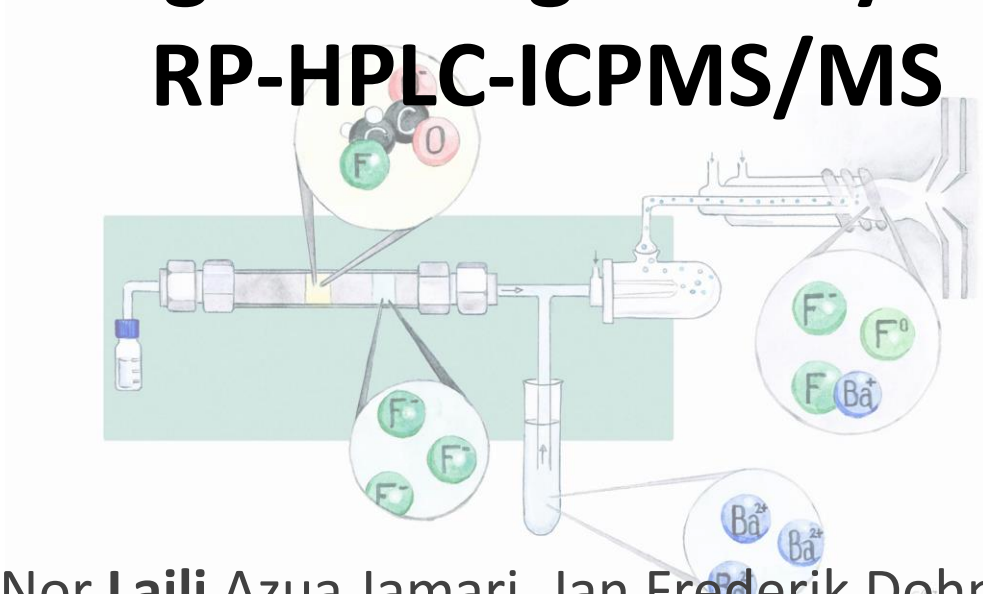
Perfluorinated compounds detection using non-target analysis of RP-HPLC-ICPMS/MS



Nor **Laili** Azua Jamari, Jan Frederik Dohmann, Andrea Raab, Eva M. Krupp and Jörg Feldmann

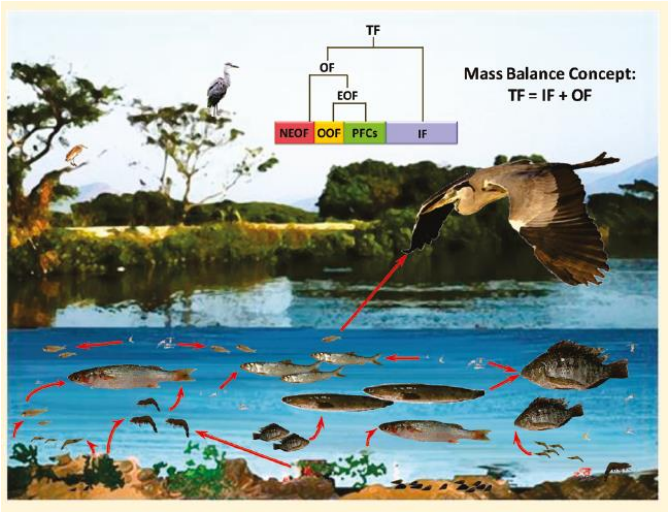
Trace Element Speciation Laboratory (TESLA)
University of Aberdeen
Scotland, UK

