GLOBAL ANALYTICAL SOLUTIONS

Analysis of Semi-Volatiles in Wastewater Using Stir Bar Sorptive Extraction

John R. Stuff, Ph.D., Jackie A. Whitecavage, and Ed Pfannkoch

Gerstel, Inc., 701 Digital Drive, Suite J, Baltimore, MD, 21009, USA

Outline

- Introduction
- Stir Bar Sorptive Extraction (SBSE) Basics
- Round Robin Study Results
- Conclusion

GERSTEL
Company Overview

- Family-owned business
- Founded in 1967
- Headquarters: Mülheim an der Ruhr, Germany
- Subsidiaries:
  - GERSTEL Inc., U.S.A.
  - GERSTEL AG, Switzerland
  - GERSTEL KK, Japan
  - GERSTEL, Brazil
  - GERSTEL, Singapore
- 200+ employees
- ISO 9001 Certified since 1997
- Represented in more than 70 countries

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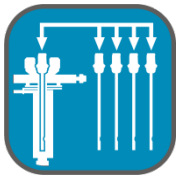
Techniques – Sample Prep and Intro for LC and GC

GERSTEL


MultiPurpose Sampler MPS


Cooled Injection System CIS


Automated Liner EXchange ALEX


easy Liner Exchange eLEX


MultiFiber EXchange MFX


Thermal Desorption System TDS


Thermal Desorption Unit TDU


Automated TDU Liner Exchange ATEX


Twister


Dynamic Headspace DHS

TDU PYRO


µFlowManager


Selectable 1D/2D GC/MS


Olfactory Detection Port OPD


Preparative Fraction Collector PFC


MultiPurpose Sampler MPS for LC/MS


LC/MS Effluent Optimizer LEO


MPS Workstation


Solid Phase Extraction SPE


Disposable Pipette Extraction DPX


MultiPosition Evaporation Station mVAP


MAESTRO PrepAhead


MAESTRO Software

GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

GERSTEL Twister™

- 1.5cm long magnetic stir bar sealed in glass
- High capacity PDMS phase on glass
- Extremely rugged
- Preconditioned for low background
- Stirs and extracts in one step
- Splitless desorption of stir bar gives low detection limits

GLOBAL ANALYTICAL SOLUTIONS

GERSTEL Twister™

GERSTEL

Stir Bar Sorptive Extraction SBSE

GERSTEL Twister™

Headspace Sorptive Extraction HSSE

Thermo-desorption TDU / TDS

Twister Back Extraction TBE

GC GC/MS

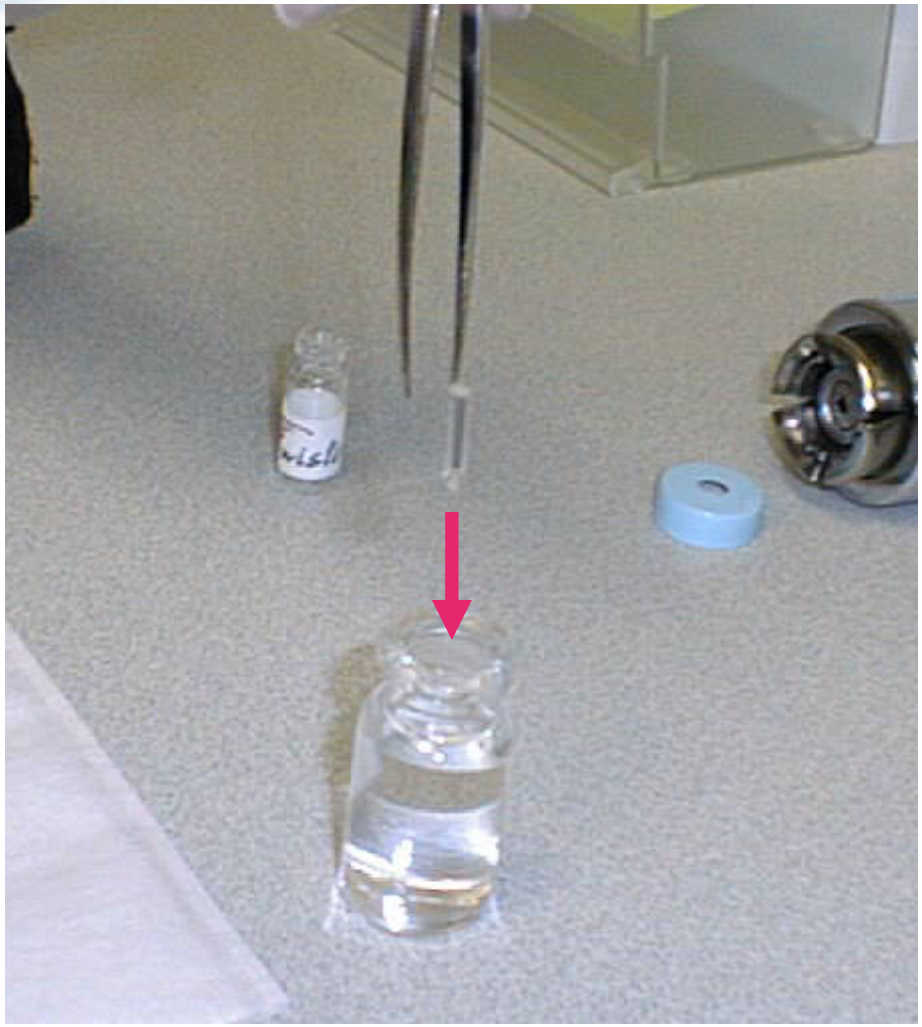
LC LC/MS

www.gerstelus.com

Stir Bar Sorptive Extraction (SBSE)

- Same principle as liquid/liquid extraction
  - But with a low amount of immobilized “solvent“ (PDMS)
- Extraction is based on sorption
  - Predictable recovery due to proportionality with log $K_{o/w}$
  - No displacement effects
- PDMS
  - Very inert
  - Retains no water
  - Selectivity eliminates polar matrix interferences
- Desorption with TDS or TDU
  - Fast and mild
  - Extremely low detection limits (ppt to ppq)

