

Analyzing the GCMS amenable compounds in water matrices according to the European Water Framework directive (2013/39/EU)

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Overview

Purpose: An overview of the results of GC amenable compounds is given for EU 2013/39/EU

Methods: For the volatile compounds headspace GCMS was used; for the semivolatiles liquid liquid extraction was applied followed by GCMSMS detection.

Results: The detection limits are calculated by standard deviation and there are some linearity examples. Not all compounds are listed in this poster, but a full list is available.

Introduction

The European Water Framework directive is a directive which commits all member states to actively control and monitor all the water bodies in the various member states on a large list of environmental contaminants. The compound levels are expressed as Environmental Quality Standard or EQS and the annual average (AA) and the Maximum Allowable Concentration (MAC) is given. The actual required quantitation limits per compound will be expressed by dividing the EQS by a factor of three. This factor was obtained following a short discussion with various environmental institutes in Europe.

The new directive 2013/39/EU will be discussed; this is amending the 2008/105/EC directive. This directive contains low limits for some of those contaminants. The compounds have been divided into several groups which will be discussed separately below.

1. Volatile Organic Compounds

Sample preparation

- 10 ml of lake water
- 2g NaCl

Headspace conditions

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

Column

Rtx®-VMS, 20 m, 0.18mmID, 1.00 µm

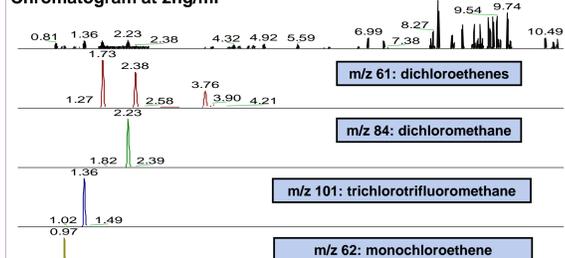
Methodology

GC method: 30° C (4min);
18° C/min; 100° C (0min);
40° C/min; 230° C (3min).
Injector: 200° C

ISQ LT MS: TimedSIM mode

Source temperature: 250° C

Chromatogram at 2ng/ml



compound	LOQ in µg/L	EQS/3 in µg/L	passed
Dichloromethane	0.07	6.7	passed
Trichloromethane	0.07	0.8	passed
Carbontetrachloride	0.05	4	passed
benzene	0.1	3.3	passed
1,2 dichloroethane	0.1	3.3	passed
Trichloroethylene	0.05	3.3	passed
Tetrachloro-ethylene	0.05	3.3	passed

Carbontetrachloride in lake water at 0.1 µg/L and cal curve r² = 0.9998

2. Polybrominated diphenyl ethers

Methodology

GC method: 120° C (1min); 20° C/min; 320° C (5min).
Injector PTV: 80° C (0.1min); 10° C/sec; 300° C (6min);
14.5° C/sec; 340° C (20min);
2 min splitless.

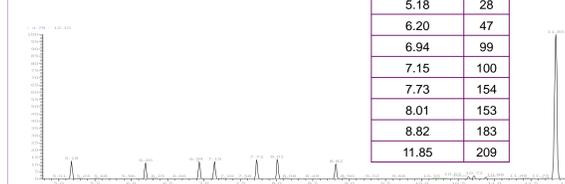
GCQuantum Ultra: TimedSRM mode and/or Cineg with NH₄

Source temperature: 260° C

Column:

TG5HT, 15m, 0.25mmID, 0.1µm

Chromatogram



Comp.	DL in pg abs.	DL in pg abs.
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

BDE100, BDE99 and BDE 85 at 0.4pg abs. EI SRM 563.65>403.81

BDE100, BDE99 and BDE 85 at 0.4pg abs. Cineg SIM m/z79

3. Organotin Compounds

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.

Column

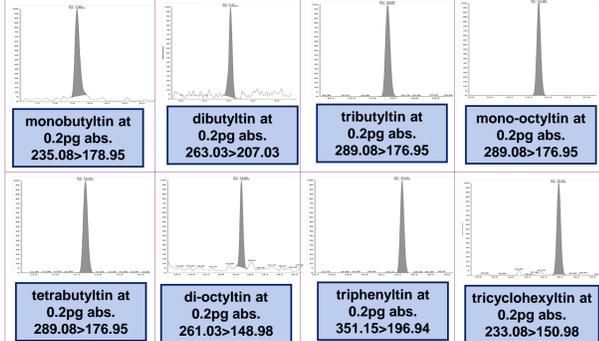
TG5MS; 30m, 0.25mmID, 0.25µm

Methodology

GC method: 45° C (2min);
55° C/min; 175° C (0min);
35° C/min; 300° C (2min).
Injector PTV: 50° C (0.1min);
8° C/sec; 280° C (1min);
350° C (11 min, clean flow 50m/min);
1 min splitless.

TSQ8000: TimedSRM mode

Source temperature: 250° C



Compound	LOQ in µg/L	EQS/3 in µg/L	passed
tributyltin	0.00007	0.00007	passed

4. Polychlorinated alkanes

Methodology

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

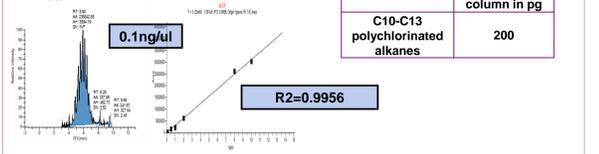
TSQ8000: TimedSRM mode

Source temperature: 280° C

Column:

TG5MS; 20m, 0.18mmID, 0.18µm

Chromatogram and calibration curve



5. Remaining semi volatiles

The remaining compounds consist of various pesticides, PAH, phthalates and alkylphenol compounds. Below just a selection of these will be depicted. The complete list of remaining compounds are extracted together and determined in one run only. Limits of quantitation have been determined by spiking river water at low levels; injecting ten times and multiplying the standard deviation times three. The water was sampled from the belgian "Mark" river.

