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Δημοσίων Εσόδων

Γ.Χ.Κ.
Γενικό Χημείο του Κράτους

GREEK PROJECTS ON TARGETED AND SUSPECT SCREENING ANALYSIS OF PAPER & BOARD FOOD CONTACT MATERIALS

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Projects

I. Determination of targeted PFAS in paper FCMs by HS-GC-MS/MS (2020 PROJECT)

HELLENIC REPUBLIC
National and Kapodistrian University of Athens
EST. 1837

Post-Graduate Thesis (MSc) I. Maggina - Supervisor: Prof. N. Thomaidis

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S.Kontou and E. Lampi

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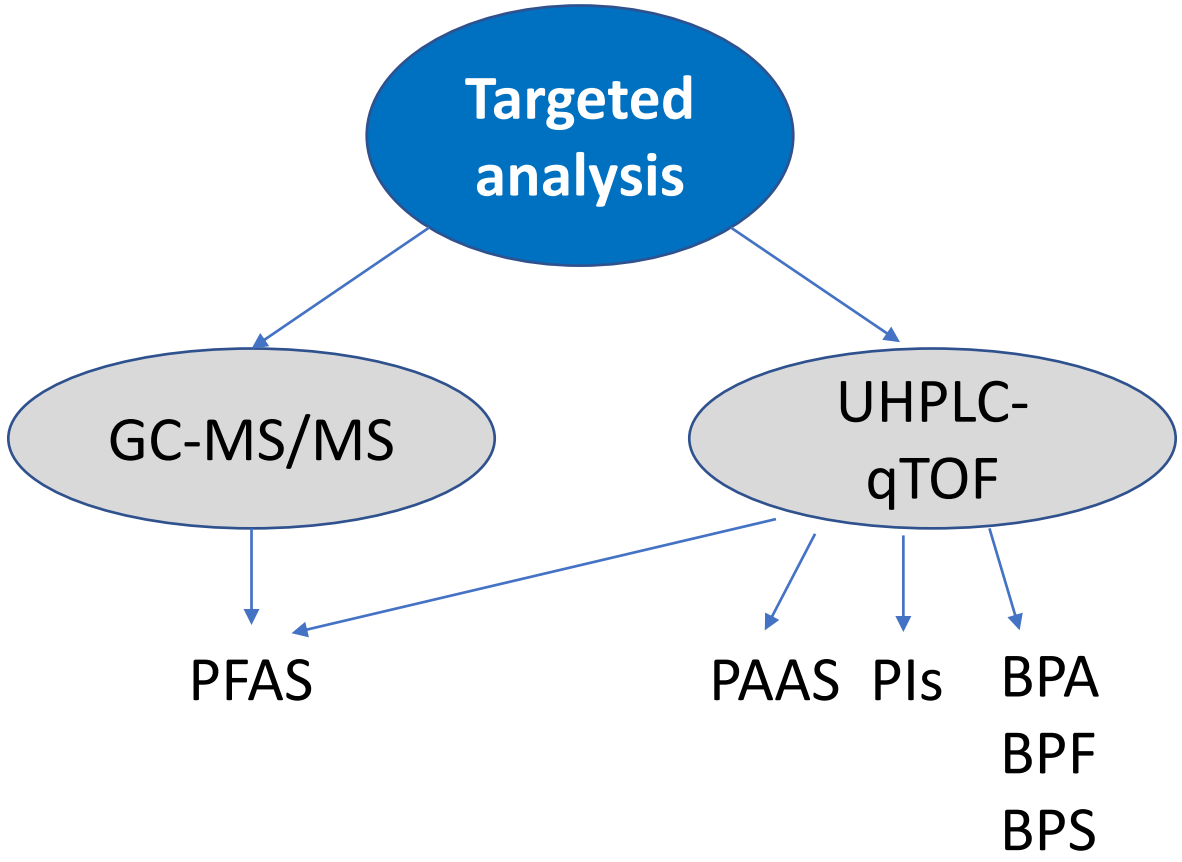
Projects