Extremely Easy to Use

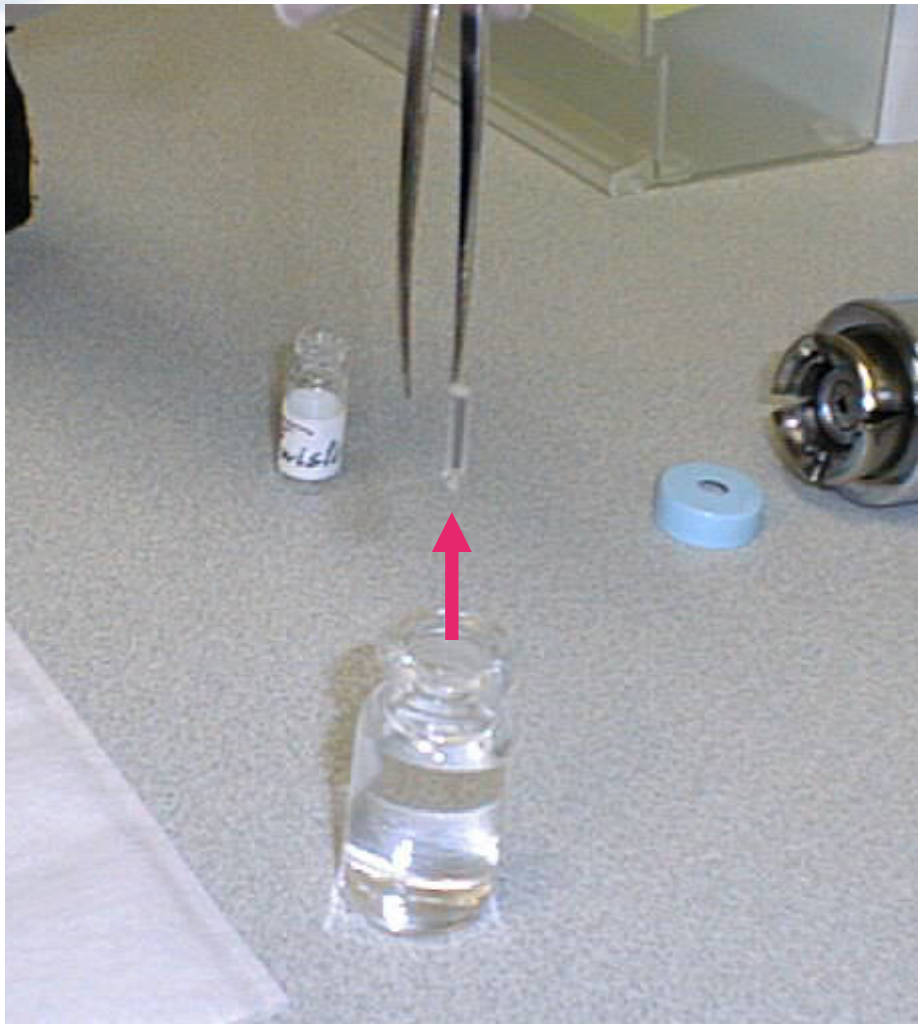


- Add stir bar to vial

Extremely Easy to Use

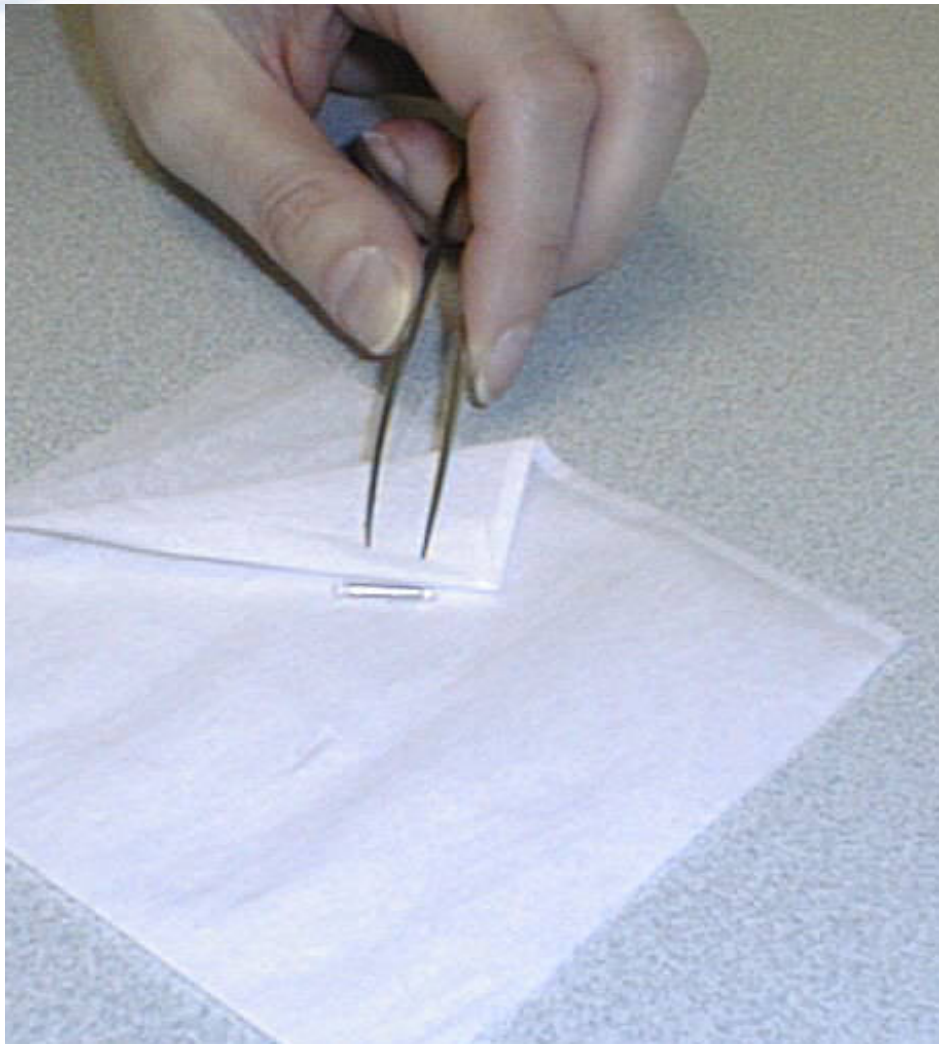
- Add stir bar to vial
- Stir 1hr to overnight

Extremely Easy to Use



- Add stir bar to vial
- Stir 1hr to overnight
- Remove stir bar with forceps and rinse briefly in distilled water

Extremely Easy to Use



- Add stir bar to vial
- Stir 1hr to overnight
- Remove stir bar with forceps and rinse briefly in distilled water
- Dry with lint-free tissue