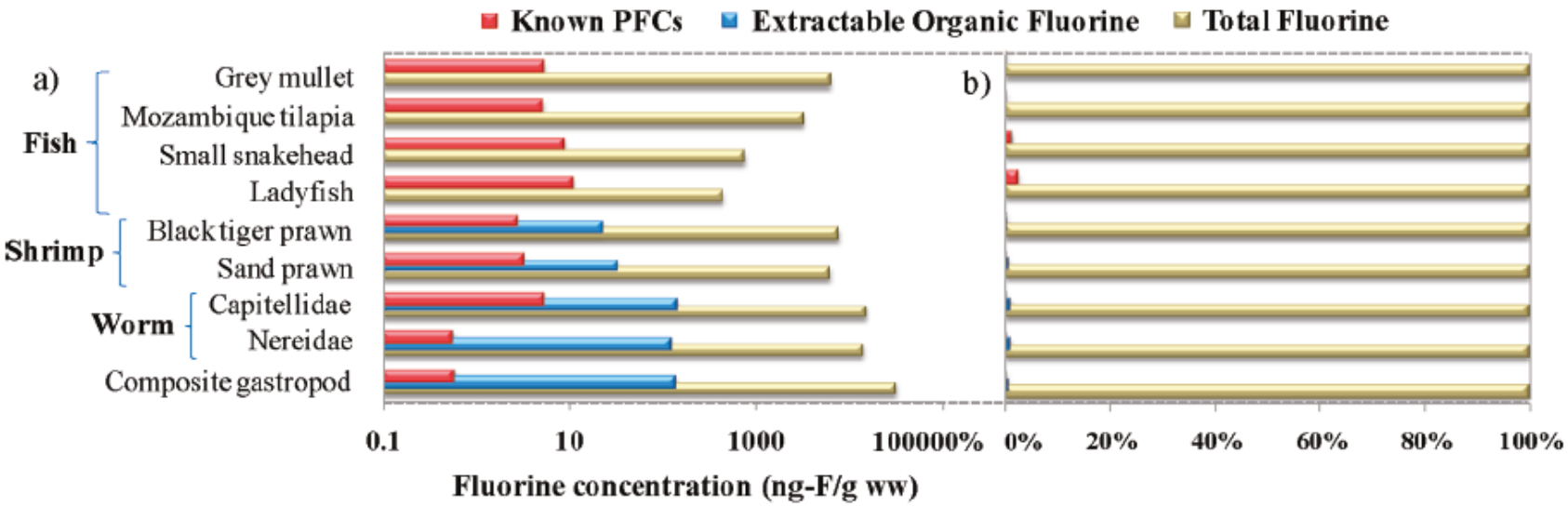
Aims

Mass balance of fluorine reveals…..
most organofluorines unknown !!

→ only target analysis (ESI-MS)

→Need for fluorine-specific detection!!

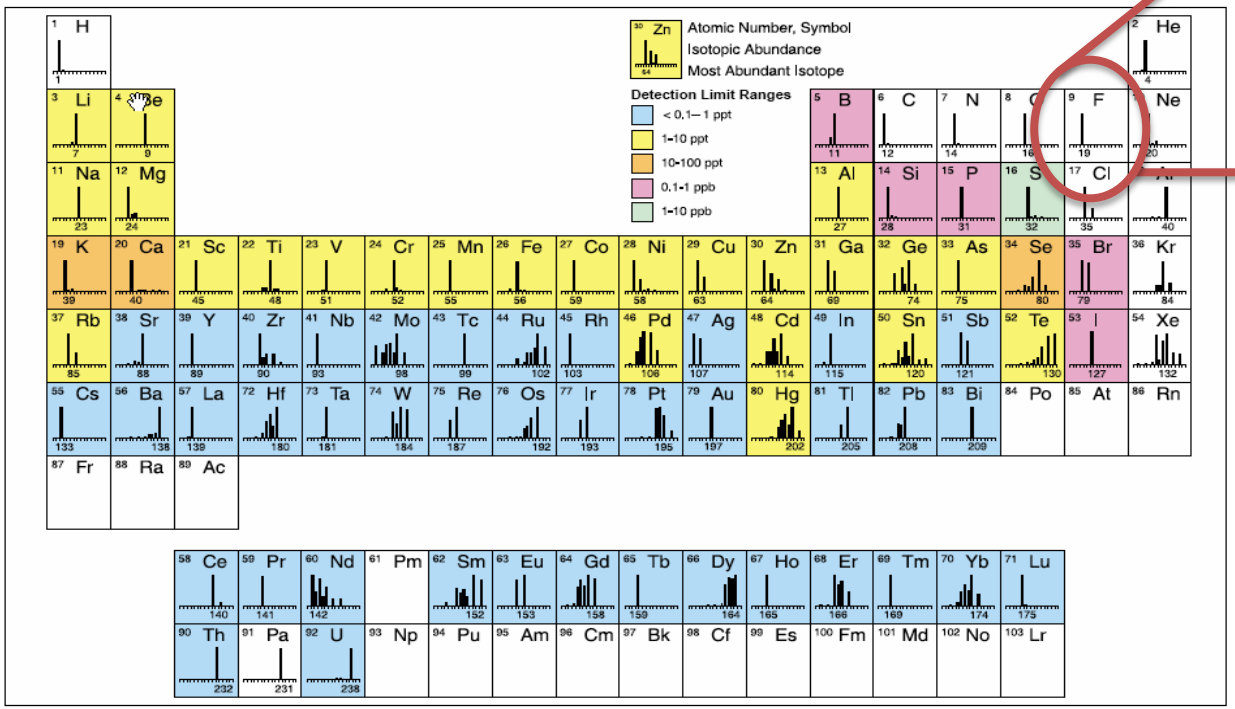




N. Yamashita and co-workers ES&T (2011) **45**, 5906

Inductively coupled plasma mass spectrometer (ICPMS)

