Table of Contents

The European Water Framework Directive

Thermo Scientific Environmental Solutions Reference Guide

Thermo SCIENTIFIC

Introduction to EU WFD 2013/39/EU

Introduction

- The EU Water Framework Directive (WFD) was introduced in August 2013, amending the EU directives 2000/60/EC, 2008/105/EC, 2000/60/EC, and 2008/105/EC.
- The European Water Framework Directive is a directive that commits all member states to actively control for a long list of environmental contaminants in all water bodes of the various member states.
- It lays down a strategy against water pollution, to be applied in all European Union member states.
- It involves identifying priority substances and monitoring different classes of contaminants; and it includes the first watch list (used for future prioritization exercises).
- Member States have the flexibility to apply an EQS (Environmental Quality Standard) for an alternative matrix or, where relevant, an alternative biota taxon, for example sub-phylum Crustacea, paraphylum “fish”, class Cephalopoda or class Bivalvia (mussels and clams).
- Compound levels are expressed as Environmental Quality Standard or (EQS) and the annual average (AA) and the Maximum Allowable Concentration (MAC) is given.
- The EU WFD encourages the development of novel monitoring methods such as passive sampling and other tools

Thermo SCIENTIFIC

Click here to link to the EU regulatory page

UK Specific Regulations: Introduction to CIP 2

- The UK Chemical Investigations Programme (CIP 2) looks into the occurance, sources, and removal of trace substances in waste water treatment facility effluent.
- This regulation helps to establish priorities for remediative action to ensure surface waters meet new Environmental Quality Standards (EQS).
- The CIP 1 program was managed by UK Water Industry Research (UKWIR) and implemented from 2010-2013.
- The CIP 2 program is a follow-up program of sampling and analysis to be implemented between 2014 and 2020.
- The primary objective of CIP 2 is to identify and characterize sites where EQS levels are breached.
- In the program, 70 priority substances were determined from 162 sewage treatment works (STW) effluents.
- Additionally, 11 pharmaceuticals were identified as priority monitoring candidates. It is important to note that EQS is defined for only three pharmaceutical compounds: Diclofenac, E2, and EE2. All substances selected for monitoring analysis were detected previously in waste water effluent samples.
- The determined environmental concentrations of many priority substances in effluent exceeded EQS.

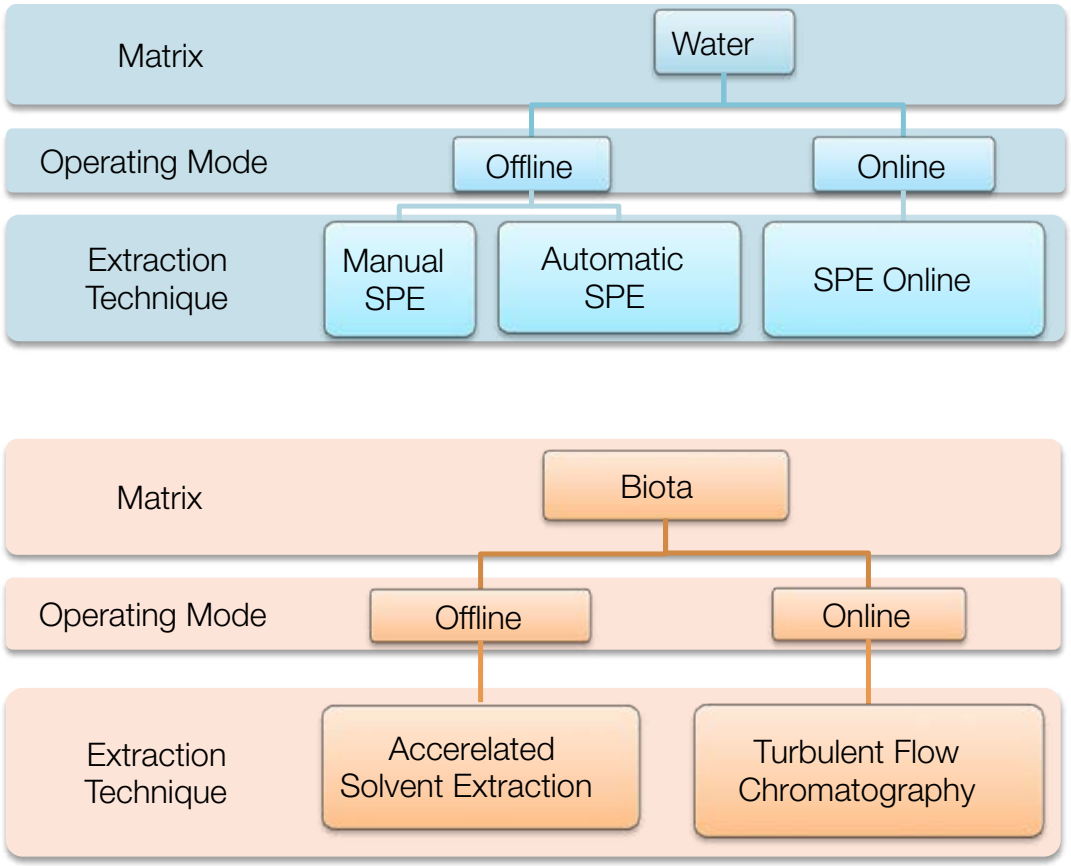
Thermo SCIENTIFIC

Chapter 1: Index of Compounds and Techniques

Priority hazardous substances	GC-MS	LC-MS	ICP-MS	Priority hazardous substances	GC-MS	LC-MS	ICP-MS	Priority hazardous substances	GC-MS	LC-MS	ICP-MS
Anthracene	√			Perfluorooctane sulfonic acid and its derivatives (PFOS)		√		Naphthalene	√		
Brominated diphenylethers	√			Quinoxyfen	√	√		Nickel and its compounds			√
Cadmium and its compounds			√	Dioxins and Dioxin-like compounds	√			Octylphenols	√		
C_{10-13} Chloroalkanes	√			Hexabromocyclododecane (HBCDD)		√		Pentachlorophenol	√		
Di-(2-ethylhexyl)phthalate (DEHP)	√			Heptachlor and heptachlor epoxide	√			Simazine	√	√	
Endosulfan	√			Alachlor	√			Trichlorobenzenes	√		
Hexachlorobenzene (HCB)	√			Atrazine	√	√		Trichloromethane (chloroform)	√		
Hexachlorobutadiene (HCBD)	√			Benzene	√			Aclonifen	√		
Hexachlorocyclohexane	√			Chlorfenvinphos	√	√		Bifenox	√		
Mercury and its compounds			√	Chlorpyrifos (ethyl)	√			Cybutryne	√		
Nonylphenols	√			1,2-dichloroethane	√			Cypermethrin	√		
Pentachlorobenzene	√			Dichloromethane	√			Dichlorvos	√		
Polyaromatic hydrocarbons (PAHs)	√			Diuron		√		Terbutryn	√	√	
Tributyltin compounds	√			Fluoranthene	√			Diclofenac (watchlist)		√	
Trifluralin	√			Isoproturon		√		17-beta-estradiol (watchlist)	√	√	
Dicofol	√			Lead and its compounds			√	17-alpha-ethinylestradiol (watch list)	√	√	

Thermo SCIENTIFIC

General sample preparation workflow



Thermo SCIENTIFIC

Automated Sample Preparation Solutions

The Thermo Scientific™ Dionex™ AutoTrace™ 280 Solid-Phase Extraction instrument saves time, solvent, and labor ensuring high reproducibility and productivity for analytical laboratories. The instrument can process up to six samples in 2–3 hours with only 15 minutes of operator involvement. The Dionex AutoTrace 280 instrument uses powerful pumps (no check valves) and proven constant-flow technology to efficiently process even the most difficult samples.

Save time, save solvent

With Dionex AutoTrace and Thermo Scientific™ Dionex™ ASE™ Accelerated Solvent Extraction systems, laboratories can effectively automate the solvent extraction process for liquid and solid matrices.

Learn more about the accelarared solvent extraction systems

Download the accelerated solvent extraction environmental summary application notebook

Thermo SCIENTIFIC

Solid Phase Extraction (SPE)

LC-MS amenable compounds

Loading	• Material: Thermo Scientific™ HyperSep™ Retain PEP cartridge • pH 2
Wash	• 10% MeOH/H_2O
Elution	• ACN (0.1%FA) – ACN – ACN (0.1% NH_4OH) • EtOAc (PFCs, HBCDD, Phenols, Triclosan, Triazoles)
Evaporation	• Final Volume (0.5 mL)
Reconstitution	• Addition of 4.5 mL of 0.1% FA
Analysis	• 10 µL direct injection • 1-5 mL Injection Thermo Scientific™ EQuan Max™ LC-MS system

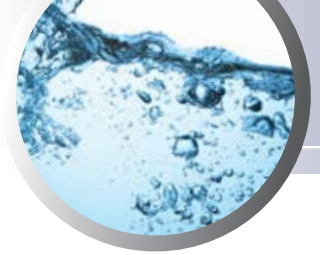
Classical off-line sample preparation: Liquid-liquid extraction or LLE

To 100 mL of surface water, 10 g of NaCl was added. The extraction solvent was 10 mL dichloromethane with 1 % iso-octane. The sample was shaken vigorously for 20 minutes. The organic phase was removed and dried with $NaSO_4$.

The extract was evaporated to 1 mL under a low flow of nitrogen and transferred to a 2 mL (12x32 mm) GC vial for injection.

No extra clean up was performed.

Iso-octane acted as a keeper to retain the most volatile compounds, such as trichlorobenzene and naphthalene. The starting temperature of the GC was increased to 65 °C, saving cooling time and decreasing the run-to-run time.



