Sample Preparation Techniques for Emerging Contaminants in Water

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Agilent Technologies
Today’s Agenda

• Analysis of emerging contaminants in water – an overview
• Offline sample preparation options for drinking water analysis
  – Solid-supported liquid/liquid extraction
  – Solid phase extraction
• New developments in online SPE
• Summary of each approach
• Question and answer period
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Why the Interest in Emerging Contaminants?

- > 3,000 drugs and PPCPs
- Interest and fate of drugs, hormones
- Limited knowledge of treatability for all contaminants
- High public visibility and concern
Examples of EC Concerns

<table>
<thead>
<tr>
<th>Category</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pharmaceuticals</td>
<td>- Veterinary and human antibiotics&lt;br&gt;- Analgesics, anti-inflammatory drugs&lt;br&gt;- Psychiatric drugs&lt;br&gt;- Lipid regulators&lt;br&gt;- β-blockers&lt;br&gt;- X-ray contrasts&lt;br&gt;- Steroids and hormones&lt;br&gt;- Personal care products&lt;br&gt;- Fragrances&lt;br&gt;- Sun-screen agents&lt;br&gt;- Insect repellents&lt;br&gt;- Antiseptics&lt;br&gt;- Surfactants and surfactant metabolites&lt;br&gt;- Flame retardants&lt;br&gt;- Industrial additives and agents&lt;br&gt;- Gasoline additives</td>
</tr>
<tr>
<td></td>
<td>- Trimethoprim, erythromycin, lincomycin, sulfamethoxazole&lt;br&gt;- Codein, ibuprofene, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen&lt;br&gt;- Diazepam&lt;br&gt;- Bezafibrate, clofibric acid, fenofibric acid&lt;br&gt;- Metoprolol, propanolol, timolol&lt;br&gt;- Iopromide, iopamidol, diatrizoate&lt;br&gt;- Estradiol, estrone, estriol, diethylstilbestrol&lt;br&gt;- Nitro, polycyclic and macrocyclic musks, benzophenone, methylbenzylidene camphor&lt;br&gt;- N,N-diethyltoluamide&lt;br&gt;- Triclosan, Chlorophene&lt;br&gt;- Alkylphenol ethoxylates, 4-nonylphenol, 4-octylphenol, alkylphenol carboxylates&lt;br&gt;- Polybrominated diphenyl ethers (PBDEs), Tetrabromo bisphenol A, C_{10}-C_{13} chloroalkanes&lt;br&gt;- Tris (2-chloroethyl)phosphate&lt;br&gt;- Chelating agents (EDTA), aromatic sulfonates,</td>
</tr>
</tbody>
</table>
Requirements for Emerging Contaminant Analysis Methods

- Selectivity/Specificity
- Sensitivity: MRL determination
- Target List
- QA/QC
- Ruggedness/matrix effects
- Cost
Innovative LC-MS/MS Approaches to EC Analysis

- Cost-effective screen for as many analytes as possible
- Reporting levels: 5 to 10 ng/L (ppt)
- Known target analytes and identification from experts
- Accuracy and precision comparable to existing drinking water methods: 70-130% recovery
- Use multiple ion transitions (MRM) to prevent misidentification
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• Analysis of emerging contaminants in water – an overview

• Offline sample preparation options for drinking water analysis
  – Solid-supported liquid/liquid extraction
  – Solid phase extraction

• New developments in online SPE

• Advantages of each approach

• Question and answer period
Historical Sample Preparation Scheme for Low Level Analyte Detection

- Large sample vessels transported to/from sampling sites
- Collection of water samples, typically 1000 mL
- Transport promptly to laboratory for analysis
- Preservation of backlog in walk-in coolers
- Bench-top serial sample preparation
- Instrumental analysis and reporting

Turnaround time?  *Typically long*
Sample prep cost?  *Typically high*
Sample Preparation

Offline SPE

- 1000 mL transported to the lab
- Trace enrich onto a cartridge or disk
- Elute with few mL solvent, dry, reconstitute in solvent amenable to LC or GC for separation
- 1 mL sample loaded into autosampler vial
- 2-20 µL injected for instrumental analysis
Sample Preparation – Supported LLE (SLE)

**Hydromatrix** - diatomaceous earth sorbent

- Composed of fossilized diatoms
- Purified at high temperatures
- High surface area for water adsorption
- Very polar surface