Sample preparation

- 100 mL water sample
- Add 10g NaCl
- Extraction with 10ml of dichloromethane;
- Shake vigorously for 20min.;
- dry the extract with Na₂SO₄
- evaporate to 1ml;
- 2 µL injection volume.

Column

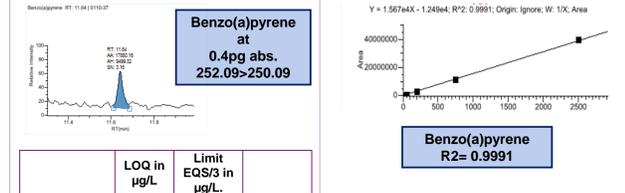
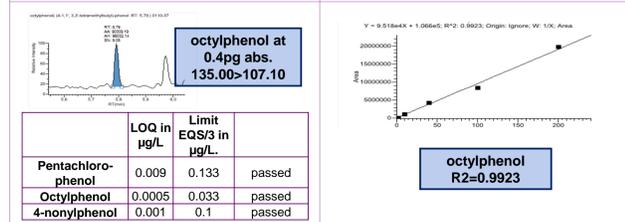
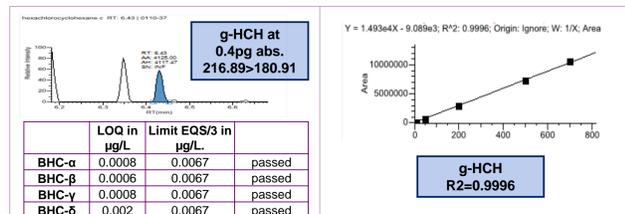
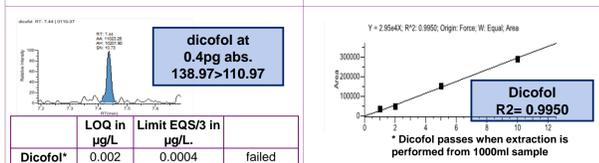
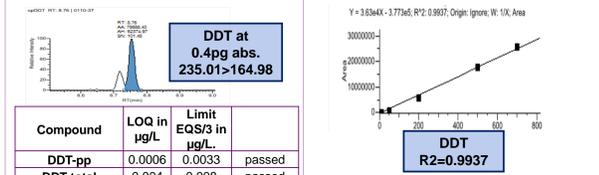
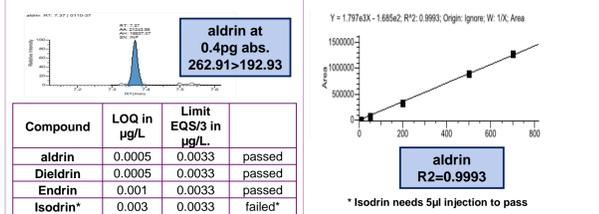
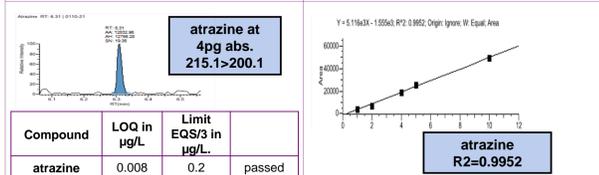
TG5MS; 20m, 0.18mmID, 0.18µm

Methodology

GC method: 65° C (2min);
40° C/min; 200° C (0min);
15° C/min; 320° C (3min).
Injector PTV: 60° C (0.1min);
5° C/sec; 300° C (1min);
330° C (1min)
1 min splitless.

TSQ8000: TimedSRM mode

Source temperature: 350° C



Compound	LOQ in µg/L	Limit EQS/3 in µg/L	passed
naphthalene	0.001	0.67	passed
anthracene	0.001		passed
Fluoranthene	0.001	0.0021	passed
Benzo(a)-Pyrene**	0.001	0.000057	failed
Benzo(b)-Fluoranthene	0.001	*	*
Benzo(k)-Fluoranthene	0.001	*	*
Benzo(ghi)-perylene	0.001	*	*
Indeno-pyrene	0.002	*	*

Conclusions

- For analyzing the volatile compounds in the EU WFD a simple headspace approach is more than sufficient to reach the required detection limits;
- More research is needed for :
 - heptachloro - and its epoxides
 - Cypermethrin
 - These compounds will need an alternative sampling like passive sampling with SPE
- The lowest detection limits for the semivolatile compounds can be achieved using SRM and triple quad technology. For the BDE compounds the lowest levels are achieved using negative chemical ionization; however for water matrix only;
- A large scope of the compounds can be performed using one method only; extraction and injection.

References

- EU directive 2013/39/EU
- Stockholm Convention on persistent organic pollutants (POPs) STARTUP GUIDANCE for the 9 new POPs (general information, implications of listing, information sources and alternatives) December 2010
- Retention-time database of 126 polybrominated diphenyl ether congeners and two Bromkal technical mixtures on seven capillary gas chromatographic columns Peter Korytar, Adrian Covacic, Jacob de Boer, Anke Gelbind, Udo A.Th. Brinkman
- Analytical Methods for the new proposed Priority Substances of the European Water Framework Directive (WFD) Revision of the Priority Substance List (2012) Robert Loos European Commission - DG Joint Research Centre (JRC) Institute for Environment and Sustainability (IES) Water Resources Unit (H01)Ispra.

Remark

Dioxin analysis in the EU WFD is limited to biota and not embedded in the scope of this poster

Application note on dioxins: AN 52266

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