EPA method 508 – Analysis of chlorinated pesticides, herbicides and organohalides

Using 10 g 75 mL Thermo Scientific™ HyperSep™ C18 SPE cartridge (P/N 60108-703)

Sample preparation
1 L water collected
Add $MgCl_2$ (final conc. 10 mL/L)

Condition HyperSep C18 SPE cartridge
1 x 1 mL 1:1 EtAC/CH_3Cl_2
1 x 10 mL CH_3OH
1 x 10 mL H_2O

Apply sample
Add 1 x 5 mL CH_3OH to sample
Mix
Take 50 µL of sample and mix

Load sample at 1 to 2 mL/minute

Elute
Insert fresh collection tubes into manifold
1 x 10 mL EtAc
1 x 10 mL CH_3Cl_2
1 x 3 mL EtAc/CH_3Cl_2

Evaporation
Evaporate cluates to 0.8 mL under a gentle stream of nitrogen in a heated water bath 40 °C
Add internal standard
Adjust volume to 1 mL

Analysis
Add 1 to 2 µL onto GC

Recommended GC column	Part number
Thermo Scientific™ TraceGOLD™ TG-OCP I 30 m x 0.25 m x 0.25 µm	26078-1420

GC-MS determination of phenols in drinking water

Using 500 mg 6 mL HyperSep Retain PEP SPE cartridge (P/N 60107-206)

Sample preparation
Collect 1 L of H_2O
Adjust pH to 2 with 6N HCl

Condition HyperSep Retain PEP SPE cartridge
1 x 3 mL CH_3Cl
1 x 3 mL CH_3OH
1 x 3 mL 0.05N HCl

NOTE: *Do not allow the cartridge to dry out*

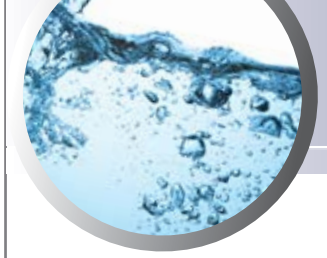
Apply sample
Load 1 L of water sample at 20 mL/minute
Dry column for 10 to 15 minutes

Wash column
1 x 10 mL H_2O
Dry column (1 minute at > 10 °Hg)

Elute
1 x 10 mL CH_3Cl
1 x 3 mL CH_3Cl
Concentrate the extract to 0.9 mL in water bath (40 °C) under a gentle stream of nitrogen

Analysis
Adjust final volume to 1.0 mL with CH_3Cl
Analyze the extract with using GC-MS

Recommended GC column	Part number
TraceGOLD TG 5MS 30 m x 0.25 m x 0.25 µm	26098-1420



Automated Solvent Extraction (ASE) Procedure

Dioxins in biota by GC-MS

Environmental contaminants in fish and egg samples

Equipment

Dionex ASE 200 accelerated solvent extractor* with ASE solvent controller

Choose either 11 mL stainless steel extraction cells (P/N 049560) or

22 mL stainless steel extraction cells (P/N 049561) or

33 mL stainless steel extraction cells (P/N 049562)

Cellulose filters (P/N 049458)

Collection vials, 40 mL (P/N 048783) or 60 mL (P/N 048784)

Dionex SE 500 solvent evaporation system (P/N 063221)

Analytical balance (to read to nearest 0.0001 g or better)

Tissue homogenizer (Buchi B-400 or equivalent)

Freeze drier (for PCB extraction)

Centrifuge (for organotin extraction)

Mechanical shaker (for organotin extraction)

Dionex ASE 150 and 350 systems can be used for equivalent results

Analysis

GC

GC-MS

GC-ECD

HPLC

Extraction conditions

Pressure:	1500 psi
Temperature:	175 °C
Solvent:	100% Toluene
Static time:	10 min
Static cycles:	2
Flush volume:	60%
Purge time:	60 sec
Static time:	1 or 2 min**
Flush volume:	60%
Purge time:	60 sec
Cycles:	2
Total time:	12 min
Total solvent:	20 mL

* *Petroleum ether and hexane were found to be equivalent as extraction solvents for fat in meat.*

***When extracting more than 1 g of a high-fat sample, a 2 min static time may be beneficial.*

Results

PCDDs/PCDFs in fish tissue samples (ng/kg or ppt)using ASE.

Compound	Soxhlet	ASE	Certified
2,3,7,8-TCDD	7.6	7.6	6.6
1,2,3,4,8-PCDD	4.3	4.3	4.4
1,2,3,4,7,8-HCDD	1.4	1.4	1.9
2,3,4,7,8-TCDF	13.4	12.6	11.9
1,2,3,7,8-PCDF	5.4	5.1	5.0
1,2,3,4,7,8-HCDF	12.5	12.2	12.2
OCDD	12.4	6.4	6.3
Total TEQ	21.4	21.1	21.0

ICP-MS amenable components

Aqueous samples

Aqueous environmental samples that contain less than 0.2% (m/v) dissolved solids at the point at which the sample enters the plasma can be measured directly with ICP-MS, following filtration of the samples if they contain suspended particles that could block the nebulizer of the instrument. For samples containing more than 0.2% (m/v) dissolved solids at the point of entry to the plasma, dilution is required either of the sample itself, by on-line or off-line liquid dilution, or by dilution of the nebulized sample aerosol using an additional flow of argon gas. Liquid dilution of samples is most commonly achieved using diluted nitric acid (typically 1 to 2% (v/v)), with addition of Au (at 0.2 to 1 ppm) to stabilize Hg to minimize memory effects with this element.

Solids and slurry samples

These samples generally require digestion with concentrated nitric acid followed by dilution with water and then filtration to remove undigested material. Digestion can be achieved using hot plate or microwave-based methods.

GC-MS amenable compounds

The section below describes the GC amenable contaminants for the surface water directive, containing the following compound classes:

- Volatile organic compounds analyzed with Headspace GC-MS in SIM mode
- Polybrominated diphenyl ethers using GC-MS/MS
- Organotin with derivatization with GC-MS/MS
- Chlorinated alkanes using GC-MS/MS
- Dioxins and PCB using GC-MS/MS
- The remaining pesticides, PAHs, phthalate, and phenol compounds with GC-MS/MS

The groups of compounds above are divided according to analytical workflows and required detection limits. Measurement in SIM mode requires monitoring three ions for each compound for which the ion ratio deviation is monitored. Measurements in MS/MS mode require two transitions per compound for which the ion ratio will be monitored according to the European Directive 2002/657/EC.

GC-MS Highlights

The Thermo Scientific™ TriPlus™ RSH autosampler offers:

- Automated sample preparation capabilities
- Unattended switching from headspace to liquid injection to SPME
- Support for dual GC injection configuration

The Thermo Scientific™ TRACE™ 1300 series GC offers:

- Instant connect modularity for easy maintenance, removal, and module replacement
- Fast and reliable heating and cooling of the oven for rapid analysis

The Thermo Scientific™ TSQ™ series triple quadrupole and ISQ™ single quad series offers:

- The Thermo Scientific™ Extractabrite™ removable ion source, for removal without venting the mass spec
- Enhanced Velocity Optics (EVO), allowing the optimal number of transition scans without comprimising data quality for large sample compound lists.
- User-friendly software, providing tools for automated method development and integration of compound names, retention times, and transitions between the instrument and processing methods

Recommended GC-MS System Configurations

Compound group	Autosampler	TRACE GC 1300/1310	MS analyzer (acquisition mode)
VOC	Headspace	SSL or PTV	ISQ or TSQ Series (EI-Timed SIM)
BDE	LV option	SSL or PTV	TSQ Series (EI-SRM or NCI-SIM)
Organotin compounds	Standard	SSL or PTV	TSQ Series (EI-SRM)
Polychlorinated alkanes	Standard	SSL or PTV	TSQ Series (EI-SRM)
Dioxins/Dioxin-like compounds	Standard	SSL or PTV	TSQ Series (EI-SRM) Thermal Scientific™ DFS™ High Resolution GC/MS
Pesticides	Standard	SSL or PTV	TSQ Series (EI-SRM)
PAHs	Standard	SSL or PTV	TSQ Series (EI-SRM)
Phenols	Standard	SSL or PTV	TSQ Series (EI-SRM)
Phthalates	Standard	SSL or PTV	TSQ Series (EI-SRM)

Volatile Organic Compounds (HS) GC-MS

Sample preparation

- 10 mL of surface water
- 2 g NaCl

Headspace conditions

60 °C, 20 min., 1.5 mL injection; 1/40 split

Column

TraceGOLD TG-VMS 20 m x 0.18 mm ID x 1.00 µm (P/N 26080-4950)

Instrument methodology

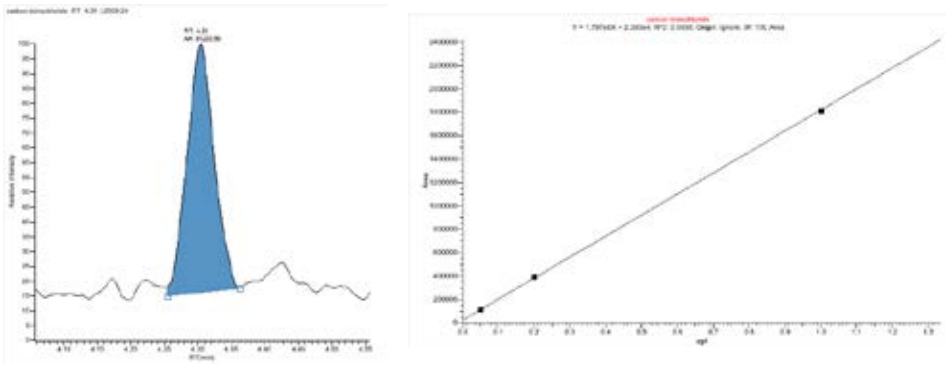
GC method: 30 °C (4 min); 18 °C/min; 100 °C (0 min); 40 °C/min; 230 °C (3 min).