- Capable in detecting multi-elements and isotope from ppm to ppt level

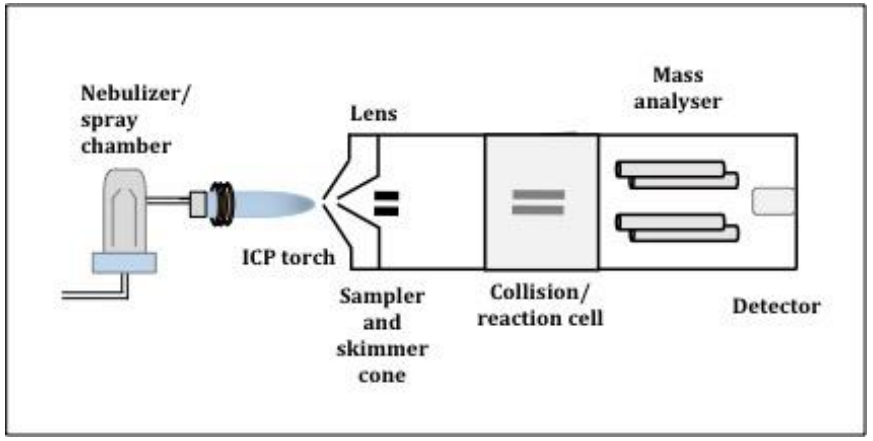


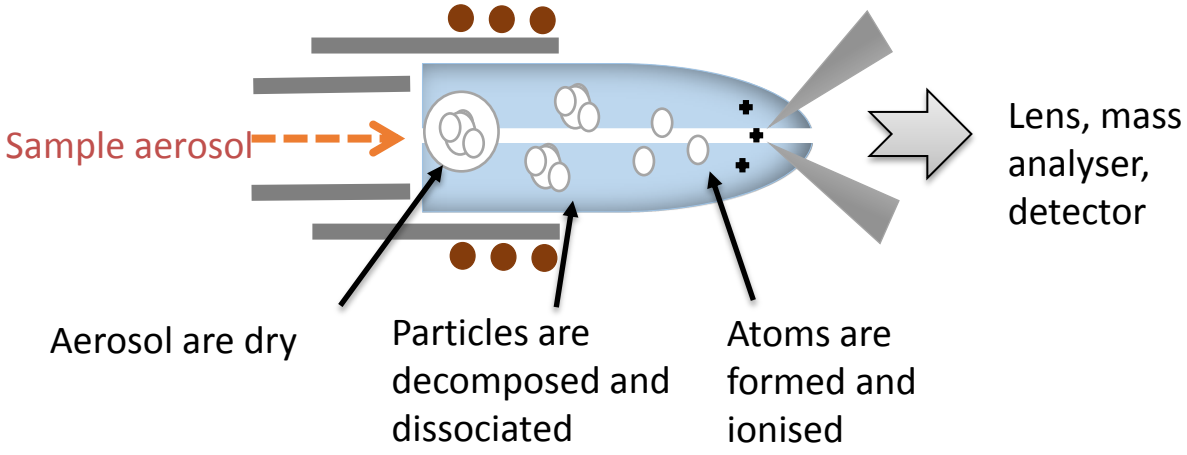
^{9}F
19
Fluorine

https://icp-ms.wikispaces.com/

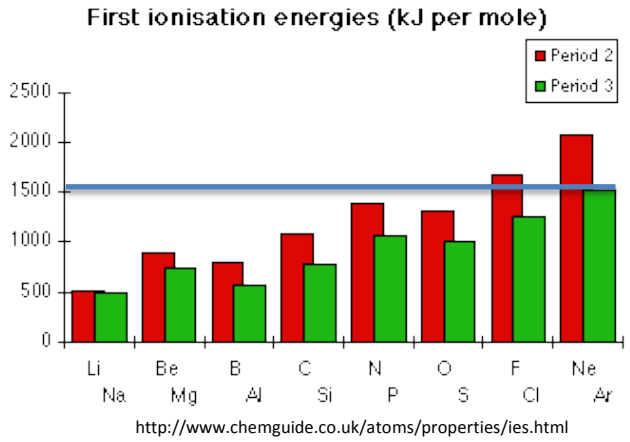
Inductively coupled plasma mass spectrometer (ICPMS)

- A very high temperature plasma discharge (~10 000 K) → generates positively charged ions.
- Mass spectrometer acts as a mass filter to allow only the target ions based on the mass-to-charge ratio (m/z) to separate and quantify those ions.
- **Element-specific rather than molecular specific!**