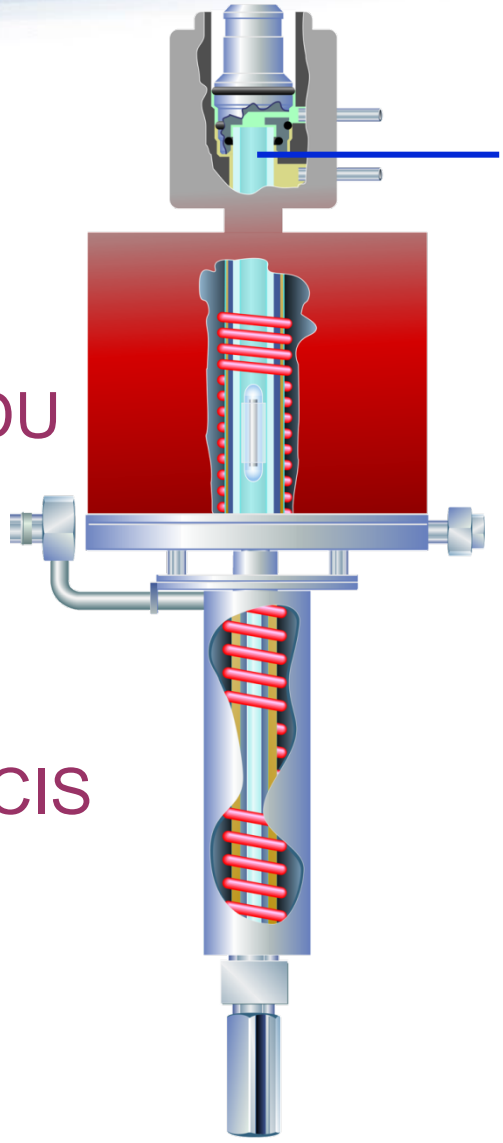
Extremely Easy to Use

- Add stir bar to vial
- Stir 1hr to overnight
- Remove stir bar with forceps and rinse briefly in distilled water
- Dry with lint-free tissue
- Place in a thermal desorption tube

TDU

Thermal Desorption Unit - TDU

Cooled Injection System - CIS



Predicting Twister Extraction Results

- Extraction is assumed to be an equilibrium process
- Predictions are based on the assumption that the PDMS:water partition coefficient (unknown) is similar to the octanol:water partition coefficient (extensive published tables)

Distribution of Analytes Between Water and PDMS

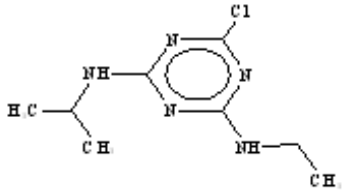
$$\frac{m_s}{m_o} = \frac{\left\{\frac{k_{o/w}}{\beta}\right\}}{1 + \left\{\frac{k_{o/w}}{\beta}\right\}}$$

m_S: Amount of Analyte in PDMS
m_0: Amount of Analyte in Water
$K_{O/W}$: Octanol/Water Distribution Coefficient
ß = V_W / V_S: Phase Ratio
V_W, V_S: Sample-, PDMS-Volume

*Baltussen et al.

Example: Atrazine in Water

log $K_{o/w}$ Atrazine = 2.61 ($K_{o/w}$ = 407.4)
Sample Volume: 10 ml



SBSE:

Twister: 24 µl PDMS

Phase Ratio: 0.0024

$$\frac{0.0024 \times 407.4 \times 100}{0.0024 \times 407.4 + 1}$$

49.4 %

SPME:

Fiber: 0.5 µl PDMS

Phase Ratio: 0.00005

$$\frac{0.00005 \times 407.4 \times 100}{0.00005 \times 407.4 + 1}$$

2.0 %

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Twister Recovery Calculator

File Tools Help

Twister Recovery Calculator

Sample Information

Sample Size (ml): 10

CAS Number: 001912-24-9

log $K_{o/w}$

Calculate

Results

log $K_{o/w}$ 2.61

Name Atrazine

Formula $C_8H_{14}CL_1N_5$

Phase Volume (µL)	Twister	Recovery
24	10mm x 0.5mm	49.4%
47	10mm x 1.0mm	72.0%
63	20mm x 0.5mm	65.7%
126	20mm x 1.0mm	83.7%