Injector: 200 °C

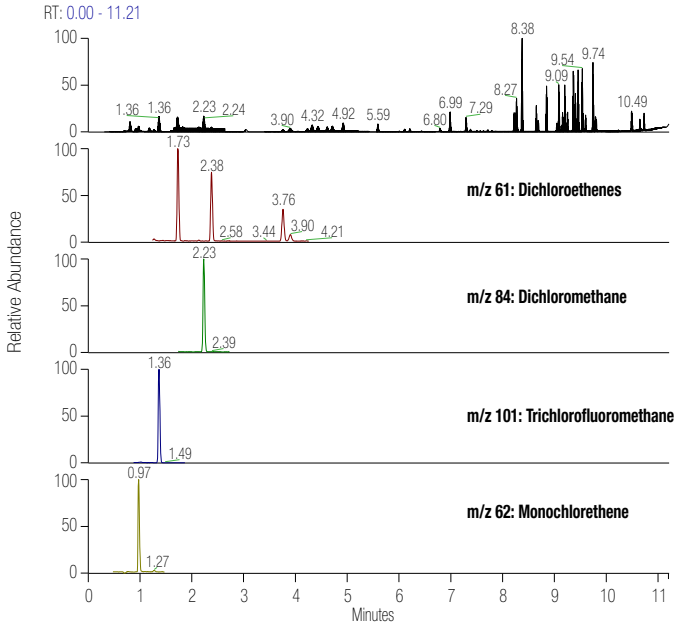
ISQ LT MS: Timed SIM mode

Source temperature: 250 °C

Compound	IDL LOQ in µg/L
Dichloromethane	0.07
Trichloromethane	0.07
Carbon tetrachloride	0.05
Benzene	0.1
1,2-dichloroethane	0.1
Trichloroethylene	0.05
Tetrachloroethylene	0.05



Carbontetrachloride in lake water at 0.1 µg/l and calibration



Chromatogram of volatile compounds monitored in Timed SIM mode with monochloro ethene eluting first.

Learn more about analyzing Volatile Organic Compounds with GC-MS

Download the poster presentation on GC-MS amenable EU WFD compounds

Polybrominated Diphenylethers by GC-MS/MS

Methodology

GC method

120 °C (1 min); 20 °C/min; 320 °C (5 min)

PTV method

80 °C (0.1 min); 10 °C/sec; 300 °C (6 min);
14.5 °C/sec; 340 °C (20 min); 2 min splitless

TSQ Quantum Ultra system Timed SRM mode and/or Cineg with NH_4

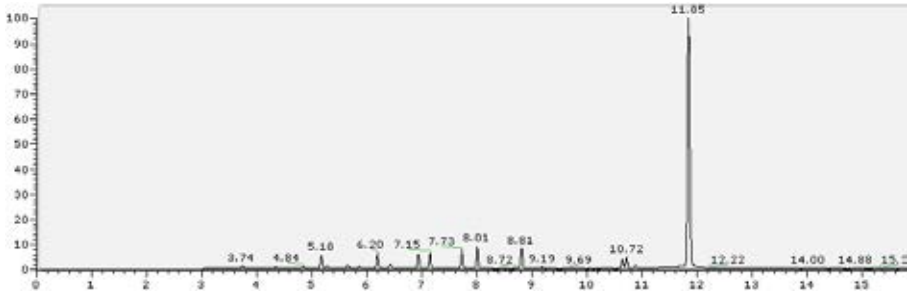
Source temperature 260 °C

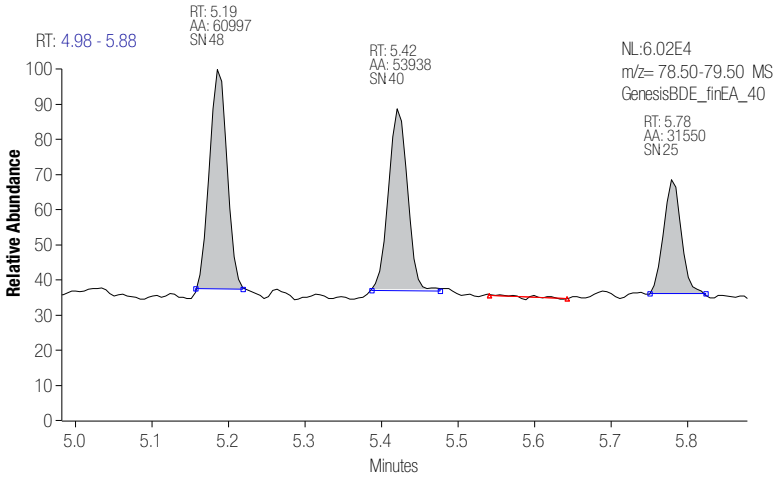
Column

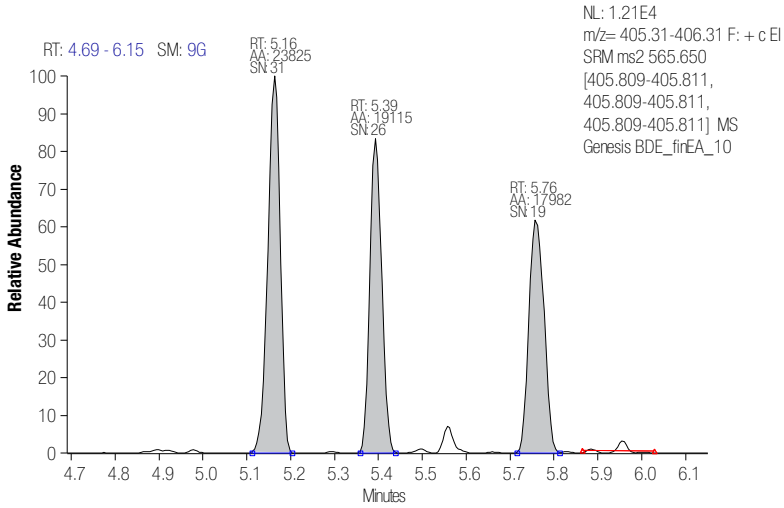
TraceGOLD TG-5HT column (5% phenyl film)
15 m x 0.25 mm x 0.10 µm (P/N 26095-0350)

Liner Siltek Baffled (P/N 453T21210)

Compound	IDL LOQ in pg in EI SRM	IDL LOQ in pg in NCI SIM
BDE28	<0.2	<0.1
BDE47	<0.2	<0.1
BDE99	<0.5	<0.1
BDE100	<0.5	<0.1
BDE154	<0.5	<0.1
BDE153	<0.5	<0.1





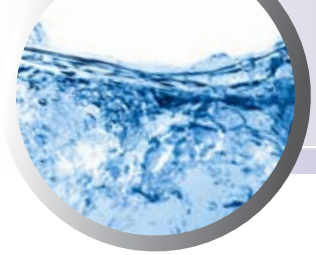


Inorganic anions, organic acids, and arsenate in a diluted apple juice sample.

Thermo SCIENTIFIC

Learn more about PBDE analysis with GC-MS/MS

Download the poster presentation on GC-MS amenable EU WFD compounds



Organotins by GC-MS/MS

GC method

Temperature program: 45 °C (Hold 2 min)

Ramp 55 °C/min – 175 °C – Ramp 35 °C – 300 °C (Hold 2 min);

Transfer line 300 °C

PTV method

Injector Temperature: 50 °C – Spitless injection 0.1 min

PTV Transfer: 8 °C/sec – 280 °C (Hold 1 min)

PTV Clean: 350 °C – 11 min – Clean flow 50 mL/min

TSQ Quantum system in EI SRM Source Temp. 250 °C

Column

TraceGOLD TG-5HT column (5% phenyl film) of 30 m x 0.25 m x 0.25 µm (P/N 26095-1420)

Liner Siltek Baffled (P/N 453T21210)

Sample preparation

400 mL water sample

Adjust pH to 5

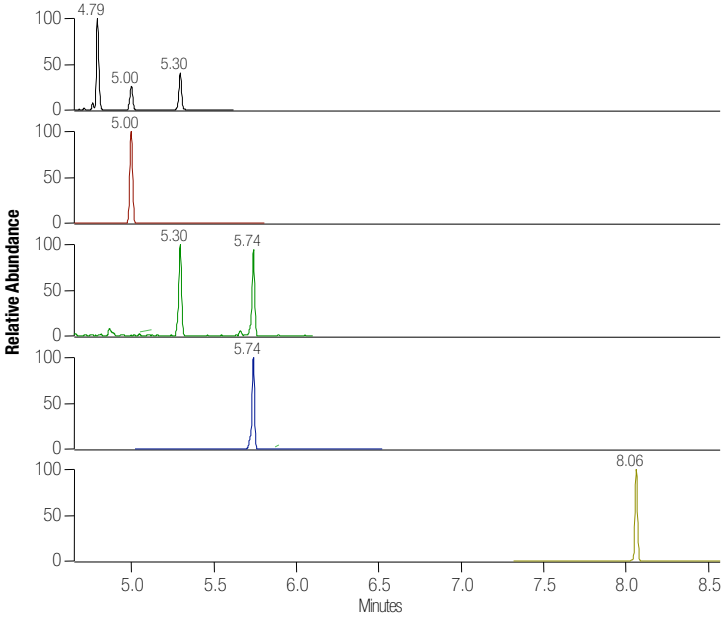
Ethylation by adding a 2% w/v sodium tetraethyl borate; solution in 0.1M NaOH;

Extraction with pentane;

Evaporate to 400 µL; 3 µL injection volume

Tributyl tin compound at 0.2 pg absolute amount

Compound	IDL in µg/l in EI SRM
Tributyl tin	0.00007



Download application note 52099 determination of organotins in water using triple quadrupole GC-MS/MS