**Chem Elut** - pre-assembled cartridges with Hydromatrix
The SLE Process

Before Extraction

Dry sorbent

Apply Sample

Aqueous layer

Extract with Organic Solvent

Organic layer
The Chem Elut Method

Aqueous sample being applied

Solid support adsorbs water onto high surface area particles

Organic extraction solvent
Solid Supported LLE - Traditional Benefits

• No emulsions
• Less glassware
• Less time
• Reduced technique dependence
• Increased reproducibility
• Automatable; batch processing
Solid Phase Extraction (SPE)

• Types of SPE
  – Reversed phase SPE
  – Cation exchange SPE
  – Anion exchange SPE
  – Mixed mode SPE
  – Specialty SPE

• Capabilities
  – Very selective
  – Clean samples
  – Wide range of applicability
  – Automation friendly
  – Concentration of analytes with removal of background
Solid Phase Extraction Protocol

↓ Pre-Treat Sample
↓ Condition
↓ Equilibrate
↓ Load
↓ Wash
↓ Elute
↓ Prep for Analysis
Solid Phase Extraction Application Example – Haloacetic Acids in Drinking Water

- Methyl chloroacetate
- Methyl bromoacetate
- Methyl dichloroacetate
- Dalapon methyl ester
- Methyl trichloroacetate
- 1,2,3-Trichloropropane (IS)
- Methyl bromochloroacetate
- Methyl 2-bromobutanoate (SS)
- Methyl bromodichloroacetate
- Methyl dibromoacetate
- Methyl dibromochloroacetate
- Methyl tribromoacetate
Plexa Method – Easy Extraction Method Covers a Wide Range of Analytes

SPE Method using 200 mg/6 mL Bond Elut Plexa polymeric SPE

<table>
<thead>
<tr>
<th>Step</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Condition with 10 mL MeOH</td>
</tr>
<tr>
<td>2.</td>
<td>Condition with 10 mL H_2O</td>
</tr>
<tr>
<td>3.</td>
<td>Load 800 mL water sample</td>
</tr>
<tr>
<td>4.</td>
<td>Dry sorbent with air for 10 minutes</td>
</tr>
<tr>
<td>5.</td>
<td>Soak and collect 2.5 mL fraction using EtOAc</td>
</tr>
<tr>
<td>6.</td>
<td>Collect 1 mL fraction using EtOAc</td>
</tr>
<tr>
<td>7.</td>
<td>Soak and collect 2.5 mL fraction using DCM</td>
</tr>
<tr>
<td>8.</td>
<td>Collect 1 mL fraction using DCM</td>
</tr>
</tbody>
</table>

HPLC-FL/UV for determination of PAHs
GC/MS for Chloro-Pesticides
LC-MS/MS for Triazines
Pesticides and PAHs from Drinking Water on Plexa

**Chloro-Pesticides**

- Alachlor
- Aldrin
- DDD o-p'
- DDD p-p'
- DDE o-p'
- DDE p-p'
- DDT p-p'
- DDT o-p'
- Dieldrin
- Endosulfan I (alpha)
- Endosulfan II (beta)
- Endosulfan sulfato
- Endrin
- HCH-alpha
- HCH-beta
- HCH-delta
- HCH-gamma
- Heptachlor
- Heptachlor Epoxide trans.
- Hexachlorobenzene

**Triazines**

- DESISPROPYLATRAZINE
- DESETHYLATRAZINE
- CIANAZINE
- SIMAZINE
- ATRAZINE
- TERBUTRINE
- PROPAZINE
- TERTBUTYLADZINE

**PAHs**

- Benzo(a)anthracene
- Benzo(b)fluoranthen
- Benzo(k)fluoranthen
- Benzo(a)pyrene
- Dibenzo(a,h)anthracene
- Benzo(ghi)perylene
- Indeno(1,2,3-cd)pyrene
- Chrysene

**Using Plexa all three compound classes can be extracted on a single cartridge**
Triazines Extracted from Drinking Water with Bond Elut Plexa

Concentration of spiked triazines: 0.4 µg/L
Max. conc. in validation: 4 µg/L
LQ : 0.05 µg/L
Recoveries > 98% (rel.recoveries calculated with IS Simazine D10)