F in ICPMS

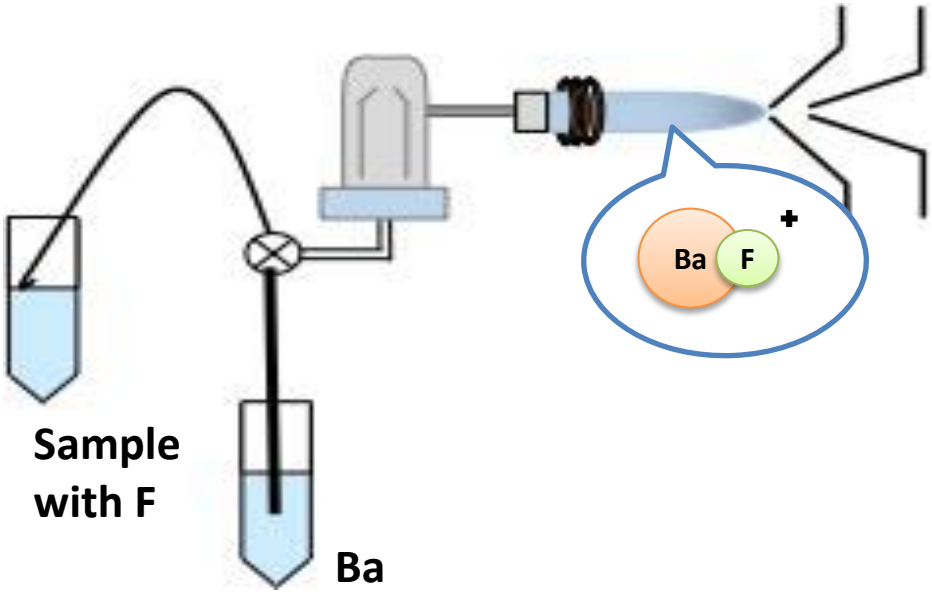


http://www.chemguide.co.uk/atoms/properties/ies.html

F impossible to be detected by ICPMS

New approach through polyatomic ions formation

F could be measured as $^{138}Ba^{19}F^{+}$ at m/z 157



$$^{138}Ba^{+} + {}^{19}F^{0} \rightleftharpoons {}^{138}Ba^{19}F^{+}$$

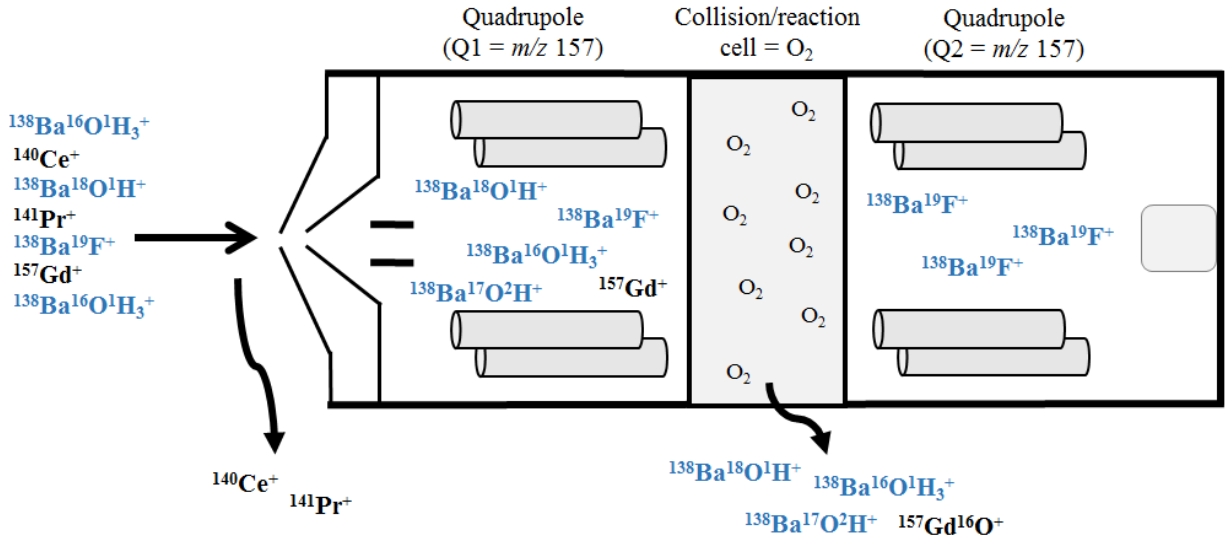
$$^{138}Ba^{2+} + {}^{19}F^{-} \rightarrow {}^{138}Ba^{19}F^{+}$$

Jamari et al., J. Anal. At. Spectrom., 2017, 32, 942-950

ICPMS/MS

- Target m/z 157: $^{138}Ba^{19}F^{+}$
- interferences: $^{157}Gd^{+}$,$^{141}Pr^{16}O^{+}$, $^{140}Ce^{16}O^{1}H^{+}$, $^{138}Ba^{18}O^{1}H^{+}$, $^{138}Ba^{16}O^{1}H_{3}^{+}$,…