Polychlorinated Alkanes by GC-MS/MS

Methodology

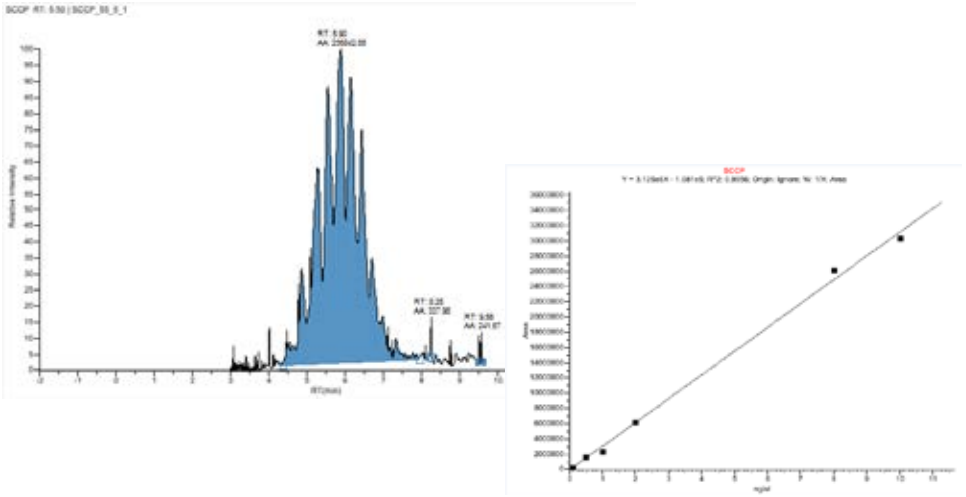
GC method: 100 °C (1 min); 40 °C/min; 320 °C (3 min).
Injector PTV: 60 °C (0.1 min); 14.5°C/sec; 280 °C (1 min);
2 µl, 1 min splitless.

TSQ Series Timed SRM mode

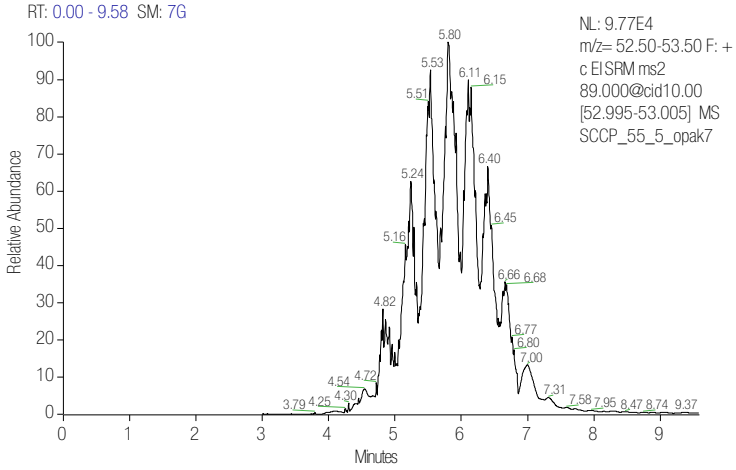
Source temperature 280 °C

Column
TraceGOLD TG-5SilMS 20 m x 0.18 mm x.18µm (P/N 26096-5780)

Liner Siltek Baffled (P/N 453T21210)



Polychlorinated alkanes 0.1ng/µl; calibration curve R^2= 0.9956



Compound	IDL abs. on column in pg
C10-C13 polychlorinated alkanes	200

Download the poster presentation on GC-MS amenable EU WFD compounds

Thermo SCIENTIFIC

Dioxins in Biota by GC-MS/MS

GC method

Initial 100 °C, hold 2 min, ramp 25.0 °C /min - 250 °C,
Ramp 2.5 °C/ min, 285 °C , ramp 10 °C/ min to 330 °C
Hold 5.0 min. transfer line: 280 °C

SSL method

Injector temperature 260 °C, splitless injection 2 min

TSQ 8000 Evo System in EI SRM mode

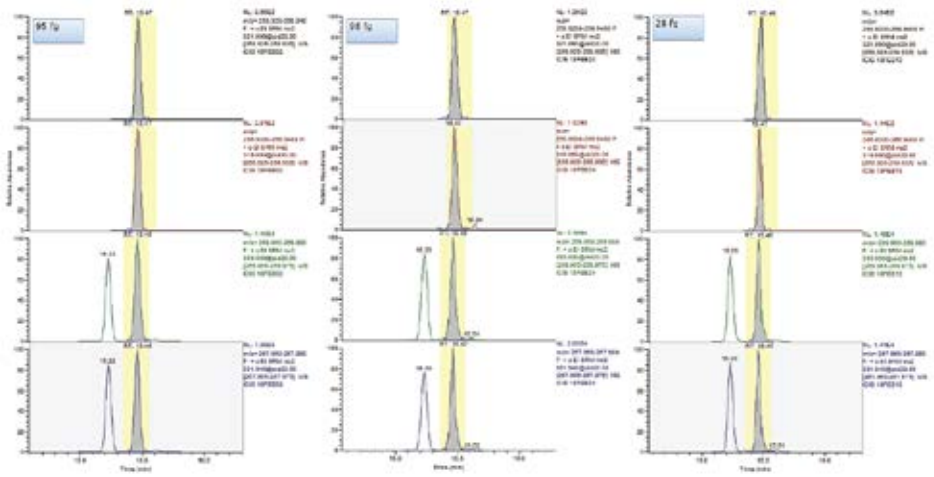
Source temp: 300 °C

Ionization: EI, 40 eV

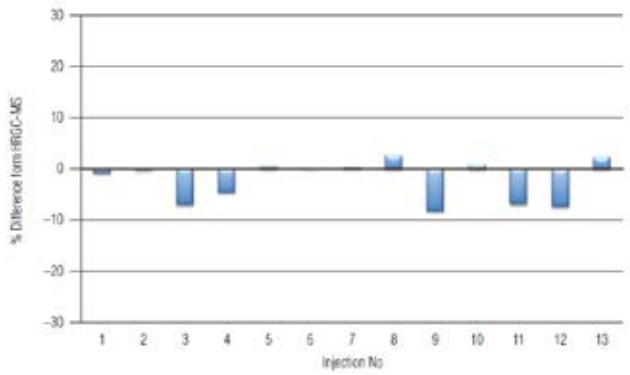
Column

TraceGOLD TG-5SilMS 60 m × 0.25 mm I.D. × 0.25 µm
(P/N 26096-1540)

Liner SSL single taper (P/N 453A2342)



2378TCDD and 13C2378 TCDD from left to right: at 95 fg in fishmeal; 98 fg in animal fat and 28 fg in egg fat sample.



Injection No	WHO-PCDD/F-TEQ ub
1	0.91
2	0.76
3	0.88
4	0.90
5	0.94
6	0.83
7	0.84
8	0.85
9	0.88
10	0.87
11	0.78
12	0.82
13	0.84
Mean	**0.85**
STDEV	0.05
%RSD	**5.97**

Results in fish meal compared with GC-HRMS

PCDD/Fs limit of quantitation	
Compound	**pg/µL**
2378-TCDF	0.01
2378-TCDD	0.01
12378-PeCDF	0.02
23478-PeCDF	0.02
12378-PeCDD	0.02
123478-HxCDF	0.04
123678-HxCDF	0.04
234678-HxCDF	0.03
123478-HxCDD	0.06
123678-HxCDD	0.03
123789-HxCDD	0.04
123789-HxCDF	0.04
1234678-HpCDF	0.02
1234678-HpCDD	0.05
1234789-HpCDF	0.02
OCDD	0.05
OCDF	0.03

Thermo SCIENTIFIC

Download the complete application note

Pesticides, PAH, and Phenols by GC-MS/MS

Methodology

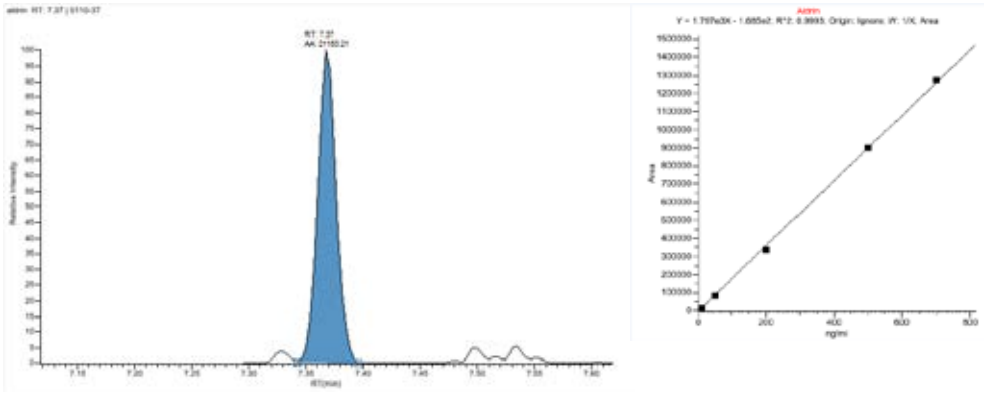
GC method: 100 °C (1 min); 40 °C/min; 320 °C (3 min).
Injector PTV: 60 °C (0.1 min); 14.5 °C/sec; 280 °C (1 min);
2 µl, 1 min splitless.

