Comparison of Analytical Methods for Analysis of Emerging Organic Contaminants in Water

Tarun Anumol
Sheher Mohsin
Jerry Zweigenbaum
Agilent Technologies
Shane Snyder
University of Arizona
Emerging Organic Contaminants Categories

- Aliphatics
- Anticorrosive
- Chlorobenzenes
- Complexing agent
- Disinfection by-products
- Fire retardants
- Fluorescent whitening agents
- Glycol ether
- Image contrast media
- Monocyclic hydrocarbons and heterocycles
- Nitrosamines
- Organotins
- Personal care product
- Pesticide
- Pharmaceutical
- Phthalate esters/plasticizers
- Polychlorinated biphenyls
- Polynuclear aromatic hydrocarbons
- Steroids, sterols & stanols
- Surfactant

WERF (2008)
Who Cares?
Why we monitor

• **Health & Safety Concerns**
  
  - £30bn bill to purify water system after toxic impact of contraceptive pill
  - Drug firms oppose an EU call for controls on potent chemicals that have been blamed for the gender mutation of freshwater fish
  
  - The Washington Post
  - Six years later, gender-bending fish in our water supply remain a mystery

• **Public Perception**

• **Potential Government Regulations**
Who Cares?
Climate Change, Draught

Drought-plagued California wants residents to drink recycled wastewater

San Diego agrees to turn recycled wastewater into drinking water

San Jose, Santa Clara mayors drink recycled sewage to push expanding reclaimed water
Analysis

Water Matrices
Traditional Extraction Techniques
Sample Preparation

Liquid-Liquid Extraction

Solid Phase Extraction
Conventional Method
Solid Phase Extraction

Sample collection

Surrogate addition (200 ng/sample)

Filtering

Evaporation

Extraction (SPE)

Analysis
Sample Volumes
Reduction in sample volume, cost of transport

Broken Sample
Sample Volume
Automated Online SPE
Reduction in labor, faster analysis
Agilent 1290 Flexcube
Integrated online SPE system

Solvents for LC

Quaternary Pump

Column Compartment

Flexible Cube

Autosampler

Thermostat

Solvents for SPE

6460 MS

Triple quad MS for quantification

Only one LC pump
Configuration

Flex cube pump

Sample Injection Loop

Analytical Column

Equilibrating

SPE cartridge 2

Mass Spectrometer

Binary Pump

SPE cartridge 1

Loading

Waste

Flexcube Pump Flow Path

Binary Pump Flow Path
Configuration

Flex cube pump

Sample Injection Loop

Analytical Column

Mass Spectrometer

SPE cartridge 2

Loading

SPE cartridge 1

Elution

Binary Pump

Waste

Binary Pump Flow Path

Flexcube Pump Flow Path
Online SPE LC-MS/MS Workflow

Sample Collection (1-20 mL)

Surrogate Addition (0.3 ng/sample)

Automated Extraction (Online)

Analysis
Evolution of Mass Spectrometers

Agilent 6410 (50:1)

Agilent 6430 (300:1)

Agilent 6490/6495 (10,000:1)

Agilent 6460 (1,000:1)

( ) denotes minimum S/N for 1 pg reserpine on column
Large Volume Injection (LVI) LC-MS/MS Workflow

Sample Collection (0.1-5 mL)  Surrogate Addition (0.1 ng/sample)  NO Extraction  Analysis
Emerging Organic Chemicals

- **Atenolol** (ß-blocker)
- **Bisphenol A** (plasticizer)
- **DEET** (Insect-repellant)
- **Estrone** (Hormone)
- **Atrazine** (Herbicide)
- **Caffeine** (stimulant)
- **Dexamethasone** (glucocorticoid)
- **Fluoxetine** (Anti-depressant)
- **Benzophenone** (UV-blocker)
- **Carbamazepine** (Anti-seizure)
- **Trimethoprim** (Antibiotic)
- **Fluoxetine** (Anti-depressant)
- **Gemfibrozil** (Anti-cholesterol)
Emerging Organic Chemicals