→ ICPMS/MS: exclusion of ions in Q1 and reactions products exclusion in Q2

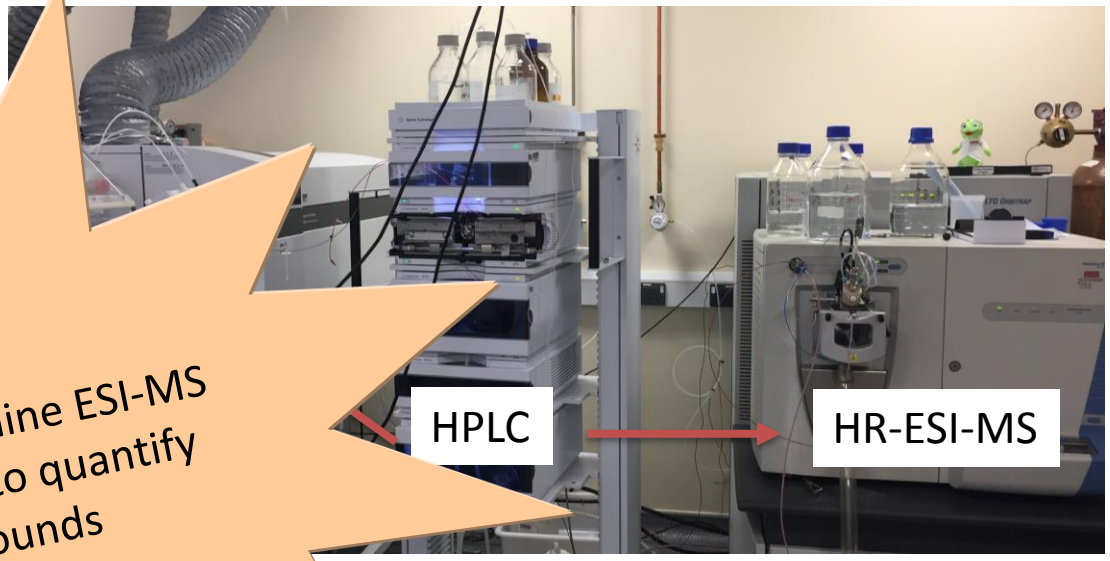


Jamari et al., J. Anal. At. Spectrom., 2017, 32, 942-950

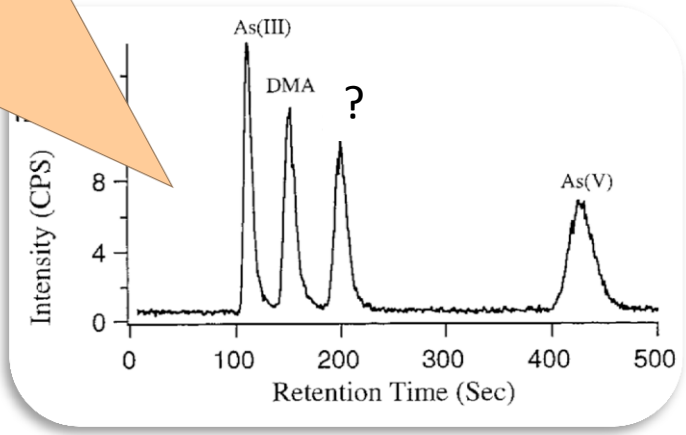
Speciation: non-target analysis

- Use the same concept as arsenic speciation using simultaneous MS
- By monitoring m/z of the target elem… di… specie… elemen… identifi… q…
- ICPMS … for ele… MS … the m… specific inform…tion simultaneously.

Quantify Separation Identify

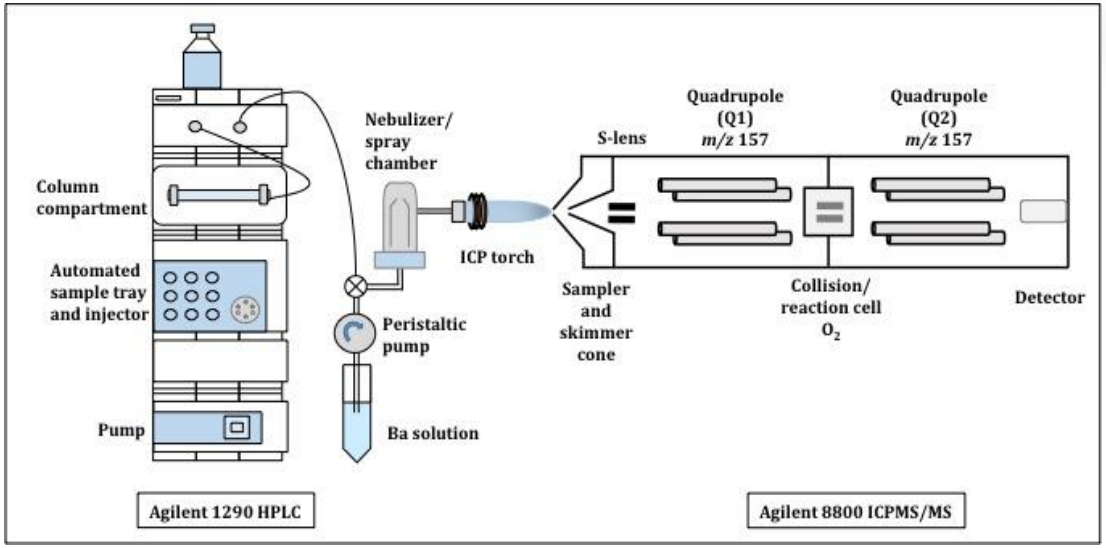


ICP-MS helps to mine ESI-MS data and is able to quantify the compounds



Feldmann et al, 1999

Method development



ICPMS/MS optimisation:

- ✓ Reaction gas
- ✓ RF power
- ✓ Gas flow rates (nebuliser and makeup gas)
- ✓ Sampling position

Speciation: HPLC-ICPMS/MS

- Water based buffer
- Solvent based buffer

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Optimisation and speciation in water based buffer

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Cite this: *J. Anal. At. Spectrom.*, 2017, 32, 942

Novel non-target analysis of fluorine compounds using ICPMS/MS and HPLC-ICPMS/MS†

N. Laili A. Jamari, J. Frederik Dohmann, Andrea Raab, Eva M. Krupp and Joerg Feldmann*

Measuring sub-ppm levels of fluorine (F) directly with a commercial ICPMS is not possible due to the high ionisation potential of F. Mixing of barium and fluorine solutions enabled a new approach in fluorine analysis through the formation of the polyatomic ion BaF^+ using ICPMS/MS. Different parameters such as reaction gas flow rate, sampling position, nebuliser and makeup gas flow rate, waiting and acquisition time as well as RF power were optimized in order to obtain the highest possible sensitivities for $^{138}Ba^{19}F^+$, as these parameters were important for polyatomic ion formation, avoiding barium oxide and barium hydroxide ion interference and sensitive detection in MS/MS. A limit of detection (LOD) of 0.043 mg L^{-1} was achieved with a good recovery of fluoride spiked in deionised water. For fluorine speciation analysis, coupling of anion exchange chromatography online with ICPMS/MS allowed separation and fluorine specific detection of fluoride and fluoroacetate. The response was compound independent as expected for ICPMS. The LODs of fluoride and fluoroacetate were 0.022 mg L^{-1} and 0.11 mg L^{-1}, respectively. Both compounds were baseline separated and detected quantitatively, making this newly developed method a promising candidate for non-target fluorine speciation analysis in environmental samples.