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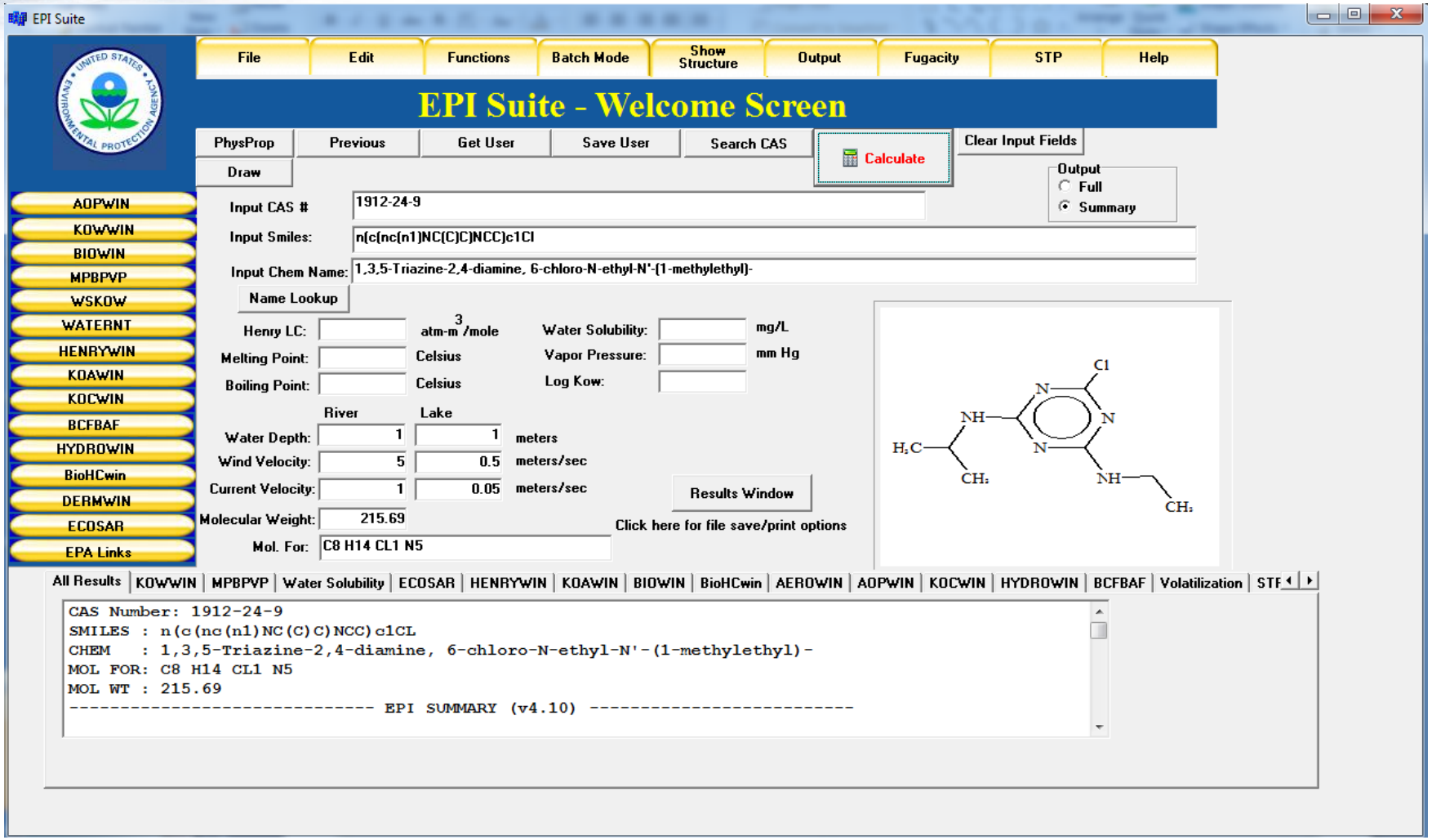
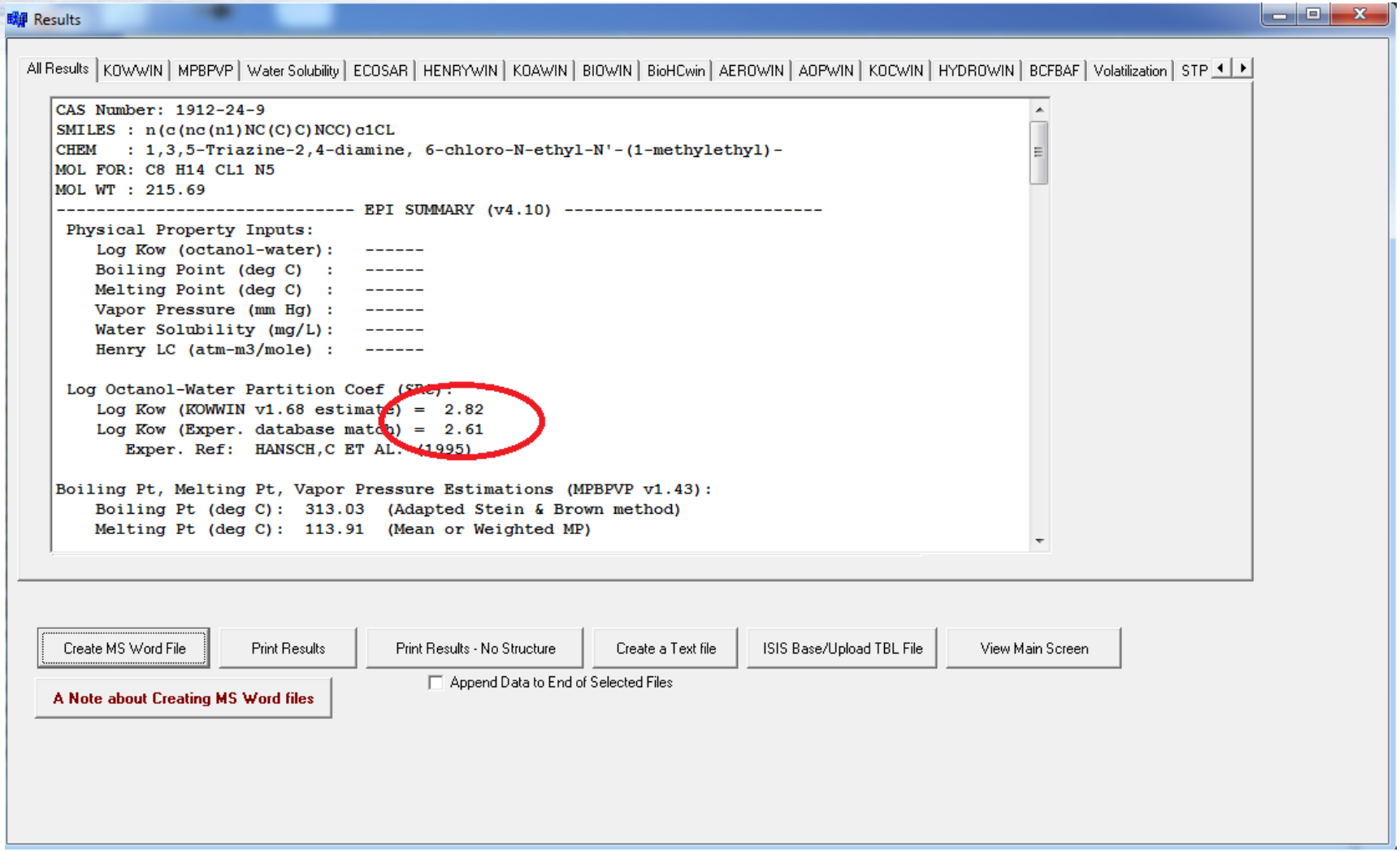
EPI Suite




Results
All Results
KOWWIN
MPBPVP
Water Solubility
ECOSAR
HENRYWIN
KOAWIN
BIOWIN
BioHCwin
AEROWIN
AOPWIN
KOCWIN
HYDROWIN
BCFBAF
Volatilization
STP
CAS Number: 1912-24-9
SMILES : n(c(nc(n1)NC(C)C)NCC)c1CL
CHEM : 1,3,5-Triazine-2,4-diamine, 6-chloro-N-ethyl-N'-(1-methylethyl)-
MOL FOR: C8 H14 CL1 N5
MOL WT : 215.69
---------- EPI SUMMARY (v4.10) ----------
Physical Property Inputs:
Log Kow (octanol-water): ------
Boiling Point (deg C) : ------
Melting Point (deg C) : ------
Vapor Pressure (mm Hg) : ------
Water Solubility (mg/L): ------
Henry LC (atm-m3/mole) : ------
Log Octanol-Water Partition Coef (SRC):
Log Kow (KOWWIN v1.68 estimate) = 2.82
Log Kow (Exper. database match) = 2.61
Exper. Ref: HANSCH,C ET AL. (1995)
Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPVP v1.43):
Boiling Pt (deg C): 313.03 (Adapted Stein & Brown method)
Melting Pt (deg C): 113.91 (Mean or Weighted MP)
Create MS Word File
Print Results
Print Results - No Structure
Create a Text file
ISIS Base/Upload TBL File
View Main Screen
Append Data to End of Selected Files
A Note about Creating MS Word files

