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GC-ICP-MS reference methodology to quantify polybrominated flame retardants in environmental waters relevant to the European Water Frame Directive.
European Metrology Research

- Traceable measurements for monitoring critical pollutants under the European Water Framework Directive
  - Duration 10/2011 to 09/2014
  - Participants: BAM, BRML, IJS, JRC, LGC, LNE, PTB, SYKE, TUBITAK UME, UBA, ISPRA, REG(HZG)
  - Target analytes: TBT, PAH, PBDE

- LGC involvement in ENV08 WFD
  - WP2 – Development of a validated measurement procedure for PBDE in whole water samples at a concentration level required by the WFD
  - WP4 – Advanced analytical platforms for monitoring the interaction and partitioning of pollutants in environmental aquatic compartments
Metrological aims

• Reference method for determination of PBDE in whole (non-filtered) water
  – Congeners of interest – PBDE 28, 47, 99, 100, 153, 154
  – Required LOQs – $\Sigma$ (6 PBDEs) $\leq$ 0.15 ng/L in whole water
  – Measurement uncertainty (95 % confidence) $\leq$ 50 % at EQS

• Systematic study of the interaction and partitioning of pollutants by field flow fractionation techniques
  – Distribution of the pollutants among fractions of different size and type;
  – Elucidation of interactions / partitioning
  – Mass balance data for the size based distribution
Development of a validated measurement procedure for PBDE in whole water samples at a concentration level required by the WFD

Advanced analytical platforms for monitoring the interaction and partitioning of pollutants in environmental aquatic compartments
Chromatographic separation of the target PBDEs

• Short program
  – Species separated in 3.5 min
  – Sample throughput – 4 samples per hour
  – Baseline separation of the target congeners
  – Suitable for pre-screening for “above/below EQS”

• Long program
  – Species separated in 28 min
  – Sample throughput – 0.5 samples per hour (2h/sample)
  – Separation of up to 180 PBDE congeners*
  – Suitable for more accurate congener identification in case of PBDE concentrations > EQS level

Chromatographic separation of the target PBDEs

Long GC separation method

Short GC separation method
Chromatographic separation / detection of the target PBDEs by HPLC-ICP-MS

NIST 2257
1+19 diluted in n-hexane
Chromatographic separation / detection of the target PBDEs by HPLC-ICP-MS

NIST 2257
1+19 diluted in n-hexane
Limits of detection for target PBDEs

- Limits of detection with **external calibration**
  - Instrumental detection limits – below 1ng/ml Br; calculated as 3 X noise band width, expressed concentration based on external calibration by peak height
  - Similar for both Br isotopes (\(^{79}\text{Br}, {81}\text{Br}\))
  - Similar for both Q-ICP-MS and SF-ICP-MS detectors
  - PBDE based IDLs ~ 1ng/ml
  - Current method detection limits – 25 fg/mL as Br
  - Current preconcentration factor – 40 000 X
Detection limits of the target PBDEs

- Instrument detection limits – Q-ICP-MS

![Graph showing detection limits of PBDEs with 1.56 ng/ml Br as reference.](image-url)
Detection limits of the target PBDEs

- Instrument detection limits – SF-ICP-MS

![Graph showing detection limits with peaks at various times and signal levels]

1 ng/ml Br
Preconcentration Procedure
Recoveries

• Vary with the congener
• Consistent with relatively large uncertainty
• 3 samples, each spiked with ~ 3 ng/L of each congener:
Finnish River Water Analysis

Procedural blank vs Standards blend

ENV08 spiked vs ENV08

C = 1.25 ng/L
R = 72 to 100%
Thames River Water Analysis

PBDE 47 0.05 ng/L
PBDE 99 0.2 ng/L
Development of a validated measurement procedure for PBDE in whole water samples at a concentration level required by the WFD

Advanced analytical platforms for monitoring the interaction and partitioning of pollutants in environmental aquatic compartments
Fractionation of environmental water samples and NOMs

• Method development samples – Finnish river water, Thames River water, Suwannee River NOM and Nordic Reservoir NOM(IHSS), HA and HA-Na (Sigma)
• Size/mass calibrants – 1, 300, 1000 kDa PSS; Spherical S-PS 100, 200 nm; NIST gold nano-particles 10, 30, 60 nm spheres
• Detection:
  - Online → UV-MALS-ICPMS for size and elemental composition
  - Offline → GC-SF-ICPMS for PBDEs association / distribution on nano-particles
Fractionation of Finnish Water Sample

![Graph showing signal vs. time for various elements]

- Al27
- Mn55
- Fe57
- Cu63
- Cu65
- Zn66
- Sn118
- Sn119
- Sn120
- Br79
- Br81

Signal [kcps] vs. Time [min]
Fractionation of Thames River Water Samples

The diagrams depict the signal strength over time for various elements in Thames River water samples. The elements include Al27, Mn55, Fe57, Cu63, Cu65, Zn66, Sn118, Sn119, Sn120, Br79, and Br81. The graphs show the signal strength in counts per second (cps) as a function of time in seconds. The data suggests a distinct pattern for each element, indicating varying degrees of fractionation in the river samples.
Calibrant Fractograms

100 ppm 1, 300, 1000 kDa PSS in 0.9% NaCl, 5 mM NH₄NO₃ carrier

UV Signal at 236nm [V]

0 10 20 30 40 50 60 70 80 90 100

Time [min]

0.30

0.25

0.20

0.15

0.10

0.05

0.00

-0.05

-0.10

-0.15

-0.20

-0.25

-0.30

-0.40

-0.45

-0.50

-0.55

-0.60

-0.65

-0.70

-0.75

-0.80

Nist Au 10, 30, 60 nm spheres

UV Signal at 254nm [V]

Field release

100, 200nm S-PS in 5 mM NH₄NO₃ carrier

100 nm

200 nm

Field release

236 nm

254 nm

Signal [kcps]
Size Calibrants Fractograms and MALS Size Estimation

- MALS calculated diameters 92 nm and 212 nm
Fractograms of HA-Na and PBDE spiked HA-Na

1.0 ppm HA-Na in 5 mM NH4NO3

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

Time [min]

Signal [kcps]

Br 79  Br 81

1.00 ppm HA-Na + 250 ppb PBDE

0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0

Time [min]

Signal [kcps]

Br 79  Br 81
ASF^4 offline GC-SF-ICP-MS analysis of HA-Na

- 2 x 1 ml HA-Na 100ppm, 30 ml fraction, 50µl extract volume
ASF^4 offline GC-SF-ICP-MS analysis of HA-Na

- 2 x 1 ml HA-Na 100 mg/L + 500 ng/ml PentaBDE (DE-71)
Future prospective

- Improve the limits of detection to reach the WFD requirements
- Employ $^{81}$Br isotopically enriched PBDE species for quantification of PBDEs in natural water samples
- Use FFF in combination with conventional fractionation techniques to better characterize the interaction and partitioning of PBDEs in water samples, rich in organic and inorganic colloids.
- Validate the methodology and prepare uncertainty budget for quantification of PBDEs in natural waters after LLE, species specific double ID-ICP-MS quantification
Acknowledgements:

The authors are grateful to EMRP and NMO for sponsoring this research, to Volker Nischwitz, who helped with the method development for WP2 and WP4, to Christopher Hopley for his highly valued advice in GC method development and troubleshooting, and last but not least to all our partners and colleagues, without whom this research wouldn’t be possible.

Thank you for your attention…