TSQ series system Timed SRM mode

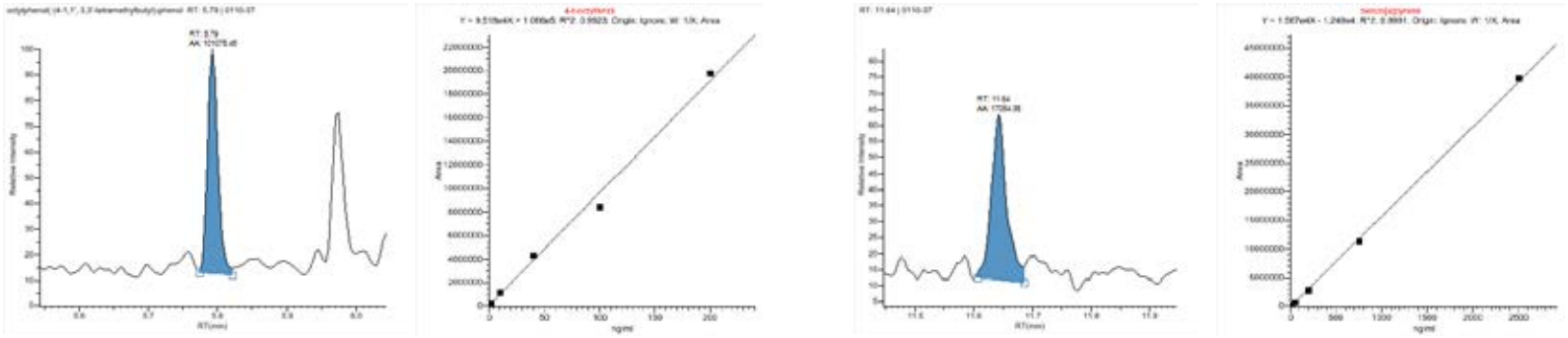
Source temperature 280 °C

Column
TraceGOLD TG-5SilMS 20 mm x 0.18 mm x 0.18 µm
(P/N 26096-5780)

Liner Siltek Baffled (P/N 453T21210)



Aldrin at 0.4 pg in river water sample and cal curve, r^2=0.9993



Octylphenol at 0.4 pg in river water, cal curve, r^2= 0.9923

Benzo(a)pyrene at 0.4 pg in river water; cal curve, r^2=0.9991

Thermo SCIENTIFIC

Combined Pesticides, PAH, and Phenols: Results

Compounds	2013/39/EU		IDL absolute amount injected in pg	Compounds	2013/39/EU		IDL absolute amount injected in pg
	AA-EQS inland surface water (µg/L)	EQS/3 required limit (µg/L)			AA-EQS inland surface water (µg/L)	EQS/3 required limit (µg/L)	
Alachlor	0.3	0.1	0.3	1,2,3-TCB			0.05
Atrazine	0.6	0.2	1.5	1,2,4-TCB			0.1
Chlorfenvinphos	0.1	0.034	4	1,3,5-TCB			0.1
Chlorpyrifos (ethyl)	0.03	0.01	0.3	Trifluralin	0.03	0.01	0.1
Cyclodiene	∑=0.01	0.0034		Dicofol	0.0013	0.0004	0.5
Aldrin	0.0025	0.0008	0.1	Quinoxyfen	0.15	0.05	0.2
Dieldrin	0.0025	0.0008	0.1	Aclonifen	0.12	0.04	2
Endrin	0.0025	0.0008	0.2	Bifenox	0.012	0.004	2
Isodrin	0.0025	0.0008	1.5	Cybutryne	0.0025	0.00083	0.5
DDT total	0.025	0.0083		Cypermethrin	0.00008	0.00003	2
pp DDT	0.01	0.0033	0.1	Dichlorvos	0.0006	0.0002	0.3
op DDT	0.025	0.0083	0.1	Heptachlor	0.0000002	0.000000067	0.5
pp DDE	0.025	0.0083	0.15	Heptachlorepoxide (Cis and Trans)	0.0000002	0.000000067	2
pp DDD	0.025	0.0083	0.5	Terbutryn	0.065	0.022	0.3
op DDE	0.025	0.0083	0.1	Anthracene	0.1	0.034	0.15
op DDD	0.025	0.0083	0.1	Benzo(a)pyrene	0.00017	0.000057	0.25
Endosulfan a	0.005	0.0017	1.5	Benzo(b)fluoranthene	0.00017	0.000057	0.25
Endosulfan b	0.005	0.0017	2	Benzo(k)fluoranthene	0.00017	0.000057	0.25
Hexachlorobenzene	(MAC) 0.05	0.017	0.08	Benzo(ghi)perylene	0.00017	0.000057	0.5
Hexachlorobutadiene	(MAC) 0.6	0.2	0.02	Indeno(123cd)pyrene	0.00017	0.000057	0.5
Hexachlorocyclohexane	0.02	0.007		Fluoranthene	0.0063	0.0021	0.25
a-HCH			0.2	Naphtalene	2	0.67	0.25
b-HCH			0.2	Pentachlorobenzene	0.007	0.0023	0.15
g-HCH			0.2	Nonylphenol (4-nonylphenol)	0.3	0.1	0.2
d-HCH			0.5	Octylphenol	0.1	0.034	0.08
Simazine	1	0.33	1.2	(4-1.1'. 3.3'-tetramethylbutyl)-phenol			
Trichlorobenzenes	0.4	0.133		Pentachlorophenol	0.4	0.14	2

Download the poster presentation on GC-MS amenable EU WFD compounds

Learn more about analyzing alkylphenoles with GC-MS/MS

Learn more about analyzing pesticides with GC-MS/MS

Learn more about analyzing pyrethroids in water with GC-MS

Thermo SCIENTIFIC

LC-MS System Highlights

The TSQ Quantiva triple quadrupole mass spectrometer exceeds the most stringent analytical requirements for quantitative performance with attogram-level sensitivity, unprecedented usability and exceptional robustness.

- Unprecedented Quantitative Performance Thermo Scientific™ active ion management (AIM™) technology — electrodynamic ion funnel, ion beam guide with neutral blocker, Thermo Scientific™ HyperQuad™ quadrupole mass filter, and active collision cell — enables attogram-level sensitivity.
- Ultrafast selected-reaction monitoring (SRM) of 500 SRM/s, with up to 30,000 definable SRMs, enables quantification of more compounds in less time.
- Easy, robust, and reliable intuitive drag-and-drop method editor software with application templates simplifies method development and operation.
- Thermo Scientific™ Ion Max NG™ ion source makes all gases and voltages automatically on installation for ease of use, while allowing flexible spray position for ultimate performance.

Thermo SCIENTIFIC

Learn more about the benefits of LC-MS/MS for the lab

Recommended LC-MS Configuration

Compound group	LC system	Injection volume (µL)	MS analyzer (Acquisition mode)
Herbicides	Thermo Scientific™ Dionex™ UltiMate™ 3000 EquanMAX Plus	10 (offline) 100 (Large Vol Inj) 1000 (online)	TSQ Endura (SRM)
Insecticides	UltiMate 3000 EquanMAX Plus	10 (offline) 100 (Large Vol Inj) 1000 (online)	TSQ Endura (SRM)
Fungicides	UltiMate 3000 EquanMAX Plus	10 (offline) 100 (Large Vol Inj) 1000 (online)	TSQ Endura (SRM)
Pharmaceuticals	UltiMate 3000 EquanMAX Plus	10 (offline) 2000 (online)	TSQ Quantiva (SRM)
Endocrine disruptors hormones	UltiMate 3000 EquanMAX Plus	50 (offline) 2000 (online)	TSQ Quantiva (SRM)
Perfluorooctane sulfonic acid (PFOS)	UltiMate 3000 EquanMAX Plus	10 (offline) 2000 (online)	TSQ Quantiva (SRM)

Thermo SCIENTIFIC

LC Method

UltiMate 3000 HPLC system

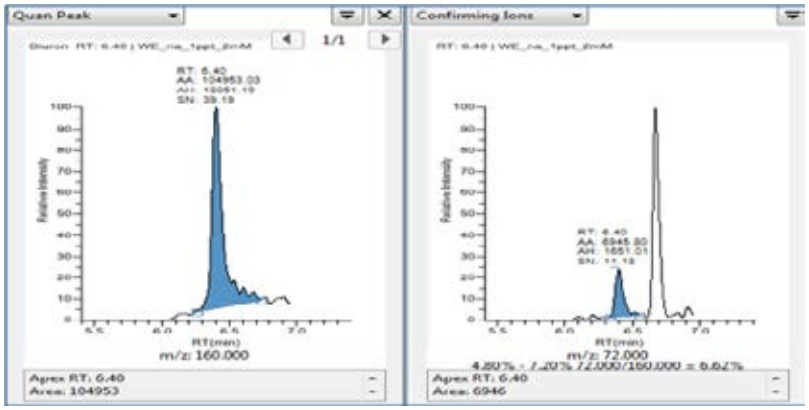
Column Thermo Scientific™ Accucore™ C18 100 x 2.1 mm, 2.6 µm (P/N 17126-102130) at 30 ºC
Mobile phase: (A) 2mM ammonium acetate (B) MeOH
Gradient: Start at 10% B (Hold 1 min), ramp to 90% B in 5min. Ramp to 100% B in 1 min (Hold 1 min). Ramp to 10% B in 0.10 min (Hold 4 min)

Flow rate 0.4 mL/min

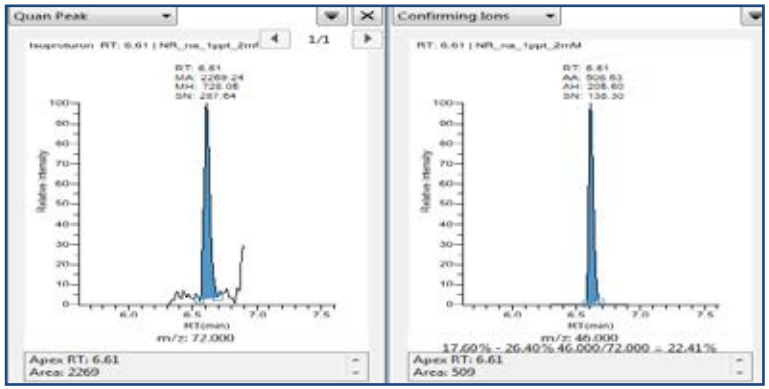
Injection Volume 10 µL

MS Quantiva ESI (SRM)