Sample Volume

Liquid Sampling

- Standard 1 cm Twister typically used for 10-40 mL liquid samples
- Standard Headspace or VOA vials
- Larger 2 cm Twister used for larger volumes (50-200 mL)
- Extraction vessel must have flat bottom surface for smooth stirring

Extraction Time

Liquid Extraction

- Extraction kinetics are slow and depend strongly on sample volume
- Use high stirring speeds (1000 rpm)
- 10 mL samples stir 60-90 min
- 40 mL samples stir 3-4 hrs
- 200 mL samples stir 16 hrs

Extraction Temperature

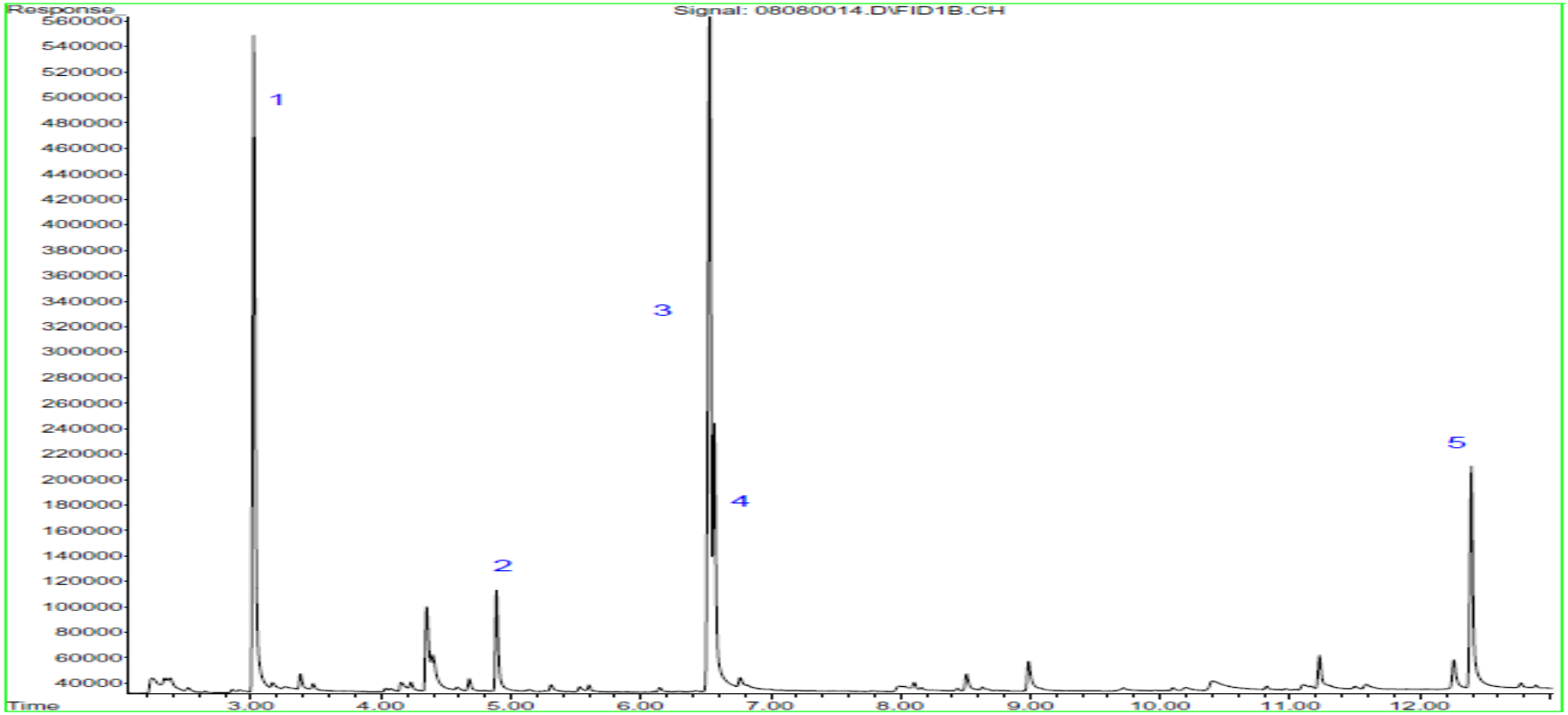
- Most Twister extractions are performed at room temperature
- Practical temperature range (0-60 ºC) has minimal effect (+/- 20%) on most compounds
- Effect can be positive or negative depending on compound

Matrix Effects

- Samples in water behave most ideally
- Presence of competing organics (nonpolar solvents, fats) or significant levels (>20%) of polar solvents (ie ethanol, acetonitrile) can reduce extraction efficiency, particularly of polar analytes
- Sample pH can strongly influence extraction of ionizable species
- Salting out can be used to enhance extraction efficiency

Twister Precision and Storage

2 mL Balsamic Vinegar + 8 mL of H_2O: SBSE for 1 Hour



Results

Peak No.	Compound	Mean Peak Area (n=10)	%RSD (n=10)	Mean Peak Area after Storage (n=2)
1	Ethyl acetate	92.8	4.01	77.5
2	Isobutyl acetate	14.5	3.68	13.5
3	Isoamyl acetate	115.0	2.06	112.4
4	2-methyl-1-butyl acetate	39.5	1.87	38.6
5	Phenethyl acetate	34.4	4.02	34.0
		Avg	**3.1**	

- No Interference from acetic acid
- Ester Peaks show good precision, Average RSD = 3.1%
- Two samples stored at room temperature for 4 days show minimal loss of apolar compounds. Ethyl acetate (log $K_{o/w}$ = 0.86) shows a 16% loss.