HPLC column: C18, 2.1 x100mm 1.7 µm
Relative Recoveries of Chloro-Pesticides

% Recovery

Chlorpesticide | % Recovery
---|---
HCH-alfa | 84
HCH-beta | 89,5
Hexachlorobenzene | 53,13
HCH-gamma | 83,13
HCH-delta | 89,25
Heptachloro | 70,38
Alachlor | 101,25
Aldrin | 62,25
Heptachloro Epoxido | 92,13
DDE o-p' | 68,75
Endosulfan I | 96
Dieldrin | 97,88
DDE p-p' | 67,75
DDD o-p' | 92,88
Endrin | 99,63
Endosulfan II | 87,75
DDD p-p' -1 | 105,13
DDT o-p'-2 | 78,88
Endosulfan sulfato | 111,5
DDT p-p' | 88,75

IS Hexachlorobenzene C\textsuperscript{13}
Advantages of Offline SPE

- Multiple published methods available utilizing the technique
- Wide variety of sorbent types suitable for different target analyte properties and to support different sample matrices
- Concentration of analytes to achieve lower detection limits in conjunction with the removal of background interferences
- Suitable for a wide variety of analytical instrumentation
- Offline preparation does not tie the instrument to the preparation, maintaining flexibility

*Flexibility and versatility for a wide range of sample types and target compounds*
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Evolution of Online SPE

1973 – Mieure and Dietrich use carrier gas to elute organics from aqueous samples concentrated onto Chromosorb 102 for online GC

1975 – Little & Fallick described “trace enrichment” for the analysis of non-polar organics in river water by LC

Mid-'70’s – LC guard column technology applied to overcome issues with dirty samples and time reduction

‘80’ to early 90’s – Continued evolution of the technology and theory of online SPE coupled with HPLC

90’s to today – Cartridge-changing systems, method development tools, and improved software integration
Requirements for Environmental Screening

- EU water framework directive and drinking water legislation requires analysis of pollutants in water samples at concentrations of 10 ng/L or below.

- Screening and quantitation in this concentration range usually requires off-line SPE to preconcentrate the target compounds in the sample solution.

- For LC/MS water is the “ideal” sample and sensitivity of QQQQ instruments is almost sufficient to meet the requirements (with large volume injection ~ 100 µL).
Online Sample Preparation for LC-MS/MS Analysis

Online SPE (trace enrichment-SPE)

- 100% of the prepared sample is loaded
- Volume can be <5 mL
- Combined with more sensitive detection (MS/MS)

- Logistics of getting sample to the lab is simplified
Early Automated Sample Enrichment/Sample Clean up Chlorophenoxy Acid Herbicides (EPA Method 555)

Load/wash Position

Elute/analyze Position

2-Position /6-Port valve

25 mL of aqueous sample is loaded through pump A, line A2
Flush loading pump with eluent from pump A, line A1
(Contamination of loading pump was problematic, requiring many blank runs)
New alternative approach: Direct inject <5ml sample from injector, eluent A1
Three Unattended Steps, from Sample to Result
Automated Online Sample Preparation, HPLC/UHPLC Separation, MS QQQ or QTOF Detection
Setup of the Agilent Online-SPE System

**SPE system:**
- Quaternary pump
- G1329A autosampler with 900 µl head
- 6 port 2 position valve
- 14 port 6 position valve
- 13 port 12 position stream selection valve (optional)

**RRLC system:**
- Binary pump SL
- Well plate sampler SL (not used)
- Column department SL
Method Implementation in Mass Hunter Acquisition – Graphic Valve Icons

Agilent MassHunter Workstation Data Acquisition

Devices

Actuals

Parameter | Value
---|---
Flow Rate | 0.3 mL/min
Valve | ELS
Column | 30°C
TIC

Graphical Valve Icons

Sample | Properties | ALS | Bypass | Quat Pump | Column SL | 2/6A Val | BCOA V | MS QQQ
---|---|---|---|---|---|---|---|---
Flow | 2 mL/min
Solvents
A | 100% | H2O
B | 0% | AcN
c | 10% | DMSO
d | 10% | DMSO

Stop Time: 10 min
Pool Time: 0 min
Pressure Limits: Min 0 bar, Max 200 bar

DOO Spectrum: MS | 7 | MRM (200.9, 173.9), ES (++) 17.36
Online-SPE – Timetable for Loading and Analysis

Equilibration of SPE cartridges, SPE and separation of pesticides is overlapped and results in a total runtime for the method of 20 minutes.
High Sensitivity Analysis of Pesticides

- Analyzed herbicide compounds

Guaranteed with a LOQ below 10 ng/L!

