High-resolution continuum-source molecular absorption spectrometry (HR-CS-MAS) – A novel approach for total organofluorine determination

Lara Schultes,[1] Urs Berger, [1,2] Marcus Frenzel,[3] Jörg Feldmann,[4] Jonathan P. Benskin[1]

[1]Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, Sweden; [2]Department Analytical Chemistry, Helmholtz Centre for Environmental Research – UFZ, Leipzig, Germany; [3]Käppalaförbundet, Lidingö, Sweden[4]; Trace Element Speciation Laboratory (TESLA), Department of Chemistry, Aberdeen University, Scotland, UK

Contact:
lara.schultes@aces.su.se

INTRODUCTION

BACKGROUND

Mass balance studies for evaluating containment and remediation strategies are hampered by the wide range of PFASs and degradation products occurring in the environment, which are not captured by routine, targeted analysis. A recent study by Miyake et al. (2007) has demonstrated that a substantial share of the total organofluorine content in water samples cannot be explained by the most common targeted fluorinated compounds.

OBJECTIVES

1) Assess the applicability of HR-CS-MAS for trace level detection of organofluorine.
2) Determine fraction of organofluorine accounted for by known PFASs at various stages in waste water treatment.

APPROACH

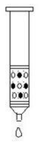
Sample Extraction → CS-MAS: Total F / HPLC-MS/MS → Fluorine mass balance → Identification of new substances?

SAMPLES, EXTRACTION & TARGETS

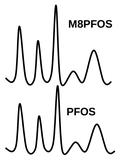
WASTE WATER: influent, effluent and upstream

SLUDGE: primary, excess, thickened, digested, dewatered

Liquid-liquid extraction with MeOH/ACN



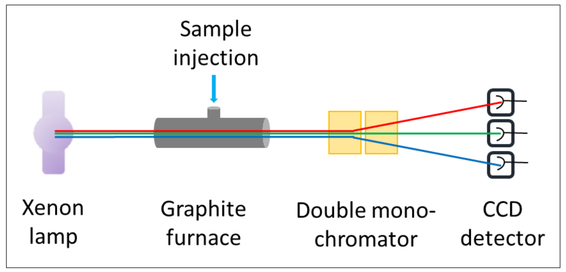
- Weak anion exchange cartridges
- Three sequential elution steps (MeOH/ acidic MeOH/basic MeOH)
  → fractionate organofluorines based on their ionic character



Targeted UHPLC-MS/MS analysis:
50 different fluorinated compounds (PFCAs, PFSAs, FOSAs, FOSAAs, FTSAs, FTCAs, FTUCAs and PAPs)

INSTRUMENTATION

HR-CS-MAS



A sensitive, fluorine-specific method to determine total organofluorine content by converting analytes into gallium fluoride.

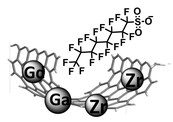
The Xenon lamp provides continuum radiation, of which GaF characteristic absorption line at 211.248 nm is selected with a CCD detector.

High resolution wave length accuracy is achieved by an Echelle double monochromator.

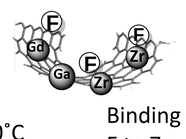
FLUORINE DETECTION

Zirconium and Gadolinium coated graphite tube

Modifier treatment & Sample injection



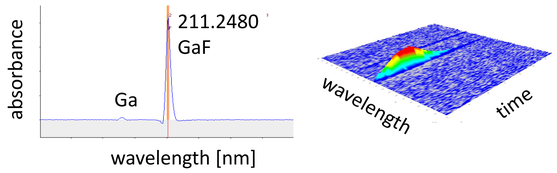
Pyrolysis at 450˚C C-F cleavage



Binding of F to Zr

Atomization at 1300˚C and formation of GaF

Detection of GaF characteristic line at 211.248 nm



RESULTS & DISCUSSION

ASSESSMENT OF INSTRUMENT SPECIFICITY

Figure 1 shows a comparison of inorganic fluoride (NaF) and organic fluorine (PFCAs: C_4-C_{14}, C_{16}, C_{18} and PFSAs: C_4, C_6, C_8, C_{10}) standards of same F-concentration.

Equivalent calibration curve slopes for organic and inorganic fluorine indicates that the method is **fluorine specific** and suggests that NaF can be used as calibration standard.

The LOD is approximately 250 pg F, for a 25 µl injection of a 10 ng/ml standard. For a 500 ml environmental sample concentrated to 4 ml, the method detection limit can be estimated to 80 ngF/L, which translates into 120 ng PFOS/L.

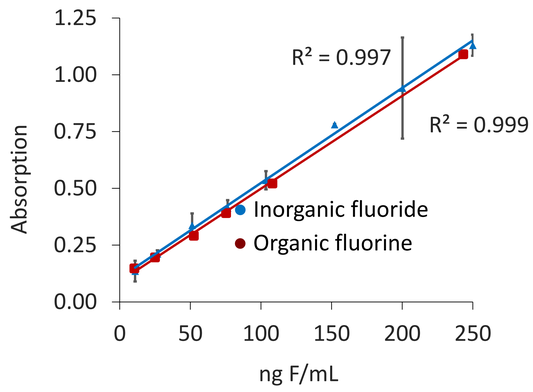


Figure 1: Calibration curve

INSTRUMENTAL OPTIMIZATION

Pyrolysis and atomization temperatures are optimized in order to obtain high sensitivity and equal response for both fluoride and organic fluorine.

Figure 2 depicts the temperature dependence of the pyrolysis efficiency - the slightly different curves for inorganic and organic fluorine can be explained by different sorption behavior to the graphite.

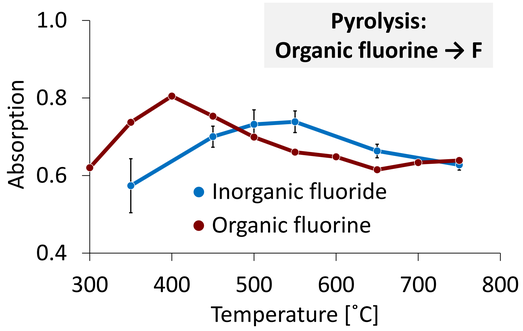


Figure 2: Optimization of pyrolysis temperature

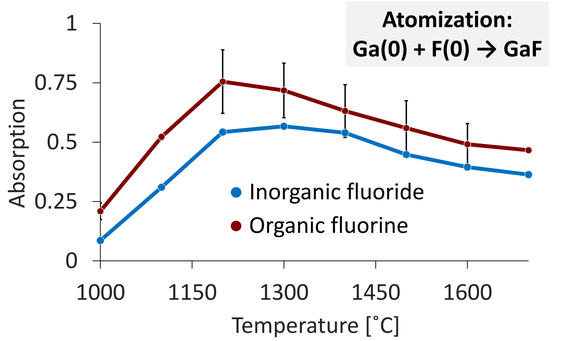


Figure 3: Optimization of atomization temperature

FUTURE OUTLOOK

Mass balance of targeted analysis and total organofluorine content in sludge and water samples

Non-targeted analysis in samples with unexplained F-content

REFERENCES

Miyake et al., J. Chrom. A 2007 1143, 98.
Qin et al., Analytical Chemistry 2012, 84, 6213.
Qin et al., J. Anal. At. Spectrom. 2013, 28, 877

ACKNOWLEDGEMENTS

FORMAS is acknowledged for funding of this project.

PDF

Feel free to download my poster as pdf!