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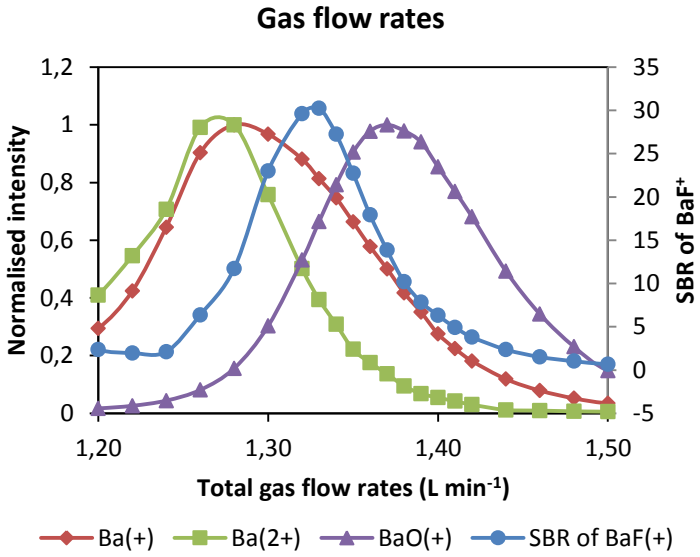
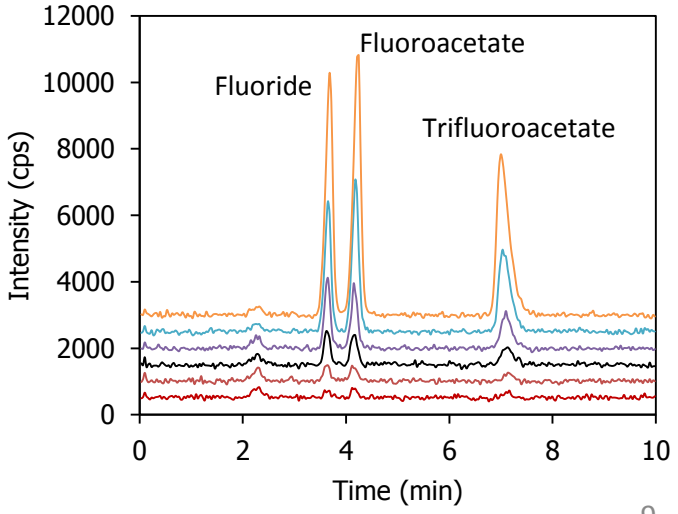
rsc.li/jaas

Introduction

Fluorine plays an important role in human nutrition, as the daily intake of fluoride (F^-) can improve dental health through its cariostatic properties.[1,2] In some countries, a sufficient supply of F^- to the population is ensured by the fluoridation of drinking water.[3] Contrary to this, high concentrations of F^- in drinking water can lead to chronic toxic effects such as dental or excess for industrial purposes and can be found in a variety of environmental samples.[11] Other compounds of interest are short-chained fluorinated acids such as trifluoroacetic acid (TFA), which originates from the atmospheric degradation of refrigerants and anaesthetics or from decombustion of perfluorinated polymers.[12,13] Fluoroacetic acid (FAA) a highly toxic compound which naturally occurs in certain plants[14] can not only be a metabolite formed by bacteria but has also been anthropogenically used as

→ Detection limits in the lower ng/mL range per F-species.