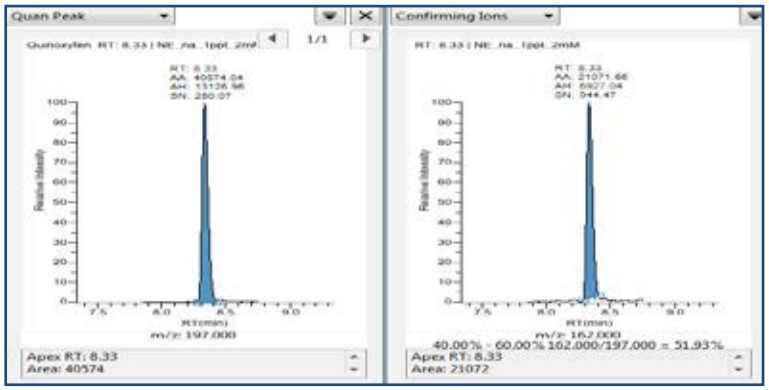
Capillary temperature (°C): 270; vaporizer temperature (°C): 400
sheath gas pressure (Arb): 50; aux gas pressure (Arb): 20
sweep gas pressure (Arb): 1



Diuron at LOD; showing two transitions

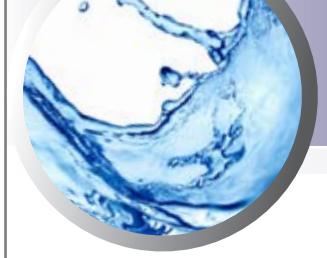


Isoproturon at LOD; showing two transitions



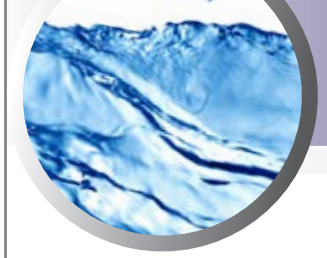
Quinoxyfen at LOD; showing two transitions

Learn how this customer benefits from the Thermo Scientific LC-MS/MS systems



Results

Compounds	2013/39/EU		Required LOD	River	Effluent	Influent
			(pg on column)	LOD	LOD	LOD
	AA-EQS inland surface water (µg/L)	EQS/3		(pg on column)	(pg on column)	(pg on column)
		(µg/L)				
Atrazine	0.6	0.2	2	0.01	0.01	0.01
Chlorfenvinphos	0.1	0.034	0.34	0.01	0.01	0.01
Diuron	0.2	0.067	0.67	0.1	0.1	0.1
Isoproturon	0.3	0.1	1	0.01	0.01	0.01
Simazine	1	0.34	3.4	0.03	0.03	0.01
Quinoxyfen	0.15	0.05	0.5	0.01	0.01	0.01
Terbutryn	0.065	0.022	0.22	0.05	0.01	0.1



Pharmaceuticals by LC-MS/MS

LC Method

UltiMate 3000 HPLC system

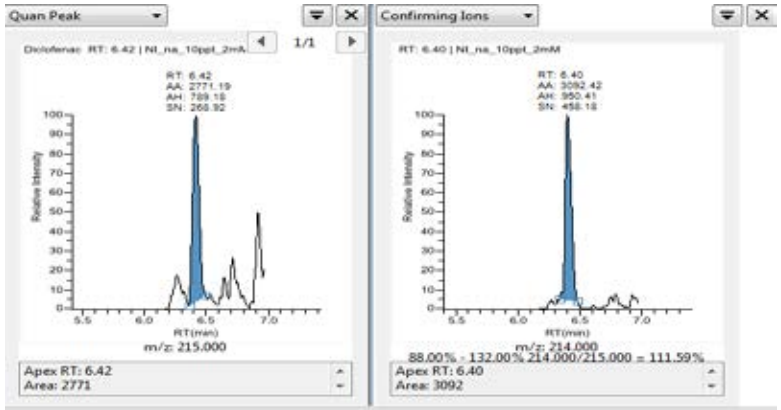
Column Accucore C18 100 x 2.1 mm, 2.6 µm (P/N: 17126-102130) at 30 ºC

Mobile phase (A) 2mM ammonium acetate (B) MeOH
Gradient: Start at 10% B (Hold 1 min), ramp to 90% B in 5 min. Ramp to 100% B in 1 min (Hold 1 min). Ramp to 10% B in 0.10 min (Hold 4 min)

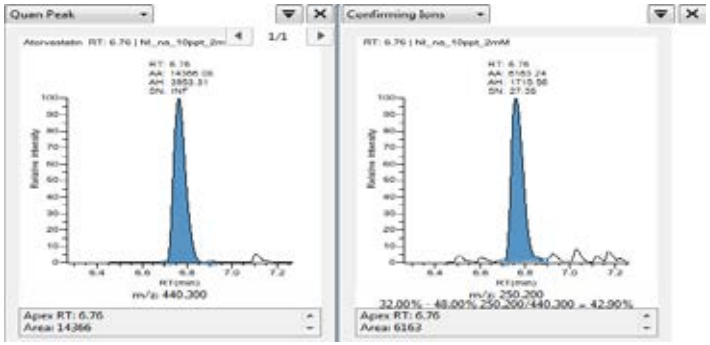
Flow rate 0.4 mL/min

Injection volume 10 µL

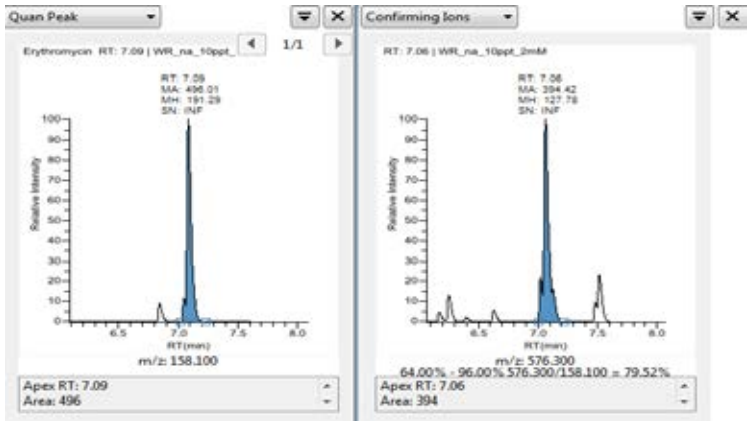
MS Quantiva ESI (SRM)
Capillary temperature (°C): 270; vaporizer temperature (°C): 400
Sheath gas pressure (Arb): 50; aux gas pressure (Arb): 20
Sweep gas pressure (Arb): 1



Diclofenac



Atorvastatin



Erthromycin

Thermo SCIENTIFIC

Download application note on analysis of basic and acidic pharmaceutical compounds

Compounds	CIP 2		River LOD	Effluent	Influent
	Required LOD (µg/L)	LOD In pg	(pg on column)	(pg on column)	(pg on column)
Diclofenac (WFD)	0.01	0.1	0.03	0.1	0.03
Ibuprofen	0.01	0.1	1	0.8	0.8
Atorvastatin	0.01	0.1	0.05	0.05	0.05
ortho-hydroxyatorvastatin	0.01	0.1	0.05	0.1	0.1
para-hydroxyatorvastatin	0.01	0.1	0.05	0.1	0.1
Propanolol	0.01	0.1	0.4	0.2	0.2
Atenolol	0.01	0.1	0.2	0.15	0.1
Amoxicillin	Not on draft - March 2014		1	1	1
Erythromycin	0.1	1	0.6	0.15	0.15
Norerythromycin	0.1	1	Standard not available		
Azithromycin	0.005	0.05	2	tbd	0.4
Clarithromycin	0.01	0.1	0.1	0.1	0.03
Ciprofloxacin	0.01	0.1	1	tbd	tbd
Ranitidine	0.1	1	0.3	0.1	0.1
Carbamazepine	0.1	1	0.01	0.1	0.1
10,11-epoxycarbamazepine	0.1	1	0.01	0.1	0.04
Sertraline	0.01	0.1	0.5	1	0.1
Norsertraline	0.01	0.1	0.5	1	0.1
Fluoxetine	0.01	0.1	0.15	0.1	0.1

Phenols and Triazoles with LC-MS/MS

LC Method

UltiMate 3000 HPLC system

Column Accucore C18 100 x 2.1 mm, 2.6 µm (P/N 17126-102130) at 30 ºC

Mobile phase (A) 2mM ammonium acetate (B) MeOH

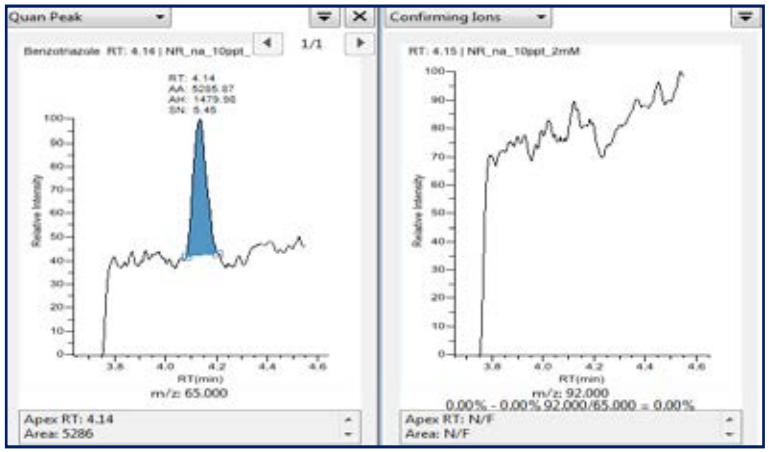
Gradient Start at 10% B (Hold 1 min), ramp to 90% B in 5min. Ramp to 100% B in 1 min (Hold 1 min). Ramp to 10% B in 0.10 min (Hold 4 min);

