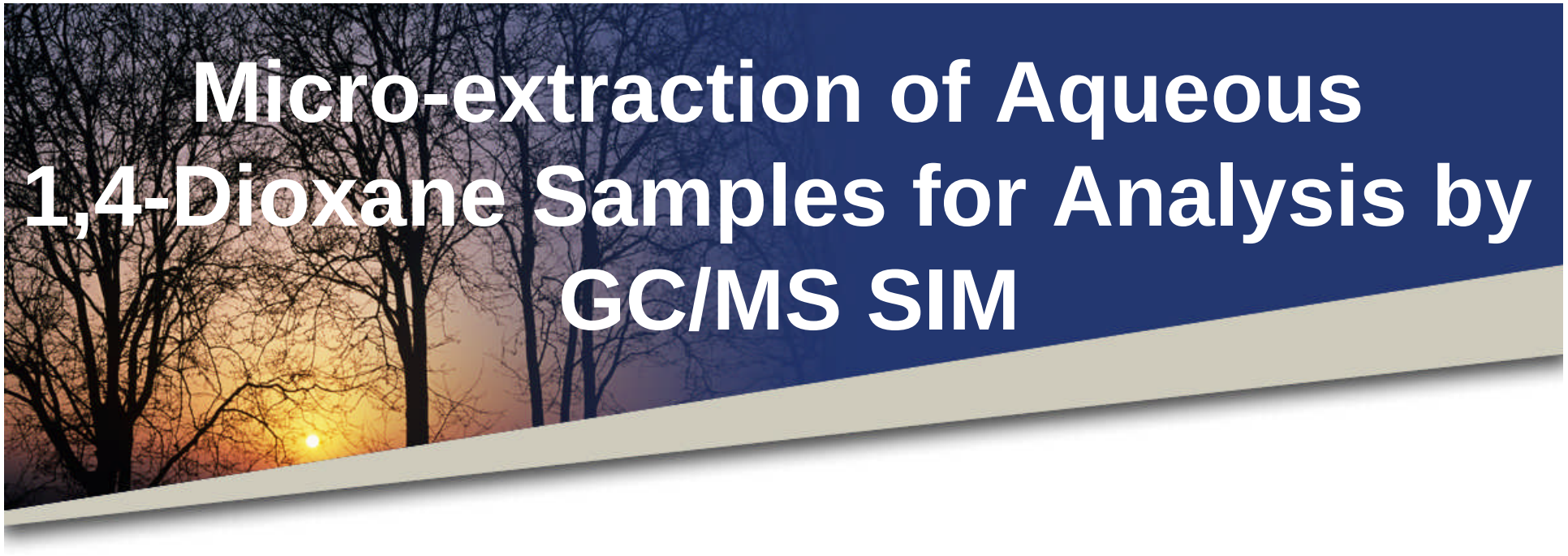

Micro-extraction of Aqueous 1,4-Dioxane Samples for Analysis by GC/MS SIM

Analytical Procedure for 1,4-dioxane extraction from 200 µL of water with a 20-µg/L reporting limit

ENVIRONMENTAL STANDARDS

Background and Assignment

- Test samples are bioremediation small-scale tests that must be sampled over time without significant change to the test system.
- Goal was to get below 50 ppb and to go as low as possible.
- Total available sample volume per test limited to 200 µL.
- Personnel time, equipment, and funding were limited.
- Target compound 1,4-dioxane has both very poor purging efficiency and poor extraction efficiency due to its high solubility.

ENVIRONMENTAL STANDARDS

Eliminations

- Testing via direct aqueous injection (DAI) sensitive to only 500 µg/L.
- Purge and Trap just not sensitive enough
- Conventional liquid-liquid extraction would require time consuming extraction and would require sample volumes beyond what was available.