<table>
<thead>
<tr>
<th>Atrazine</th>
<th>Diuron</th>
<th>Monolinuron</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbendazim</td>
<td>Fenuron</td>
<td>Monuron</td>
</tr>
<tr>
<td>Carbetamid</td>
<td>Irgarol 1051</td>
<td>Neburon</td>
</tr>
<tr>
<td>Chloridazon</td>
<td>Isoproturon</td>
<td>Prometryn</td>
</tr>
<tr>
<td>Chlorotoluron</td>
<td>Linuron</td>
<td>Propazin</td>
</tr>
<tr>
<td>Chloroxuron</td>
<td>Metamitron</td>
<td>Simazine</td>
</tr>
<tr>
<td>Desethylatrazine</td>
<td>Methabenzthiazuron</td>
<td>Terbutryn</td>
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<tr>
<td>Desisopropylatrazine</td>
<td>Metoxuron</td>
<td>Terbutylazine</td>
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<tr>
<td>Desmetryn</td>
<td>Metsulfuron methyl</td>
<td>Trietazin</td>
</tr>
<tr>
<td>Diflubenzuron</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
High Sensitivity Analysis of Pesticides

Isoproturon

- Quantifier: 207.1 → 72.0
- Qualifier: 207.1 → 46.1
- Peak width: 16.1 s
- Data points: 18
- Linear range: < 1 ng/L to 1 µg/L
High Sensitivity Analysis of Pesticides

- Isoproturon

+ ESI MRM Frag=110.0V CID@16.0 (207.1000 -> 72.0000) BlankWater-1-r001.d
  Noise (PeakToPeak) = 82.32; SNR (7.473min) = 1.0

- Isoproturon Water Blank

+ ESI MRM Frag=110.0V CID@16.0 (207.1000 -> 72.0000) Cal_1-r001.d
  Noise (PeakToPeak) = 47.74; SNR (7.514min) = 36.8

- Isoproturon Cal 1 (1.0 ng/L)

+ ESI MRM Frag=110.0V CID@16.0 (207.1000 -> 72.0000) Cal_2-r001.d
  Noise (PeakToPeak) = 69.74; SNR (7.490min) = 137.2

- Isoproturon Cal 2 (5.0 ng/L)

+ ESI MRM Frag=110.0V CID@16.0 (207.1000 -> 72.0000) Cal_3-r001.d
  Noise (PeakToPeak) = 79.88; SNR (7.487min) = 256.0

- Isoproturon Cal 3 (10.0 ng/L)

+ ESI MRM Frag=110.0V CID@16.0 (207.1000 -> 72.0000) Cal_4-r001.d
  Noise (PeakToPeak) = 89.26; SNR (7.512min) = 1507.1

- Isoproturon Cal 4 (50.0 ng/L)
High Sensitivity Analysis of Pesticides

- **Cyanazine**

- Quantifier: 241.1 → 214.0
- Qualifier: 241.1 → 68.0
- Peak width: 16.0 s
- Data points: 18
- Linear range: 1 ng/L to 5 µg/L
High Sensitivity Analysis of Pesticides

Cyanazine

- **Water Blank**
  - +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) BlankWater-1-r001.d
  - Noise (PeakToPeak) = 29.42

- **Cal 1 (1.0 ng/L)**
  - +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) Cal_1-r001.d
  - Noise (PeakToPeak) = 30.08; SNR (6.659min) = 8.8
  - Counts: 6.659
  - Counts: 266

- **Cal 2 (5.0 ng/L)**
  - +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) Cal_2-r001.d
  - Noise (PeakToPeak) = 30.80; SNR (6.632min) = 32.3
  - Counts: 6.632
  - Counts: 996

- **Cal 3 (10.0 ng/L)**
  - +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) Cal_3-r001.d
  - Noise (PeakToPeak) = 34.38; SNR (6.628min) = 53.5
  - Counts: 6.628
  - Counts: 1840

- **Cal 4 (50.0 ng/L)**
  - +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) Cal_4-r001.d
  - Noise (PeakToPeak) = 31.42; SNR (6.658min) = 436.8
  - Counts: 6.658
  - Counts: 13723

**Test Sample 1**

- +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) TestSample_1-r001.d
  - Noise (PeakToPeak) = 40.16; SNR (6.643min) = 438.3
  - Counts: 6.643
  - Counts: 17602

**Test Sample 2**

- +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) TestSample_2-r001.d
  - Noise (PeakToPeak) = 23.58
  - Counts: 6.648
  - Counts: 50190