Flow rate 0.4 mL/min

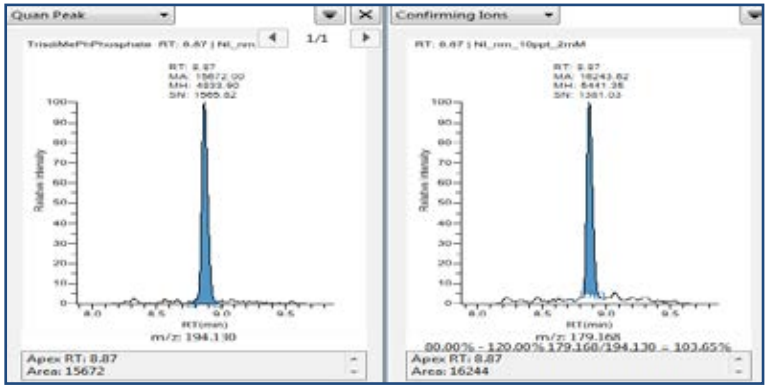
Injection volume 10 µL

MS Quantiva ESI (SRM)

Capillary temperature (°C): 270; vaporizer temperature (°C): 400
Sheath gas pressure (Arb): 50; aux gas pressure (Arb): 20
Sweep gas pressure (Arb): 1



Benzo triazole at LOD; showing two transitions



Tris(isopropylphenyl)phosphate at LOD; showing two transitions

Compounds	CIP 2				
	Required LOD (µg/L)	Required LOD pg on column	River LOD pg on column	Effluent pg on column	Influent pg on column
Nonylphenol/4-nonylphenol	0.1	0.4	GC-MS	GC-MS	GC-MS
Octylphenols	0.1	0.14	GC-MS	GC-MS	GC-MS
4-nonylphenol triethoxylate	0.1	0.4	0.2	0.1	0.1
Tris(isopropylphenyl)	0.01	-	0.1	0.1	0.1
Phosphate	0.01		0.1	0.1	0.1
Benzotriazole	0.002	-	0.1	-	0.1

Thermo SCIENTIFIC

Perfluorooctanesulfonic Acid (PFOS) by LC-MS/MS

LC Method

UltiMate 3000 HPLC system

Column Accucore C18 100 x 2.1 mm, 2.6 µm (P/N 17126-102130) at 30 ºC

Mobile phase (A) 2 mM ammonium acetate (B) MeOH
Gradient: Start at 10% B (Hold 1 min), ramp to 90% B in 5min. Ramp to 100% B in 1 min (Hold 1 min). Ramp to 10% B in 0.10 min (Hold 4 min);

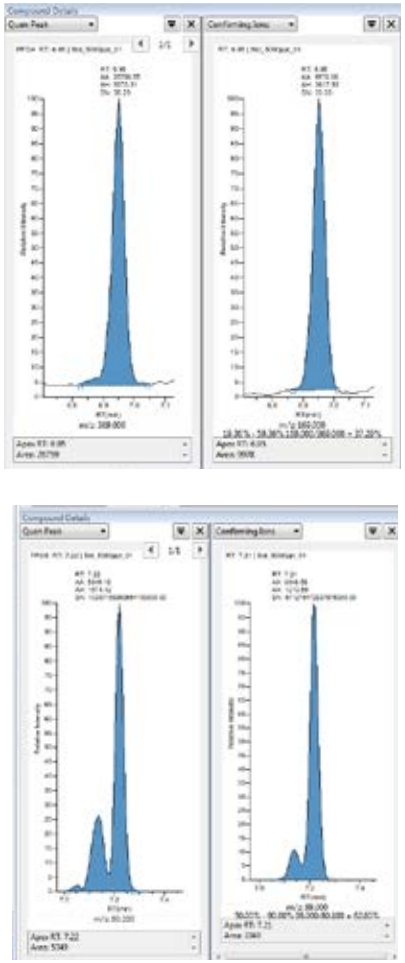
Flow rate 0.4 mL/min

Injection volume 10 µL

MS Quantiva ESI (SRM)
Capillary temperature (°C): 270; vaporizer temperature (°C): 400
Sheath gas pressure (Arb): 50; aux gas pressure (Arb): 20
Sweep gas pressure (Arb): 1

To reduce the contamination coming from the system we recommend to replace parts of the UHPLC system and introduce a trap column before the injector:
Thermo Scientific™ Hypersil GOLD™ column
50 x 2.1 mm x 3 µm (P/N 25003-052130)

Compounds	2013/39/EU			LODs
	AA-EQS inland surface water (µg/L)	AA-EQS Other surface water (µg/L)	Biota µg/kg	(µg/L)
PFOS	0.00065	0.00013	9.1	0.1
PFOA	-	-	-	0.1



PFOS linear and branched at 5 µg/l; showing two transitions

Learn how this customer benefits from the Thermo Scientific LC-MS/MS

Hexabromocyclododecane (HBCDD) by LC-MS/MS

LC Method

UltiMate 3000 HPLC system

Column Accucore C18 100 x 2.1 mm, 2.6 µm (P/N 1726-102130) at 35 ºC

Mobile phase (A) 2mM ammonium acetate B) MeOH
Gradient: Start at 0% B, ramp to 100% B in 10 min (Hold 2 min). Ramp to 0% B in 0.10 min (Hold 3.3 min)

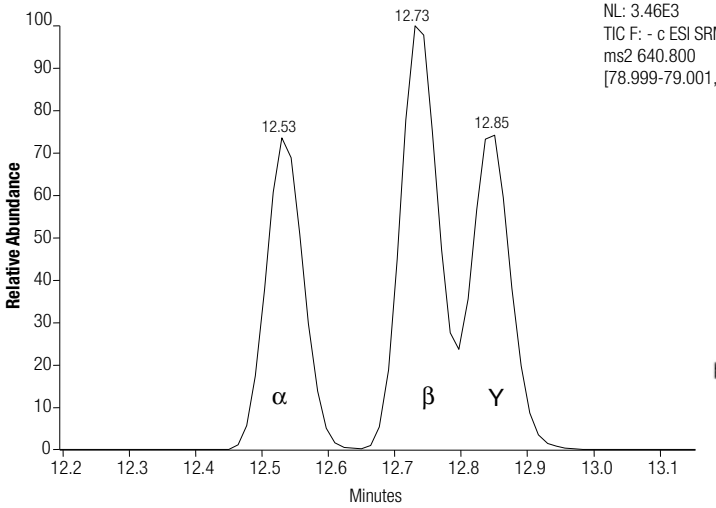
Flow rate 0.3 mL/min

Injection volume 10 µL

MS Quantiva ESI (SRM)
Capillary temperature (°C): 280; vaporizer temperature (°C): 120
Sheath gas pressure (Arb): 50; aux gas pressure (Arb): 15
sweep gas pressure (Arb): 1

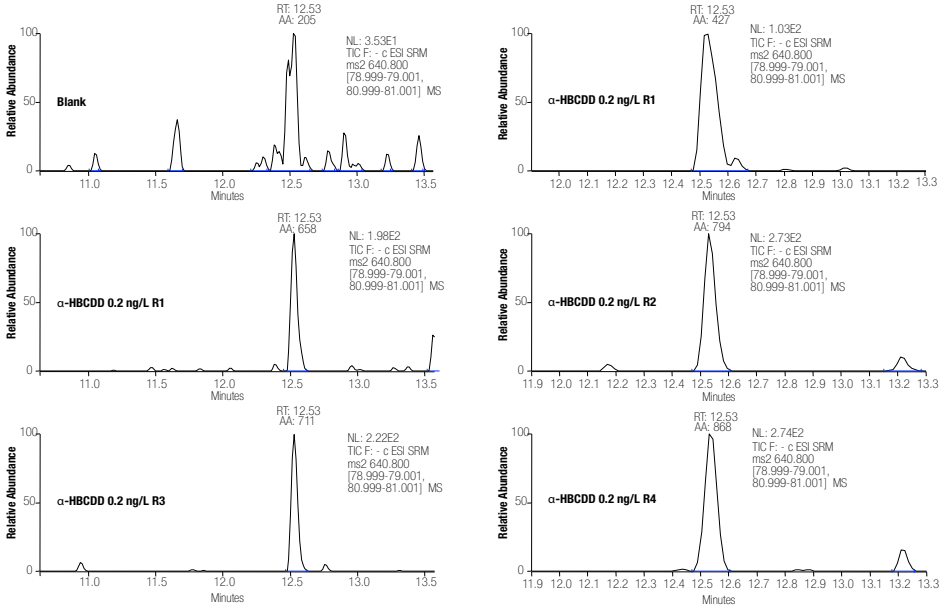
Compounds	2013/39/EU			LODs	
	AA-EQS inland surface water (µg/L)	AA-EQS other surface water (µg/L)	Biota µg/kg	(required)	achieved
HBCDD	0.0016	0.0008	167	2000	2000

Results



Gradient elution using 2mM ammonium acetate and MeOH
Accucore C18 - 100 x 2.1mm, 2.6 µm