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Project Planning Options

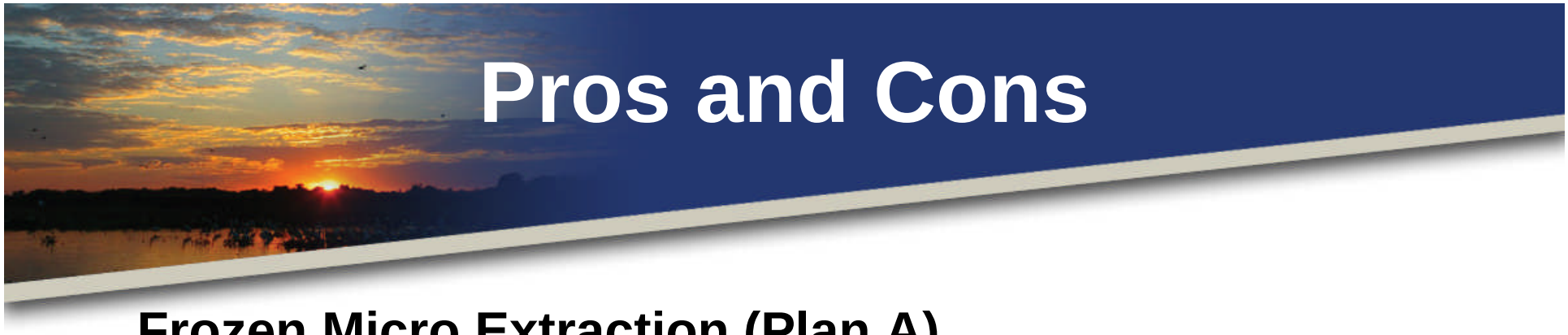
Plan A:

- Frozen micro extraction.
- Take 200 µL of sample and add 200 µL of methylene chloride in a 2 mL instrument vial.
- Freeze sample.
- Syringe off methylene chloride
- Dry and analyze

Plan B:

- Adapt Solid Phase Micro Extraction (SPME) for 200 µL sample.
- Manual extraction set up on rotatary shaker for agitation.
- Direct Manual injection

ENVIRONMENTAL STANDARDS



Pros and Cons

Frozen Micro Extraction (Plan A)

- Very low on time and materials
- Unproven technique
- Requires GC/MS SIM

SPME (Plan B)

- Potentially a sensitivity multiplier
- Generally proven technology, but untested for volume/scale limitations of project
- Typically requires autosampler requiring higher volume for high precision
- 200-µL extraction would requires manual set-up

ENVIRONMENTAL STANDARDS

Method Selection Considerations

- Micro extraction (Plan A) was selected because it appeared to be relatively simple to try and much of the equipment was readily available
- Equipment was purchased for manual SPME (Plan B) and experimental design was developed as a backup if Plan A did not work.

ENVIRONMENTAL STANDARDS

Final Experimental Design for Frozen Micro-extraction

- 200-µL aliquot of sample(s) is transferred to a screw top auto-sampler vial(s).
- Sample(s) is spiked with 200 ppb of 1,4-dioxane-d_8 and 100 ppb of 1,4-dichlorobenzene-d_4.
- Vials are placed in a -80°C freezer at a 45° angle for 30 minutes.
- Vials are taken out of freezer individually and are immediately prepared for analysis.

ENVIRONMENTAL STANDARDS

Experimental Design for Frozen Micro-extraction (Cont.)

- Methylene chloride solvent is syringed from the vial and transferred to a clean instrument vial fitted with a 200-µL insert.
- Sodium sulfate is added to vial to fill the bottom tip of the insert approximately 1/16 of an inch.
- Vials may be placed directly on an instrument for analysis.
- A 5975 instrument was set up in GC/MS SIM mode for analysis.

ENVIRONMENTAL STANDARDS

Analytical Methods

- Holding Time Considerations
- Instrumentation and Equipment
- Instrument Program Settings
- Quality Control & Acceptance Criteria

ENVIRONMENTAL STANDARDS

Holding Time Considerations

Prep	Method	Matrix	Preservation	Holding Times
Frozen – micro extraction	8270C SIM	Aqueous	Cool to 4°C	ASAP
SPME	8270C 8260B	Aqueous	Cool to 4°C	48 hours

- Holding times were shortened for Method 8270C due to risk of biodegradation of the 1,4-dioxane in study.
- Holding time for SPME represents time from extraction to injection.