Twister Reconditioning

Thermally condition for 2 hours at 300 °C
Dry Nitrogen 50-100 mL/min
For simultaneous conditioning of 10 tubes up to 40 Twisters

GERSTEL TC-2: Tube Conditioner

GERSTEL Twister™

Round Robin Study

Host Organization: Independent Laboratories Institute
Title: Solid Phase Extraction (SPE) Protocol Validation Study
Purpose: Update to EPA Method 625

Participants: SPE Manufacturer's, Commercial Environmental Labs, and Government Laboratories, 24 Laboratories

GERSTEL Twister accepted as an "SPE Material"

GERSTEL Applications Lab
Government Lab
Academic Lab

GERSTEL Twister™

SBSE Protocol

- Add 10.0 mL of sample to 10 mL vial
- Add 8.0 mL of sample + 2.0 mL of acetonitrile to a 10 mL vial
- Add internal standard to each vial
- Add a conditioned stir bar to each vial
- Extract at 1000 rpm for 60 minutes
- Remove stir bars with forceps, rinse in water, dry on tissue
- Place the stir bar from the acetonitrile extract in the TDU tube first
- Analyze the Twisters by thermal desorption GC/MS
- N = 3 Replicates
- Sample Spike Range 0-200 ppb

Only 18 mL of Sample Used !!

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GERSTEL Twister™

The heated zone of the TDU is 20 mm, so 2 Twisters can be desorbed in a single tube.

Analysis Conditions

Thermal Desorption

Pneumatics mode:	splitless
Sample mode:	sample remove
Temperature:	30°C; 720°C/min; 300°C (5.0 min)
Transfer Heater temp.:	300°C

CIS

Liner type:	quartz wool
Carrier gas:	helium
Pneumatics mode:	solvent venting
Vent flow:	100 ml/min
Vent pressure:	7.07 psi until 0.00 min
Split flow:	**100 ml/min @ 0.01 min**
Temperature:	-70°C (0.0 min); 12°C/sec; 300°C (3 min)

Analysis Conditions

Gas Chromatograph
Agilent 7890
Column: Rxi-5 MS (Restek); 30 m x 0.25 mm x 0.25 µm (Catalog #13423)
Mode: Constant Flow: 1 mL/min
Temp.: 40°C (2 min), 8°C/min; 284°C (0 min); 15°C/min; 310°C (7 min)

Mass Selective Detector
Agilent 5977
EI, Scan mode 35-450 amu

Transferline temp. 280°C
Source temperature 230°C
Quad temperature 150°C

Internal Standards

SV Internal Standard Mix (Restek #31006)

1,4-dichlorobenzene-d4
Naphthalene-d8
Acenaphthalene-d10
Phenanthrene-d10
Chrysene-d12
Perylene-d12

Surrogates

OLC 03.2 SVOA Deuterated Monitoring Compounds (DMC) (Restek #31810)

16 Compounds:

Acenaphthylene-d8
Benzo(a)pyrene-d12
4-Chloroaniline-d4
2,4-Dichlorophenol-d3
4,6-Dinitro-2-methylphenol-d2
4-Methylphenol-d8
2-Nitrophenol-d4
Phenol-d5
Anthracene-d10
Bis-(2-chloroethyl)ether-d8
2-Chlorophenol-d4
Dimethylphthalate-d6
Fluorene-d10
Nitrobenzene-d5
4-Nitrophenol-d4
Pyrene-d10

Calibration

Semivolatiles Megamix, EPA method 625 (Restek #31829) (54 Compounds)
Organochlorine Pesticide Mix AB #3 (Restek #32415) (20 Compounds)

Calibration Standards at 0, 2.5, 5.0, 10.0, 50.0 and 100.0 ηg/mL
Calibration Standards in Water (Aquafina)
One CCV and 2 LCS spiked at 10 ηg/mL run with Samples
Surrogates at 50 ηg/mL

Matrices

- Phase 1
  - Water
  - ASTM D5905-98 Wastewater – Mix of Water, Kaolin, Beer, Flour, Ocean Salts (Instant Ocean), and Surfactant (Triton X-100)
- Phase 2
  - Acetate Buffer pH = 6
  - Water (Optional)