HBCDD: α, β, γ isomer separation



Thermo SCIENTIFIC

Steroid Analysis by LC-MS/MS

LC Method

UltiMate 3000 HPLC system

Column Hypersil GOLD 50 x 2.1 mm, 1.9 µm (P/N 25002-052130) at 30°C

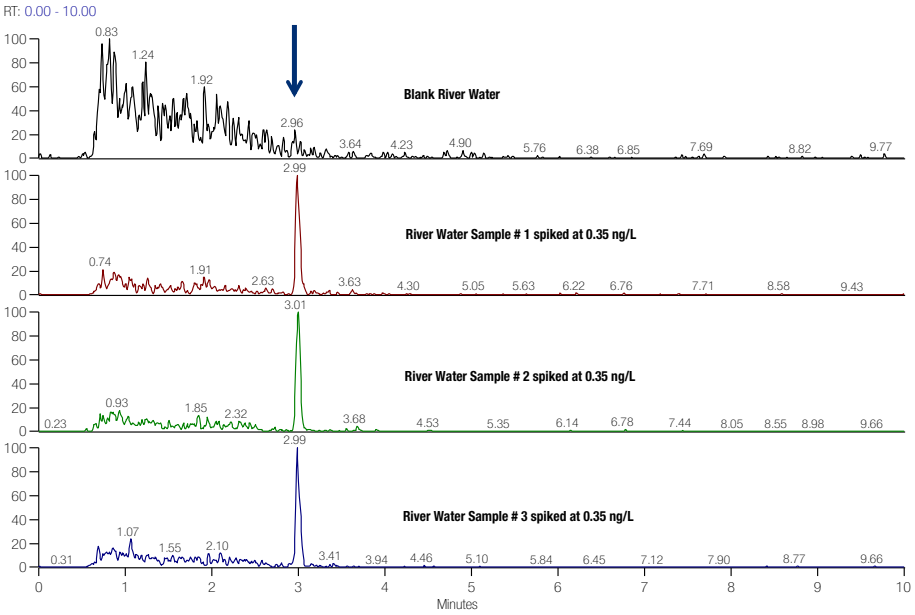
Mobile phase (A) 0.02 % ammonium hydroxyde in H_20
(B) 0.02 % ammonium hydroxyde in MeOH

Flow rate 0.4 mL/min

Injection volume 50 µL

MS Quantiva ESI (SRM)

Capillary temperature (°C): 320; vaporizer temperature (°C): 350
Sheath gas pressure (Arb): 50; aux gas pressure (Arb): 40
sweep gas pressure (Arb): 1



Compounds	CIP 2	COM(2011)876	2013/39/EU	LOD influent/ effluent
	Required LODs	AA-EQS inland surface water (ng/L)	AA-EQS inland surface water	(ng/L)
	Influent/effluent			
	(ng/L)			
17-alpha-ethinylestradiol (EE2)	0.03	0.35	Watch list	100
17-beta-estradiol (E2)	0.3	4	Watch list	10
Estrone	1	-	-	15

ICP-MS System Highlights

The Thermo Scientific™ iCAP™ Q ICP-MS system has been developed with groundbreaking technology to enable advanced high-performance analysis combined with total reliability and ultra-flexibility.

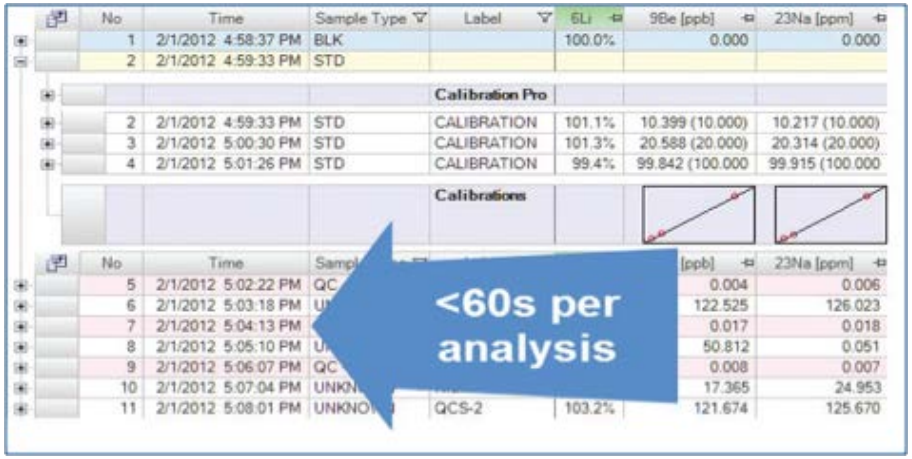
- Ergonomically designed quadrupole ICP-MS system with smallest footprint
- Innovative RAPID (Right Angle Positive Ion Deflection) lens technology (90° ion optics) for separation of ions and neutrals
- Innovative interface with skimmer cone featuring unique, user-replaceable inserts mounted behind the cone tip to minimize memory effects
- The only ICP-MS system to include proprietary QCell technology combining proven He KED interference reduction
- High-performance quadrupole analyzer pumped by a novel split flow turbo pump backed by a single rotary pump
- New, simultaneous analog/PC detector with real time multi-channel analyzer electronics provides >9 orders of dynamic range suitable for both steady state and transient signal analysis
- The combination of an advanced inlet system, the RAPID lens and QCell provide enhanced performance for outstanding signal to background
- New, exceptionally robust RF generator with fast dynamic frequency impedance matching for high plasma stability without need for a shield

Thermo SCIENTIFIC

Click here to find out more about the iCap Q ICP-MS system

Applications

Peristaltic pump speed	40 rpm
Pump	tubing orange/green tubing for both
Carrier	(sample) and internal standard
Nebulizer	PFA-ST
Interface	cones Nickel
RF Power	1550 W
Cool gas flow	14 L/min
Auxiliary gas flow	0.8 L/min
Nebulizer gas flow	0.97 L/min
Number of sweeps	20
Dwell Times	0.001 - 0.02 ms
Data points per isotope	1
Replicates per analysis	3
Signal stabilization time	15 s
FAST sample loop	0.5 mL
FAST uptake time	3 s
FAST rinse time (dual stations)	1+3 s
Total analysis time (sample to sample)	56 s



Fast analysis for all compounds is achieved

Element	Lowest required AA-EQS (in µg/L)	Method detection limit shown in AN43127 (in µg/L)
Cd	≤ 0.08	0.017
Pb	1.2	0.007
Hg	0.07	0.011
Ni	4	0.014

References

Heinz Singer et al. Determination of biocides and pesticides by on-line solid phase extraction coupled with mass spectrometry and their behavior in wastewater and surface water published at Environmental Pollution – 2010 (158) 3054-3064

Liza Viglino et al. On-line solid phase extraction and liquid chromatography/tandem mass spectrometry to quantify pharmaceuticals. pesticides and some metabolites in wastewaters. drinking and surface waters published at Journal of Environmental Monitoring – 2008 (10) 482-489

Laszlo Hollosi et al. Analytical sensitivity of direct injection LC-MS methods for the compounds of EU Water Frame Work directive presented at SETAC Glasgow 2013

Marina Gorga et al. Multi-residue analytical method for the determination of endocrine disruptors and related compounds in river and waste water using dual column liquid chromatography switching system coupled to mass spectrometry published at Journal of Chromatography A – 2013 (1295) 57-66

Rebeca López-Serna et al. Direct Analysis of pharmaceuticals, their metabolites and transformation products in environmental waters using on-line TurboFlow chromatography-liquid chromatography-tandem mass spectrometry published at Journal of Chromatography A – 2012 (1252) 115-129

Marta Llorca et al. Analysis of perfluoroalkyl substances in waters from Germany and Spain published at Science of the Total Environment – 2012 (431) 139-150

Salima Idder et al. Quantifitative on-line pre-concentration-liquid chromatography coupled with tandem mass spectrometry method for the determination of pharmaceutical compounds in water published at Analytica Chimica Acta– 2013 (805) 107-115

Thermo SCIENTIFIC

References

Sara Valsecchi et al. Optimization of an on-line SPE-UHPLC/MS/MS method for the analysis of perfluoroalkylated acid in Italian drinking and surface waters presented at SETAC Glasgow 2013

Technical note 148 : Automated extraction and determination of human hormones in drinking water using solid-phase extraction and HPLC with UV detection

Application note 52389 – Consolidated GC-MS/MS analysis of OCPs, PAHs, and PCBs in environmental samples

Application note 51899 – Latest advances in the analysis of volatile organic compounds by single quadrupole GC-MS

Technical note 10319 – Simplifying complex multi-residue pesticide methodology in GC-MS/MS

Technical note 52099 – The determination of organotins in water using triple quadrupole GC-MS/MS

Application note 30098 – DFS-analysis of brominated flame retardants with high resolution GC/MS

Application note 43098 – Speciation analysis of Cr (III) and Cr (IV) in drinking waters using anion exchange chromatography coupled to the Thermo Scientific iCAP Q ICP-MS

Application note 40849 – Lead in natural waters by graphite furnace atomic absorption using EPA Method 200.9

Application note 40851 – Arsenic in natural waters by graphite furnace atomic absorption using EPA Method 200.9

Application note 40853 – Environmental series - US EPA Method 200.7 using the iCAP 6500 Duo ICP

Thermo SCIENTIFIC

Table of Contents

www.thermoscientific.com/water-analysis

Thermo Fisher Scientific, Sunnyvale, CA USA is ISO 9001: Certified.

Africa +43 1 333 50 34 0
Australia +61 3 9757 4300
Austria +43 810 282 206
Belgium +32 53 73 42 41
Brazil +55 11 3731 5140
Canada +1 800 530 8447
China 800 810 5118 (free call domestic)
400 650 5118

Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland +358 10 3292 200
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9494
Italy +39 02 950 591

Japan +81 6 6885 1213
Korea +82 2 3420 8600
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Norway +46 8 556 468 00

Russia/CIS +43 1 333 50 34 0
Singapore +65 6289 1190
Sweden +46 8 556 468 00
Switzerland +41 61 716 77 00
Taiwan +886 2 8751 6655
UK/Ireland +44 1442 233555
USA +1 800 532 4752

Thermo SCIENTIFIC

A Thermo Fisher Scientific Brand

XX71741EN 0815S