GC/MS Instrument

Sample Introduction	Agilent 7683B AutoSampler
Instrument	Agilent 5975 GC/MS
GC Column	HP-5, 30 m x 250 μm x 0.25 μm
Injection Volume	1 μL
Solvent	Methylene Chloride
EM Offset	200

ENVIRONMENTAL STANDARDS

GC Oven Parameters

- 30°C Hold for 5 minutes
- Ramp 15°C/minute to 100°C
- Hold for 0 minute
- Ramp 50°C/minute to 275°C
- Hold for 1 minute

ENVIRONMENTAL STANDARDS

SIM Acquisition Parameters

- Solvent Delay 5.00 minutes
- SIM Group 1 Start Time 5.00
- Group 1 - (Mass, Dwell)

  (58.00, 100) (88.00, 100) (96.00, 100)
- SIM Group 2 Start Time 8.00 minutes

  Group 2 - (Mass, Dwell)
  (150.00, 100)

ENVIRONMENTAL STANDARDS

GC/MS Instrument Tune

- 1,4-dioxane is a fairly low mass compared to many semi-volatiles.
- Recommended using BFB for the tune check
- SW-846 volatile criteria used for tune acceptance every 12 hours.
- When necessary PFTBA was used for autotune on the LOMASS program

ENVIRONMENTAL STANDARDS

Initial Calibration

- Established initially with a minimum of six concentration levels with low standard at or below limit of quantitation (LOQ).
- Calibration blank is included in the curve.
- Both the initial calibration (ICAL) and the continuing calibration verification (CCV) are prepared in water and extracted in the same manner as the samples.

Initial Calibration (Cont.)

- When the percent relative standard deviation (%RSD) for target compound is ≤15%, an average response factor may be used.
- When %RSD for target compound is >15%, a linear regression or quadratic curve must be used.
- A regression curve must have a correlation coefficient (R^2) ≥ 0.99.
- Force through zero was turned off.

ENVIRONMENTAL STANDARDS

Continuing Calibration Verification

- CCV is run every 12 hours immediately after the instrument tune.
- Should be at or near the mid-point calibration range for the target compound.
- Minimum %D for CCV should be ≤ 30% (recommended).
- When possible, the CCV should be prepared using a separate dilution series from neat to verify primary calibration accuracy.

ENVIRONMENTAL STANDARDS

Method Blank

- One Di Water and reagent blank per batch of up to 20 samples per day; run with samples.
- Must undergo ***all*** sample preparative and cleanup procedures.
- All target compounds of interest must be $\leq$ LOQ.

ENVIRONMENTAL STANDARDS

Laboratory Control Sample

- Two per extraction batch per set of 20 samples per day.
- The CCV and laboratory control sample (LCS) are equivalent for this method.
- The CCV/LCS were prepared as a separate working standard from neat material.
- The default recovery recommended for this method is 100 ± 30%.
- RPD is considered acceptable if the successive LCSs are within range.

ENVIRONMENTAL STANDARDS

Sample Replicate

- One set per extraction batch per set of 20 samples per day.
- The default % RPD = 30%.
- Alternatively, project control limits may be calculated using ± 3× the standard deviation of recoveries.

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Qualitative/Quantitative Issues

- The raw result for 1,4-dioxane must be within the calibration range (≤ highest standard) for all samples.
- Compounds exceeding the instrument calibration range (highest calibration standard) must be diluted to within calibration range and reanalyzed.
- Analyst should take precautions against carryover, including reanalysis of samples when carryover is suspected.

ENVIRONMENTAL STANDARDS

Qualitative/Quantitative Issues (Cont.)

- The blank analyzed immediately after any standard must display a concentration of the 1,4-dioxane < the LOQ.
- Any unusual change in instrument chromatography should be investigated as a potential change in instrument performance.

ENVIRONMENTAL STANDARDS

Method Performance Data

The following were put together for a final demonstration of method performance before writing the SOP.

- Curve Linearity and Range demonstration.
- Initial Demonstration of Capability Study Using LCS level spike.
- Low Level Demonstration of Capability as an LOQ verification.