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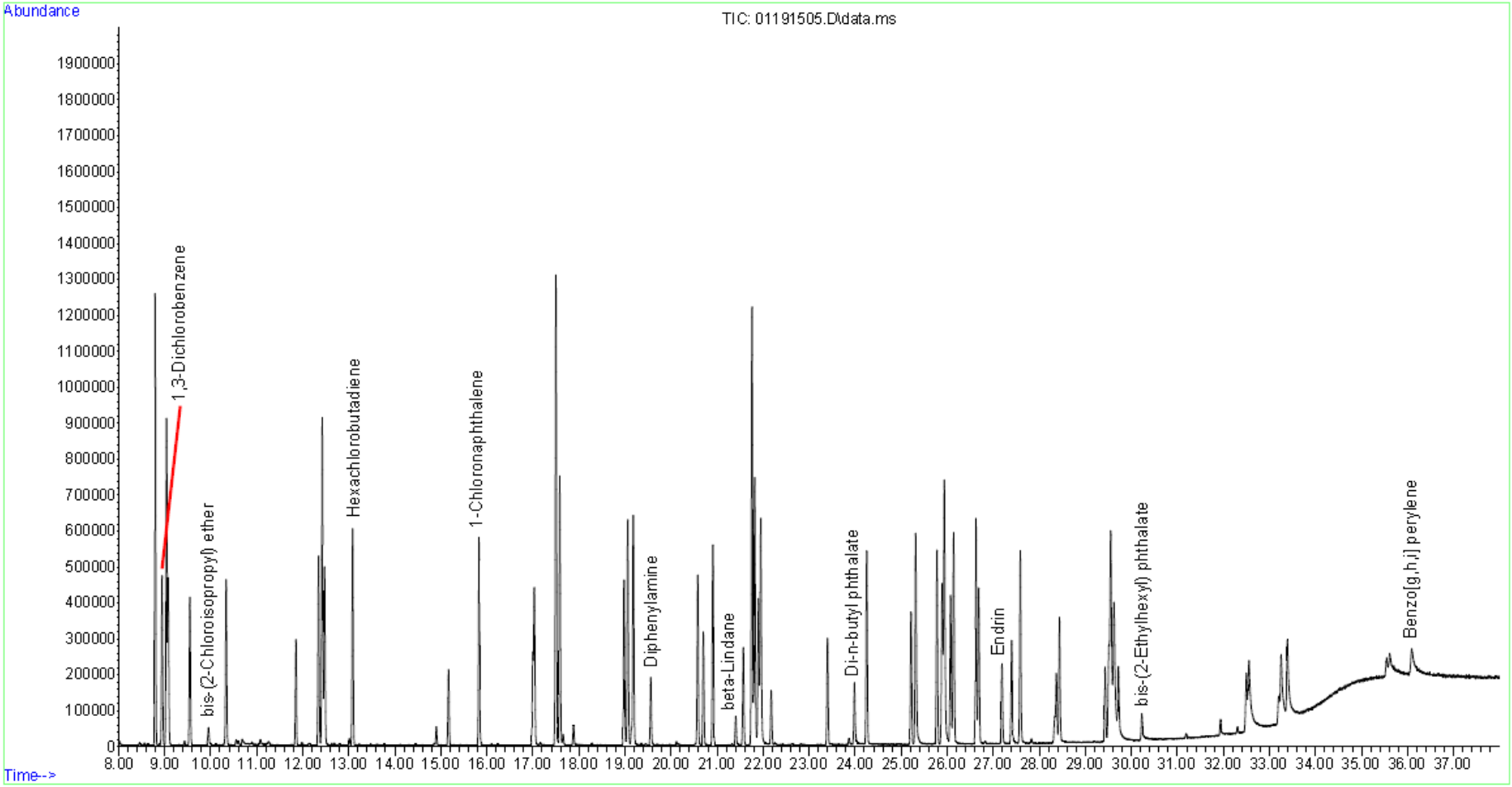
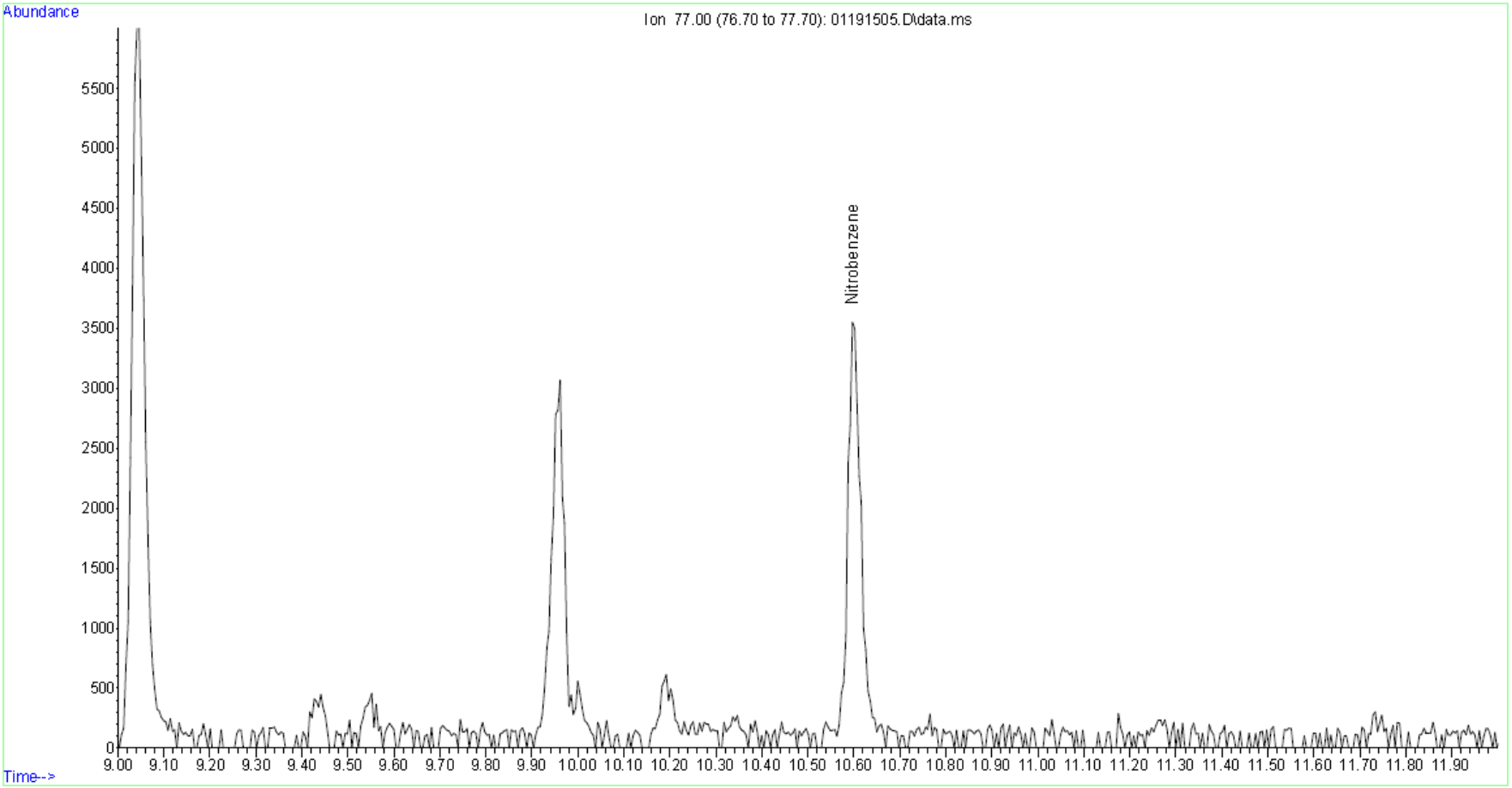
Full Scan TIC for 5 ηg/mL Standard



EIC (m/z= 77) for 5 ηg/mL Standard

Log Ko/w = 1.85 (15%)

100:1 Split Introduction



Phase 1 Results

	Twister		All SPE		EPA 625	Actual
Matrix →	**Water**	**Waste Water**	**Water**	**Waste Water**	**Criteria**	**Value**
Analyte					**Table 6**	**ng/mL**
Aldrin	116	90.4	82.0	74.3	D-166	3.66
Alpha-BHC	103	96.7	89.9	88.8		3.48
Beta-BHC	118	93.5	93.6	84.8	24-149	5.74
Delta-BHC	104	92.2	90.0	92.6	D-110	2.70
Gamma-BHC	116	105	85.8	90.0		4.78
Alpha-Chlordane	122	117	69.9	62.9		8.23
Beta-Chlordane	123	108	87.8	71.7		6.57
4,4'-DDD	115	129	76.5	62.7	17-168	8.80
4,4'-DDE	111	94.3	76.6	65.5	D-145	2.61
4,4'-DDT	104	117	88.1	67.0	D-203	6.48
Dieldrin	130	136	89.5	79.4	29-136	8.78
Endosulfan I	67.9	72.3	43.3	38.6		15.9
Endosulfan II	75.4	84.0	54.4	51.7		12.8
Endosulfan sulfate	153	165	91.4	67.2	D-107	17.4
Endrin	97.1	124	98.0	145		4.53
Endrin Aldehyde	103	129	58.1	23.2	D-209	16.4
Endrin Ketone	116	126	82.9	70.3		9.16
Heptachlor	113	93.2	73.0	70.9	D-192	8.43
Heptachlor epoxide	113	108	85.9	79.8	26-155	1.63
Methoxychlor	97.1	100	93.2	117		6.49
Average Recovery	**110**	**109**	**80.5**	**75.2**		

