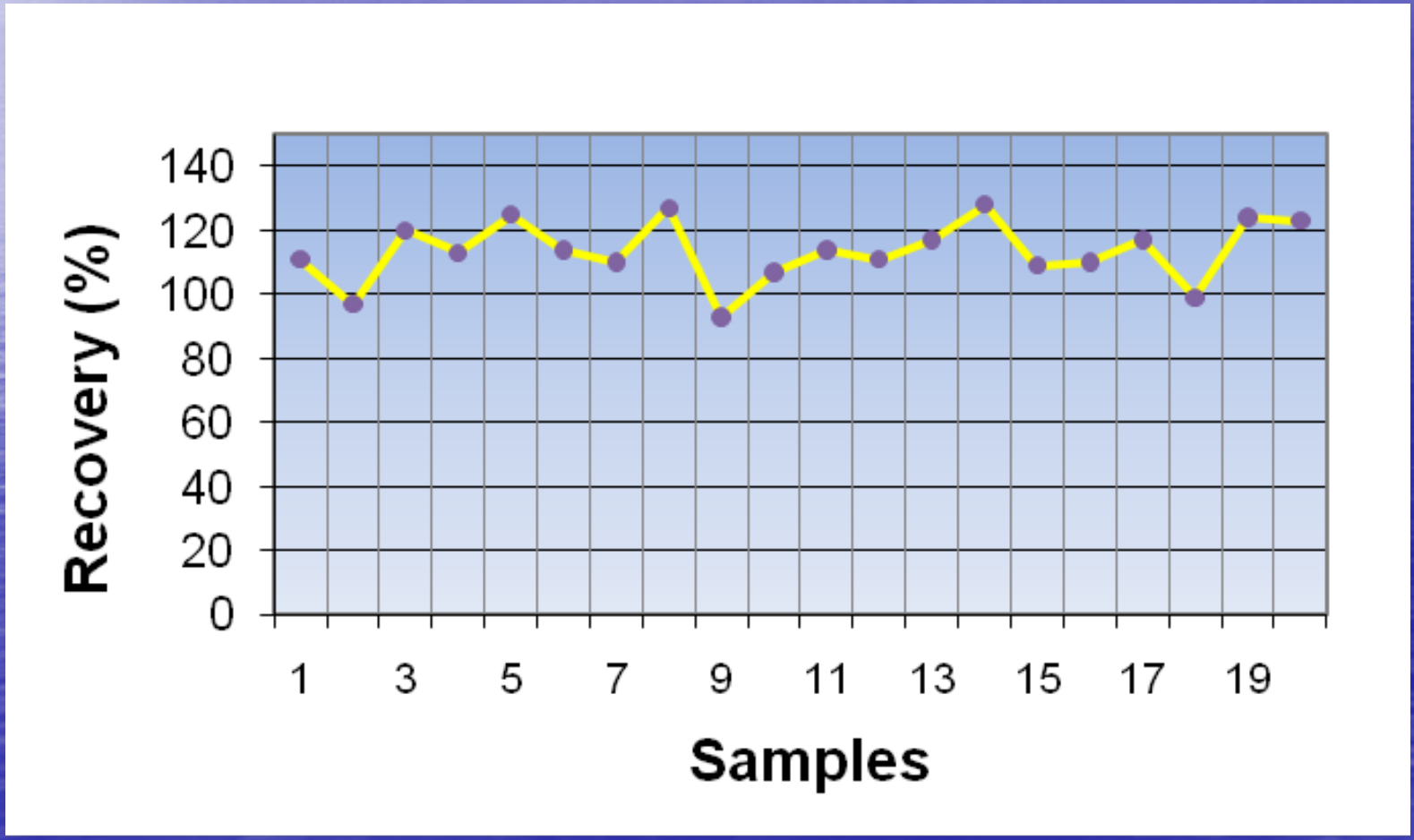
For a Batch of 20 samples

- Blank and Tune
- 3 CCV Levels (every 10 samples)
  - Low - 10 µg/L (initially)
  - Medium - 100 µg/L (alternating w/ High)
  - High - 500 µg/L
- LFB & MS/MSD
- Closing Blank and CCV