Calibration Curve

1000 ppb

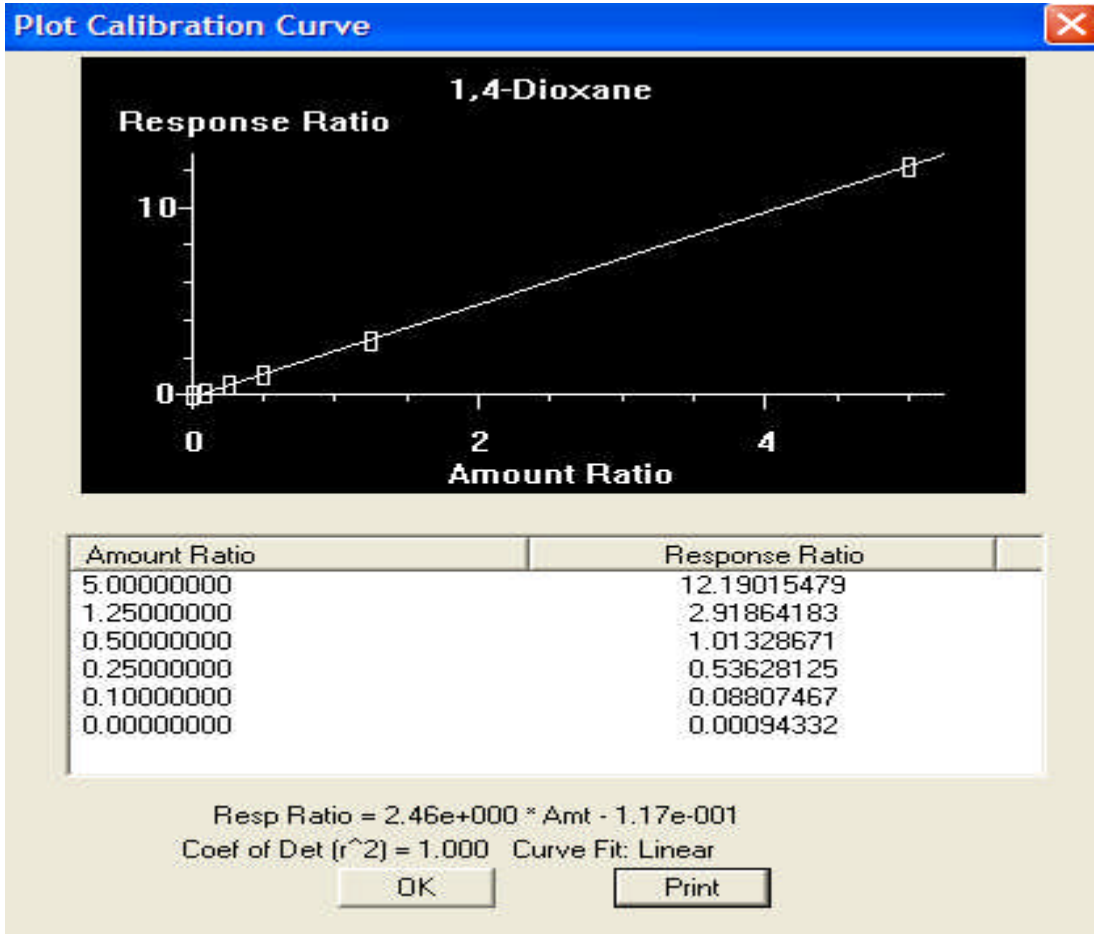
250 ppb

100 ppb

50 ppb

25 ppb

0 ppb



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Initial Demonstration of Capability

Parameter	Spiked Amt (µg/L)	Average Recovery	Acceptance Range	STD DEV (s)	RSD
1,4-Dioxane	100.00	114.98%	70% - 130%	6.21 µg/L	5.40%
1,4-DCB-d_4	200.00	111.99%	70% - 130%	13.06 µg/L	5.83%
1,4-Dioxane (Low level)	20.00	93.38%	70% - 130%	2.87 µg/L	15.36%

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In Summary

- We developed a method for preparation and analysis of 200-µL aliquot samples down to 20 µg/L for 1,4-dioxane.
- All materials used were commonly available laboratory materials.
- Very reasonable time & costs.
- Acceptable linearity and accuracy to the reporting level.
- Detected values appear to be reliable to ~ ½ the RL or 10 ppb.

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Thank You

"Setting the Standards for Innovative Environmental Solutions"

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