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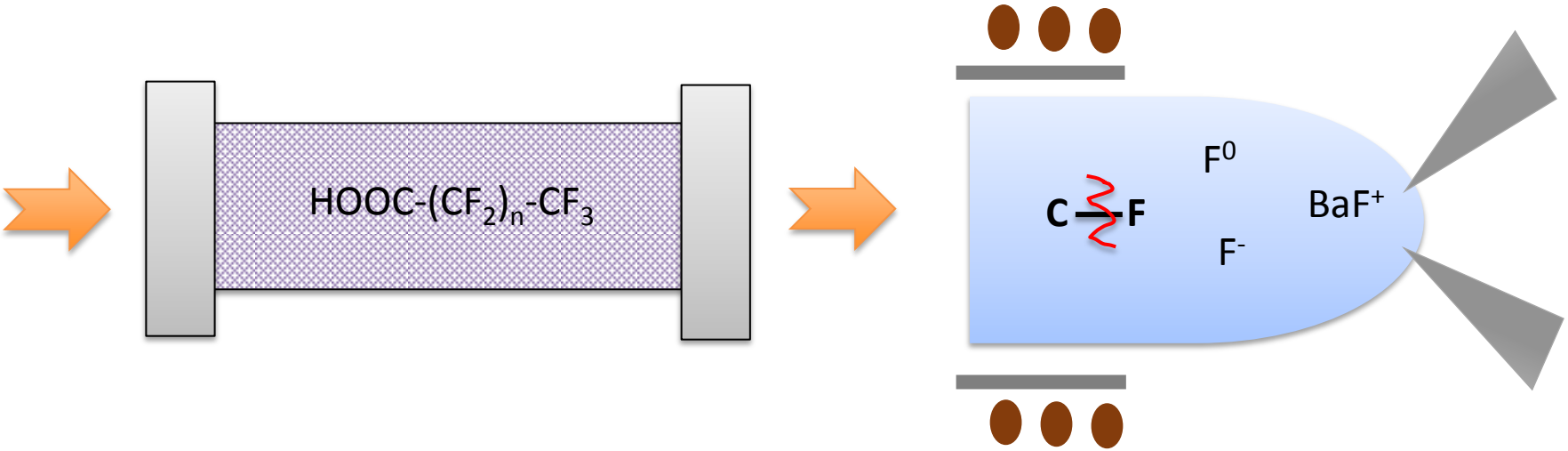
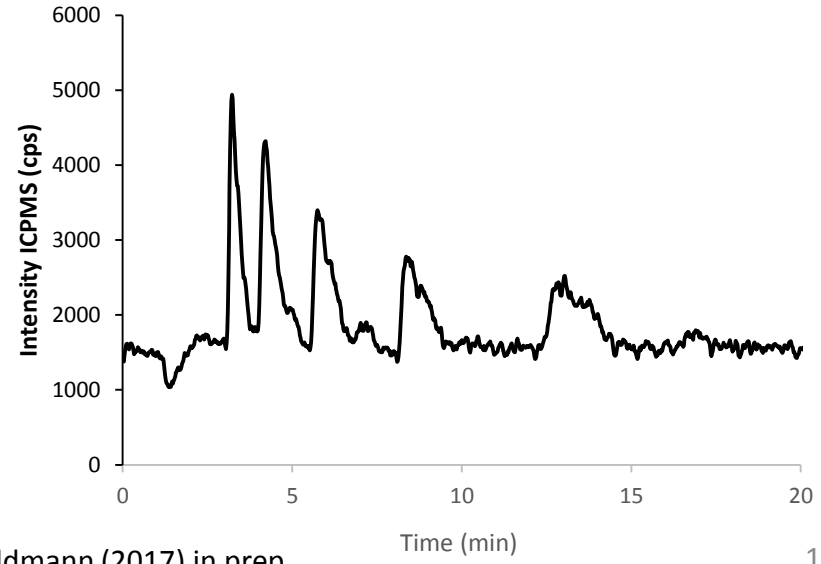
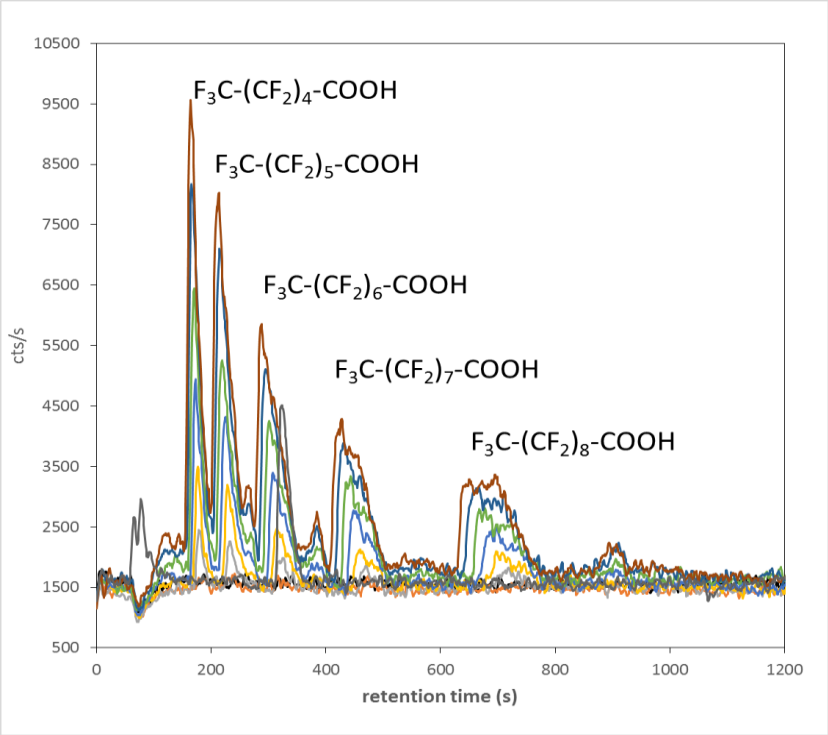
Speciation: solvent based buffer

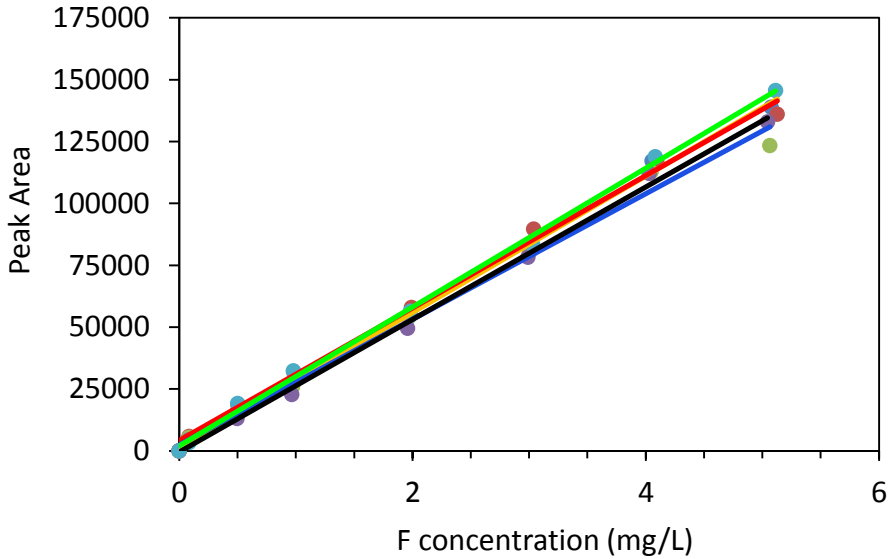


- Reverse phase C18 column (MeOH)
- Plasma gas needs additional O_2
- High temperature of plasma could break C-F bond.
- ICPMS will detect each F-containing compound.