**Test Sample 3**

- +ESI MRM Frag=125.0V CID@** (241.1000 -> 214.0000) TestSample_3-r001.d
  - Noise (PeakToPeak) = 49.56; SNR (6.648min) = 1012.7
  - Counts: 6.648
  - Counts: 50190

The Measure of Confidence

Agilent Technologies
Robust Method for Glyphosate and AMPA

- **Background**

  - Glyphosate is a global herbicide which is widely used in agriculture and urban landscape management.
  - In the environment, glyphosate is metabolized to its metabolite aminomethyl phosphonic acid (AMPA).
  - Both compounds are extremely polar due to their bipolar structure.
  - For the analysis of both compounds, a derivatization is widely accepted.

![Chemical structures of Glyphosate and AMPA](image)
Robust Method for Glyphosate and AMPA

Background

- Derivatization works at basic pH values with high excess of FMOC and both reduces the lifetime of the chromatographic column and the robustness of the method
- Sensitivity of direct injection is just enough to detect 100 ng/L
- Online SPE allows for clean-up and enrichment to comply with screening
- Experimental:
  - 1 mL of sample is fortified with 100 ng ISTD (Glyphosate 1,2 $^{13}$C-$^{15}$N, AMPA $^{13}$C)
  - Borate buffer (pH 10) and FMOC (5 mg/mL) is added and reaction takes place over night (> 4 h)
  - Acetic acid (58%) is added to neutralize sample
  - FMOC derivates are stable for > 48 hours
Robust Method for Glyphosate and AMPA

**AMPA**

- **Quantifier:** 334.0 → 179.0
- **Qualifier:** 334.0 → 112.0
- **Peak width:** 15.4 s
- **Data points:** 15
- **Linear range:** 10 ng/L to 1.0 µg/L

EIC for Cal_1 (10.0 ng/L)
Robust Method for Glyphosate

Results

• Use of internal standards needed to correct for derivatization yields in different water samples
• Online SPE increases the sensitivity to the relevant concentration range (10 to 25 ng/L) for environmental samples
• Robustness of the method is substantially increased – run already > 1000 samples on the same chromatographic column with just 2 cartridges
• AMPA has been found in concentrations up to 2000 ng/L, Glyphosate just positive if AMPA concentrations are extremely high
Screening Strategies

- Target screening for organic residues using QQQ
- Non-target screening using scan type instruments
  1. Non-target acquisition
  2. Identification of known contaminants
     Databases, libraries
  3. Identification of unknown contaminants
     Data mining tools, profiling software
- Identification based on
  - Accurate mass (linked to resolving power)
  - Isotope ratio, isotope spacing, isotope matching
  - Retention times
  - Fragment information (including accurate mass)
- Software workflow is of utmost importance
Agilent’s Ultra High Definition Accurate Mass Q-TOFs

Exceptional accurate mass, sensitivity, dynamic range and resolution … perfect match for 1290 Infinity UHPLC

• 500 ppb mass accuracy
• Femtogram sensitivity
• 5 decades dynamic range
• 40,000 resolving power
• 20 Spectra/sec
• Excellent Linearity and Isotopic Fidelity
• Supports Agilent Jet Stream and HPLC-Chip
Ultra High Definition QTOF

Maintaining Resolving Power – Across the Mass Range

Counts vs. Mass – to – Charge (m/z)

Scan Rate Independent

m/z 622 and isotopes
Requirements for Identification and Confirmation

- New guidelines for identification of pesticide residue analysis in food and feed available since January 1st 2010 (SANCO/10684/2009)

- High resolution/high mass accuracy MS instruments other than magnetic sector instruments are specified for the first time

- Minimum resolution: \( \frac{M}{DM} > 10,000 \) (@ 10% valley) 
  \(~ 20,000 \) (@ FWHM)

- Positive identification: \( \geq 2 \) diagnostic ions 
  (including one fragment) 
  Mass accuracy < 5 ppm

- TOF/QTOF instruments are typically factor 10 less sensitive than QQQ instruments

- Online SPE and TOF/QTOF is an ideal combination
The spectra of the standards at the LOQ (1B) were evaluated for the reproducibility of the mass accuracy (MS1). In the following table the results obtained for the negative ion mode analytes are given (standard used for the determinations shown in brackets).