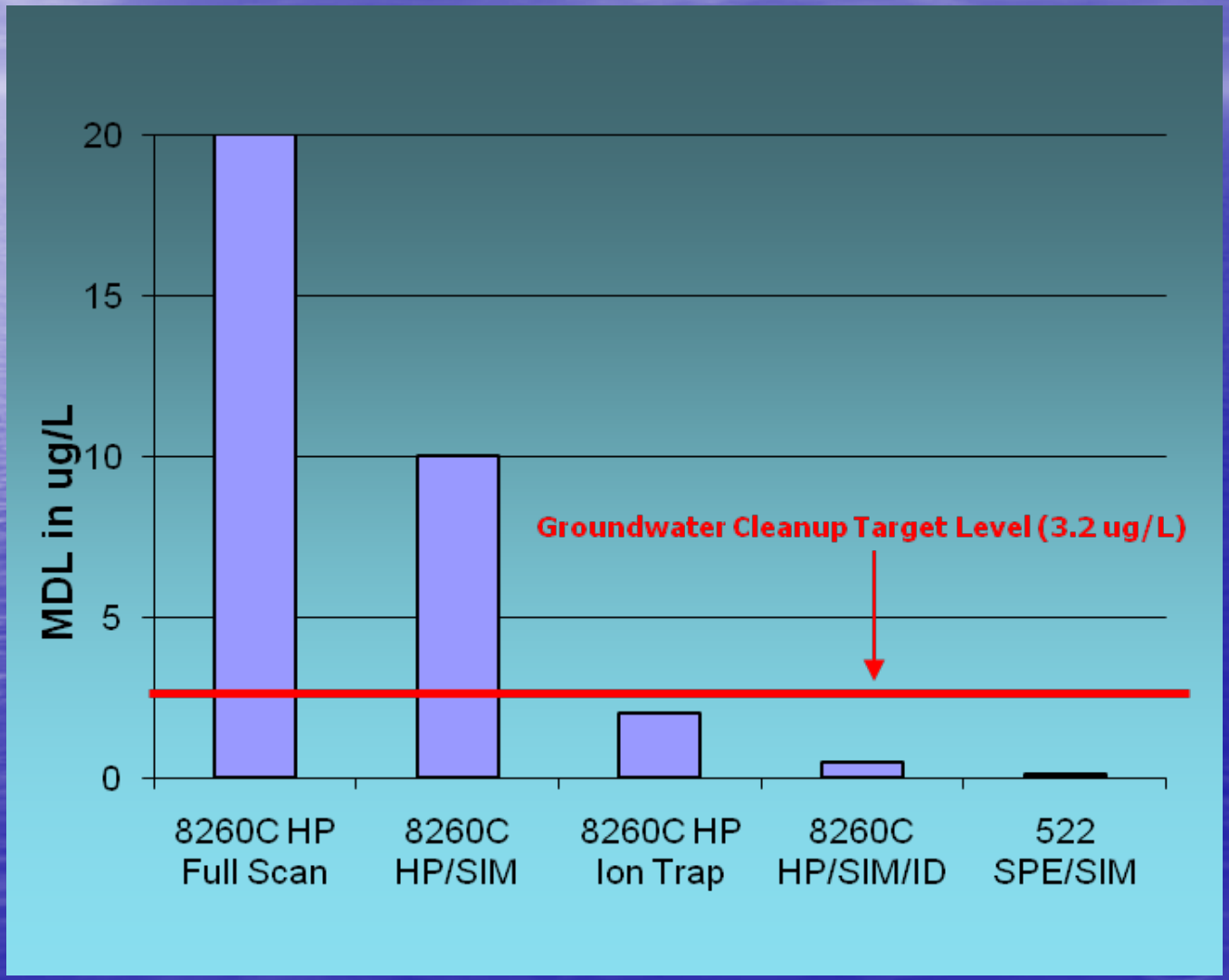
Initial 1,4-Dioxane Validation Study Results by EPA Method 522



Typical 1,4-Dioxane-d8 Surrogate Recoveries by EPA Method 522



MDLs for 1,4-Dioxane by Various EPA Methods



EPA Method 522 Advantages

- Relatively Easy Sample Preparation
- Very Low Detection Limits (< 0.05 ppb)
- Long Sample and Extract Hold times
- Excellent standard shelf life.
- 1,4-Dioxane-d_8 Surrogate

EPA Method 522 Disadvantages

- Low Mass Ions for Analyte, Surrogate, and Internal Standard.
- Selected Ion Monitoring limitations
- Cost-per-Analyte high relative to multi-component methods.

1,4-Dioxane as a Volatile

Method 8260 SIM, Heated Purge, and Isotope Dilution (ID)

- Minimal sample preparation involved
- Automation possible for high throughput
- Method can achieve MDL objective of < 5 µg/L by using both heated purge and SIM
- Very Low Relative Response Factor due to poor purging efficiency.