NLA Jamari, JF Dohmann, A Raab, EM Krupp, J Feldmann (2017) in prep.



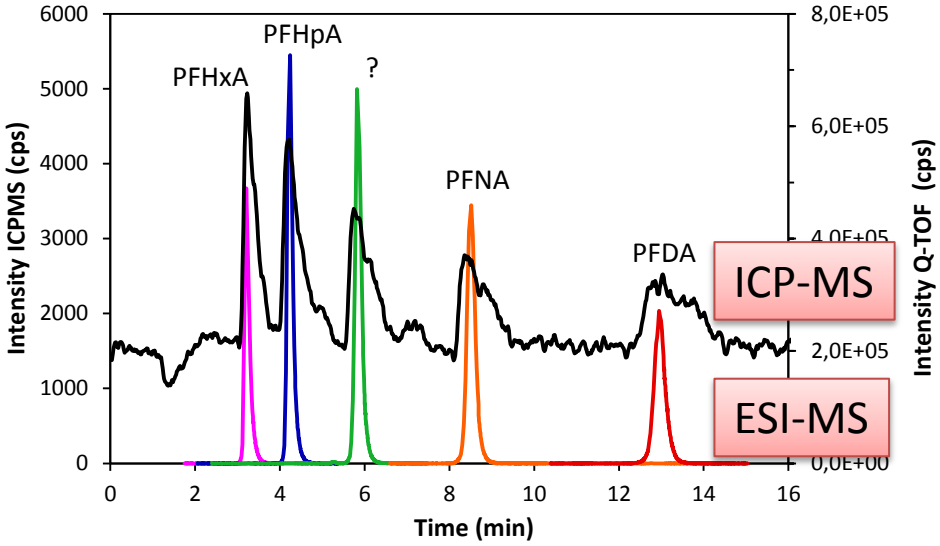


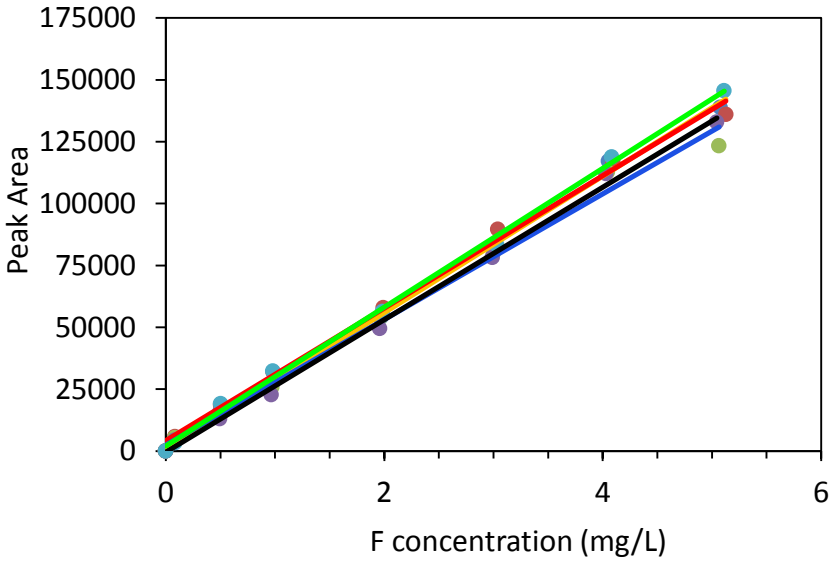
- Linear correlation for all compounds.
- LOD ~0.15 mg F/L
- Sensitivity similar for each compound→ method is F specific, not compound specific!

→ quantification is possible by using one F species only.

→ Mass balance is possible.

NLA Jamari, JF Dohmann, A Raab, EM Krupp, J Feldmann (2017) in prep.





- Mining ESI-MS data will give the identity of the unknown peak
- Identification of unknown compounds is possible without a standard
- Quantification of the unknown compound also possible

NLA Jamari, JF Dohmann, A Raab, EM Krupp, J Feldmann (2017) in prep.

Conclusion

- F is possible to be detected by ICPMS through the formation of polyatomic ions, BaF^+ in the ng/mL range.
- The developed method is F specific, since the sensitivity depends only on mass fraction of F, not the species.
- New method can quantify unknown F- containing compounds using HPLC-ICPMS/MS and makes mass balance possible.
- Offer great potential to be a non-target F specific method which might be the key method to identify unknown organofluorine compound in the future.
- Future work need to improve chromatographic resolution and sensitivity of the ICPMS/MS.

Thank you

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  - Analytical Chemistry Trust Fund (RSC): Overseas Conference Travel Grant
  - University of Aberdeen: travel scholarship
  - Ministry of Higher Education Malaysia
  - TESLA members