<table>
<thead>
<tr>
<th>SPS (III, 50ng/L)</th>
<th>MCPB (III, 50ng/L)</th>
<th>pp-DDA (III, 50ng/L)</th>
<th>24-DB (III, 50ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>Diff (ppm)</td>
<td>m/z</td>
<td>Diff (ppm)</td>
</tr>
<tr>
<td>228.0335</td>
<td>0.54</td>
<td>227.0484</td>
<td>1.54</td>
</tr>
<tr>
<td>228.0336</td>
<td>-0.06</td>
<td>227.0484</td>
<td>-1.69</td>
</tr>
<tr>
<td>228.034</td>
<td>-1.66</td>
<td>227.0478</td>
<td>0.98</td>
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<tr>
<td>228.0339</td>
<td>-1.12</td>
<td>227.0474</td>
<td>2.72</td>
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<td>228.0338</td>
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<td>228.0341</td>
<td>-1.99</td>
<td>227.0479</td>
<td>0.78</td>
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<tr>
<td>228.0335</td>
<td>0.41</td>
<td>227.0485</td>
<td>-2.16</td>
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<tr>
<td>228.0336</td>
<td>0.21</td>
<td>227.0484</td>
<td>-1.36</td>
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<tr>
<td>228.034</td>
<td>-1.79</td>
<td>227.048</td>
<td>0.11</td>
</tr>
</tbody>
</table>
PCDL Databases & Libraries for the QTOF

Forensic and Toxicology Database & Library
Pesticide Database & Library
Personal Databases
Waste Water Effluent
500 µL injection with 3-minute wash

Search results from 130-compound database
Waste Water Effluent
500 µL injection with 3-minute wash

Additional search for Pentazocine
Accurate Mass Library Search

Forward Score = 51
(low due to d3-ISTD)

Reverse Score = 81

Forensics/Toxicology accurate mass library
7300 + compounds

Includes many searchable spectra at
3 different CE’s (10/20/40)
Advantages of Online SPE

- Utilizes entire prepared sample to achieve low detection limits
- Small sample volumes (mL) needed – lower logistics and storage costs
- Reduced chance of error caused by sample handling
- Save on solvent costs – both purchase and disposal of waste
- No evaporation step
- No reconstitution required
- Integrated system increases sample throughput

*Exploit the native sensitivity of the LC-MS/MS system with online SPE*
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• Analysis of emerging contaminants in water – an overview
• Sample preparation options for drinking water analysis
  – Solid-supported liquid/liquid extraction
  – Solid phase extraction
• New developments in online SPE
• Summary of each approach
• Question and answer period
## Review: Online versus Offline SPE

<table>
<thead>
<tr>
<th>Online SPE</th>
<th>Offline SPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utilizes entire prepared sample to achieve low detection limits</td>
<td>Only a fraction of concentrated sample is used</td>
</tr>
<tr>
<td>Small sample volumes (mL) needed – lower logistics and storage costs</td>
<td>Large initial sample volume required (100-1000 mL)</td>
</tr>
<tr>
<td>Reduced chance of error</td>
<td>Increased chance of error</td>
</tr>
<tr>
<td>No evaporation step</td>
<td>Concentration step may be necessary</td>
</tr>
<tr>
<td>No reconstitution required</td>
<td>Reconstitution may be required</td>
</tr>
<tr>
<td>Integrated system increases sample throughput</td>
<td>Sample preparation independent of analysis system - ↑ flexibility</td>
</tr>
<tr>
<td>Requires high-end instrumentation</td>
<td>Suitable for low-end instruments</td>
</tr>
</tbody>
</table>
Summary and Conclusions

- A wide range of offline SPE products support emerging contaminant analysis using established methods and protocols.
- Online SPE combined with a LC-QQQ system allows a relatively simple, fast and reliable determination of herbicides in the low ng/L range in filtered water samples.
- The whole system is fully controlled with the MassHunter acquisition software.
- Adding a more sensitive QQQ system allows for even better sensitivity or compounds which are less weakly ionizable.
- Good recovery values and reproducibilities can be achieved even in complex samples and for very polar compounds.
- Online SPE not only increases the sensitivity but adds robustness to the method (e.g. for glyphosate).
- The use of online SPE with the QTOF allows for unknown screening and quantitation in complex environmental samples.

**Agilent offers a wide range of solutions for potable water analysis**
Today’s Agenda

• Analysis of emerging contaminants in water – an overview
• Sample preparation options for drinking water analysis
  – Solid-supported liquid/liquid extraction
  – Solid phase extraction
• New developments in online SPE
• Summary of each approach
• Question and answer period
Thank you for your time and attention