Phase 1 Results Continued

	Twister		All SPE		EPA 625	Actual
Matrix →	**Water**	**Waste Water**	**Water**	**Waste Water**	**Criteria**	**Value**
Analyte					**Table 6**	**ng/mL**
Bis(2-chloroethyl) ether	126	103	60.4	59.4	12-158	93.1
2-Chlorophenol	169	103	63.0	68.3	23-134	61.6
1,3-Dichlorobenzene	113	104	46.9	46.4	D-172	104
Nitrobenzene	146	117	56.0	64.6	35-180	158
Naphthalene	106	91.9	57.4	58.5	21-133	176
4-Chloro-3-methylphenol	127	119	68.7	83.1	22-147	113
Dimethylphthalate	112	91.9	72.4	77.6	D-120	124
Fluorene	116	104	53.5	73.2	59-121	142
4-Chlorophenyl phenyl ether	115	105	61.3	66.3	25-158	95.9
Hexachlorobenzene	138	101	62.9	67.0	D-152	63.9
Anthracene	119	98.3	63.0	67.1	27-133	173
Dibutyl phthalate	150	140	71.2	73.4	1-120	101
Fluoranthene	134	116	69.9	67.7	26-137	79
Benzyl butyl phthalate	167	162	69.3	71.4	D-152	69.3
Benz[a]anthracene	111	109	63.7	58.0	33-143	29.5
Bis(2-ethylhexyl) phthalate	99.9	103	66.4	58.2	8-158	42.8
Benzo[k]fluoranthene	92.6	69.2	56.6	52.7	11-162	45.9
Benzo[a]pyrene	120	90.5	59.7	54.0	17-163	144
Dibenz[a,h]anthracene	107	95.4	56.8	48.6	D-227	46.1
Benzo[ghi]perylene	115	112	62.0	54.8	D-219	42.9
Average Recovery	**124**	**107**	**62.1**	**63.5**		

Phase 2 Surrogate/LCS Results

Surrogate	Percent Recovery	Acceptance Criteria
		Table 8
d8-Bis(2-chloroethyl) ether	66.0	25-222
d4-2-Chlorophenol	67.2	33-180
d8-4-Methylphenol	43.6	25-111
d5-Nitrobenzene	67.0	15-314
d4-2-Nitrophenol	90.6	37-163
d3-2,4-dichlorophenol	82.8	34-182
d6-Dimethyl phthalate	54.2	1-500
d8-Acenaphthylene	99.8	33-168
d10-Fluorene	94.0	38-172
d10-Anthracene	105	23-142
d10-Pyrene	101	28-196
d12-Benzo[a]pyrene	80.4	32-194

LCS Data (10 ppb):
Average Recovery = 106%
RSD = 15%
Range = 5.9-15.3

Phase 2 Results

	Twister		SPE		EPA 625	Actual
Matrix →	Water	Waste Water	Water	Waste Water	Criteria Table 6	Value
Analyte						
1,4-dichlorobenzene	122	99.5	29.4	31.7		82.2
1,2-dichlorobenzene	90.6	87.7	33.3	35.8		171
Nitrobenzene	99.5	83.6	77.5	66.4	35-180	83.0
2-Nitrophenol	121	112	80.0	85.1	29-182	135
2,4-Dimethylphenol	109	84.8	90.1	84.0	32-120	131
1,2,4-trichlorobenzene	127	102	28.7	34.3	44-142	150
Naphthalene	101	85.7	50.1	57.8	21-133	170
Hexachloro-1,3-Butadiene	169	126	17.6	17.2	24-120	118
2,4,6-trichlorophenol	79.0	220	119	140	37-144	56.1
Acenaphthylene	86.6	84.4	63.4	74.1	33-145	108
Acenaphthene	99.5	97.1	65.3	73.0	47-145	36.6
Fluorene	94.1	96.7	80.9	75.8	59-121	104
Diethyl Phthalate	153	108	84.9	87.2	D-120	152
4-chlorophenyl phenyl ether	119	105	72.6	67.5	25-158	157
4-bromophenyl phenyl ether	116	109	87.6	75.4	53-127	129

Phase 2 Results

	Twister		SPE		EPA 625	Actual
Matrix →	**Water**	**Waste Water**	**Water**	**Waste Water**	**Criteria Table 6**	**Value**
Analyte						
Hexachlorobenzene	111	106	86.3	64.6	D-152	72.3
Phenanthrene	101	79.0	102	98.2	54-120	169
Anthracene	72.7	73.1	81.8	43.5	27-133	154
Dibutyl phthalate	117	93.7	102	97.7	1-120	132
Fluoranthene	110	87.0	93.3	73.3	26-137	165
Pyrene	79.8	107	101	85.2	52-120	48.6
Benzyl butyl phthalate	74.1	110	108	94.7	D-152	132
Chrysene	83.5	98.7	97.6	79.4	17-168	53.8
Bis(2-ethylhexyl) phthalate	60.7	108	121	109	8-158	159
Di-n-octyl phthalate	68.1	118	121	103	4-146	115
Benzo[k]fluoranthene	48.7	91.9	97.4	75.3	11-162	114
Benzo[a]pyrene	55.7	83.4	104	80.3	17-163	178
Indeno[1,2,3-cd]pyrene	85.6	163	214	165	D-171	86.9
Dibenz[a,h]anthracene	136	159	100	70.0	D-227	40.6
Average Recovery	**99.7**	**106**	**100**	**77.4**		

Conclusion

- Solid Phase Extraction is a suitable substitute for LLE
- Twister is an excellent choice for a subset of the 625 List
- Further optimization is required for phenols
- Phthalates can be problematic

- Eliminates solvent extraction steps
- Eliminates most non-volatile and polar matrix interference
- Allows parallel sample preparation minimizing instrument run time
- Stir bars are reusable
- Analytes are stable for days on stir bar allowing field sampling
- Extremely low detection limits possible (low ppt)
- Excellent bar-to-bar reproducibility
- Analyte recovery is predictable

GERSTEL Website

- On-Line Store and Catalog
- Product Information
- Application Bibliography
- GERSTEL Solutions

"Vielen Dank für Ihre Aufmerksamkeit"

Questions??