1,4-Dioxane as a Volatile

Method 8260 SIM, Heated Purge, and Isotope Dilution (ID)

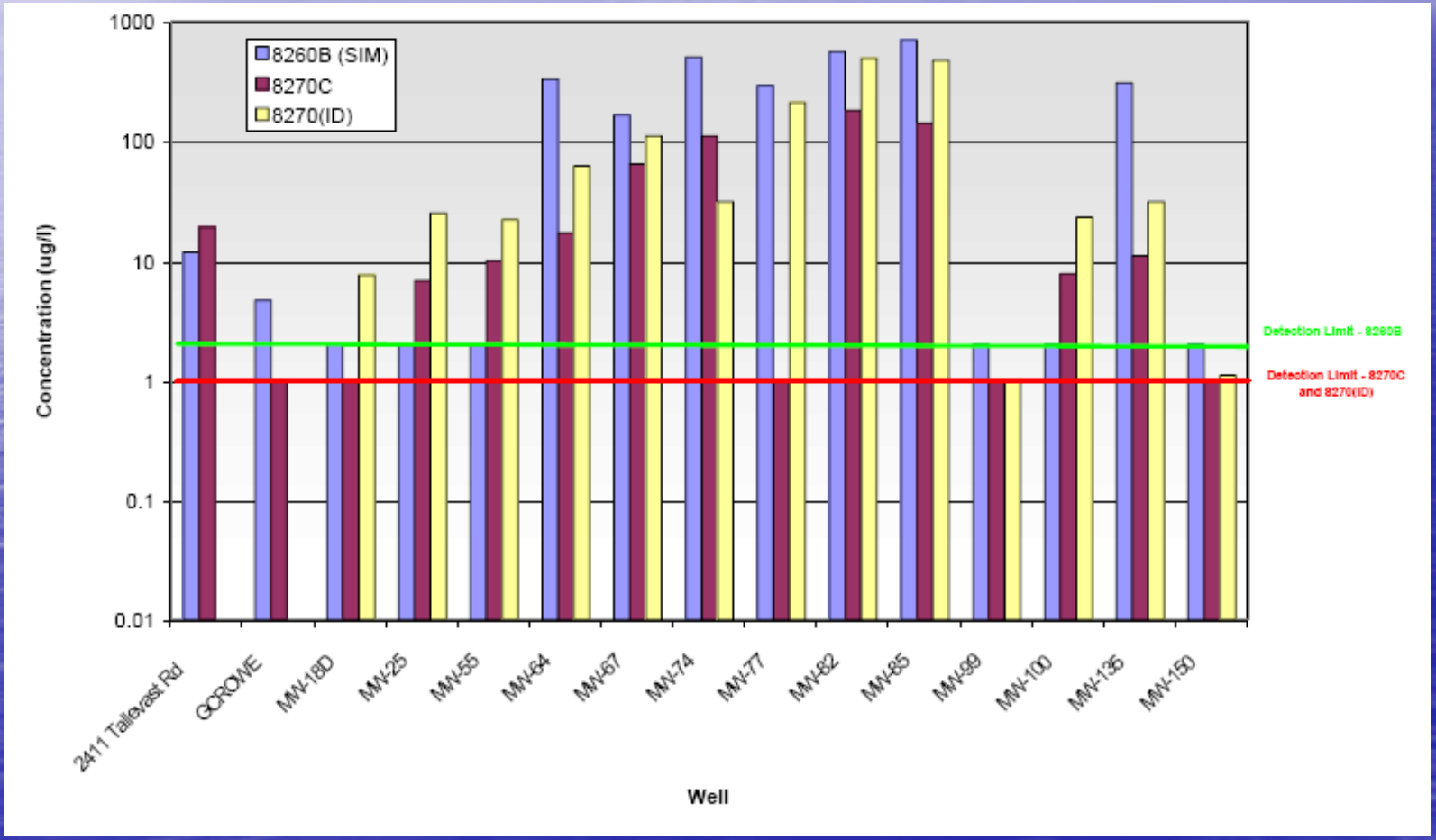
- Requires a limited sample volume.
- Typical recovery limits 60 to 130%.
- Isotope Dilution compensates for poor purge efficiency and method variability.
- Prone to carryover problem.

1,4-Dioxane as a Semi-Volatile
Method 8270 and 8270 Isotope Dilution (ID)

- 1,4-Dioxane elutes very early
- Potentially large extraction losses and correction factors w/ ID (increases uncertainty in results)
- Potential for losses during sample collection and transportation due to equilibrium with headspace
- Accreditation Problems by 8270

EPA Method 8260 and 8270 Comparison

BBL Environmental Services Inc (2006)



1,4-Dioxane Analysis:

Summary

- 1624 or 8260C w/ Heated Purge-Isotope Dilution-SIM is recommended for quantitative analyses, but have difficulty performing in the low-ppb range.
- Method 8270D SIM also has difficulty in the low-ppb range.
- 8261A is a good quantitative method but availability is limited;
- EPA Method 522 provides a robust, trace-level analytical approach for the analysis of 1,4-dioxane in water.

1,4-Dioxane Analysis:

Summary

EPA Method 522

- Provides best low-level performance.
- 28 Day hold times.
- Excellent calibration range and linearity.
- Requires small sample size (100 mL).
- Data readily meets typical data quality objectives.
- Recommended by the FDEP lab for routine environmental water matrices analysis.

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