- **Ibuprofen** (Analgesic)
- **Meprobamate** (Anti-anxiety)
- **Naproxen** (Pain-reliever)
- **PFBS** (Fluoro-surfactant)
- **PFOA** (Fluoro-surfactant)
- **PFOS** (Fluoro-surfactant)
- **Primidone** (Anticonvulsant)
- **Simazine** (Herbicide)
- **Sulfamethoxazole** (Antibiotic)
- **TCPP** (Flame-retardant)
- **Triclocarban** (Anti-microbial)
- **Triclosan** (Anti-microbial)
LC Conditions
Linear Gradient

A: Water + 0.1% Acetic Acid
B: ACN + 0.1% Acetic Acid

Agilent 1290 Infinity LC
Poroshell EC 120 C-18, 2.1x50 mm
Method Detection Limits

MDL Method:
Glaser et al. (1981)
7 replicates
Ion Suppression
Comparison of methods

**Conventional SPE**
- Carbamazepine_d10
  - Concentration: 50 pg/mL
  - Injection Vol: 3 μL
  - Mass: 150 pg
- Wastewater effluent (0.2 um filtered)
- Ultrapure water

**Online SPE**
- Carbamazepine_d10
  - Concentration: 100 pg/mL
  - Injection Vol: 1.5 mL
  - Mass: 150 pg
- Wastewater effluent (0.2 um filtered)
- Ultrapure water

**Direct Injection**
- Carbamazepine_d10
  - Concentration: 1.5 pg/mL
  - Injection Vol: 100 μL
  - Mass: 150 pg
- Wastewater effluent (0.2 um filtered)
- Ultrapure water
Matrix Effects in Surface Water

Conventional SPE
Online SPE
Direct Injection

Matrix Effects (%)
Matrix Effects in Wastewater Effluent

The graph shows the matrix effects (%) for various compounds under different sample preparation methods: Conventional SPE, Online SPE, and Direct Injection. The compounds include Atenolol, Atrazine, Benzophenone, Caffeine, Carbamezapine, DEET, Diclofenac, Diphenhydramine, Diltiazem, Gemfibrozil, Ibuprofen, Meprobamate, Naproxen, PFOA, PFOS, Primidone, TCEP, Triclocarban, and Trimethoprim.
Method Detection Limits

![Graph showing method detection limits for various substances. The x-axis represents the substances (e.g., Atenolol, Atrazine, Benzophenone), and the y-axis represents the method detection limit in ng/L. The graph compares Conventional SPE, Online SPE, and Direct Injection methods.](image-url)
Method Reporting Limits in Wastewater Effluent

$MRL = \frac{MDL \times 100}{\text{Surrogate Recovery}} \%$

28 July 2015

Atenolol
Atrazine
Benzophenone
Caffeine
Carbamazepine
DEET
Ditiazem
Ibuprofen
Naproxen
PFOA
Primidone
TCEP
Trimethoprim
Reproducibility
Seven replicates of WW effluent samples
Conclusions

- Online SPE allows sensitive analysis of trace organics in water while allowing significant time, labor and reagent savings.

- Conventional SPE can be significantly affected by ion suppression compared with online SPE and LVI techniques especially for multi-residue methods.

- LVI may currently not be sensitive enough to attain desired MRLs in finished drinking water but offers promise with rapid increase in sensitivity of newer mass spectrometers.

- Use of online SPE with accurate mass detectors (ToF & Q-ToF) could allow for real-time analysis of trace unknowns in water.
Conventional offline SPE method:


Automated online SPE method:

- Anumol, T.; Snyder, S. A., Rapid analysis of trace organic compounds in water by automated online solid-phase extraction coupled to liquid chromatography–tandem mass spectrometry. Talanta 2015, 132, (0), 77-86.

Direct injection method:

QUESTIONS ???

tarun.anumol@agilent.com
Ph (O): 302-636-1517