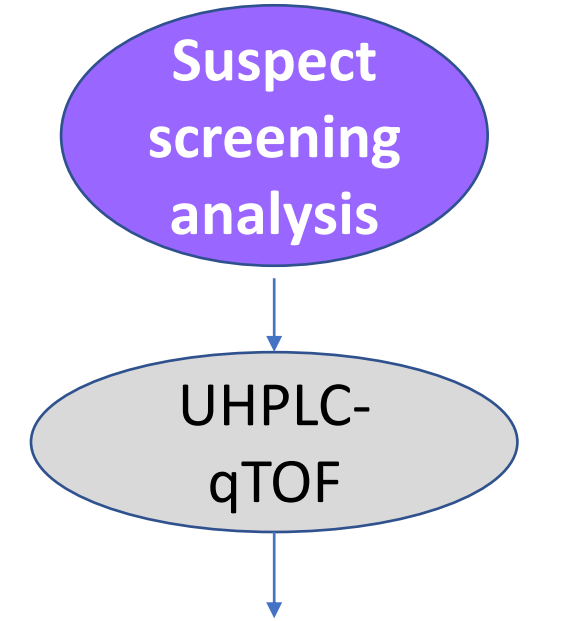
II. Targeted and suspect screening analysis of paper & board FCMs by UHPLC-qTOF (ON-GOING PROJECT)

General Chemical State Laboratory

S. Kontou, E. Dessipri, E. Kokkalis, D. Triantou and E. Lampi

Overview


Targeted analysis
GC-MS/MS
UHPLC-qTOF
PFAS
PAAS
PIs
BPA
BPF
BPS


Suspect screening analysis
UHPLC-qTOF
In-house suspect list of potential migrants

Overall Objectives

- To identify and quantify toxic chemicals present or migrating from paper and board FCMs (targeted analysis of representative chemicals belonging to the groups of PFAS, PAAS, PIs, Bisphenols)
- To identify potential migrants from paper and board FCMs focusing on chemicals of emerging concern (suspect screening)
- To prioritize migrants for monitoring based on occurrence (suspect screening)

Determination of targeted PFAS in paper & board FCMs by HS-GC-MS/MS (2020)

Fluorotelomer alcohols (FTOHs)

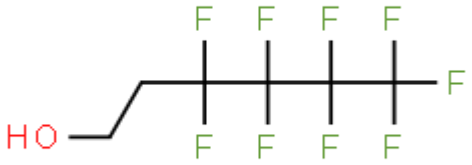
Perfluorinated Sulfonamides (FASAs)

Perfluorinated Sulfonamidoethanols (FASEs)

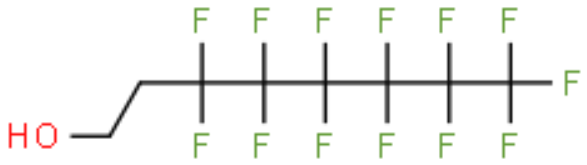
- Not readily analyzed by the LC-MS/MS (ESI) methods used for the other PFAS
- Not easily ionizable
- Volatile (short-chain PFAS of the group)

To overcome these analytical challenges a HS-GC-MS/MS method was developed, optimized and validated

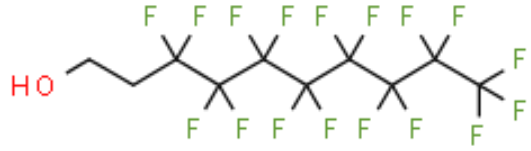
Targeted PFAS



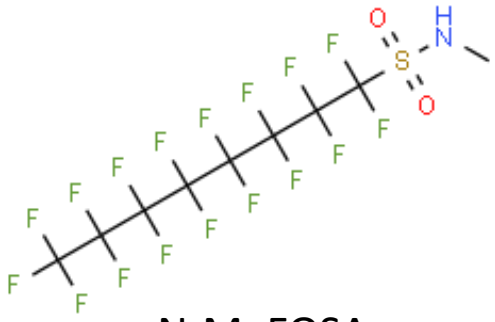
FTOH 4:2
(MW: 264.09)



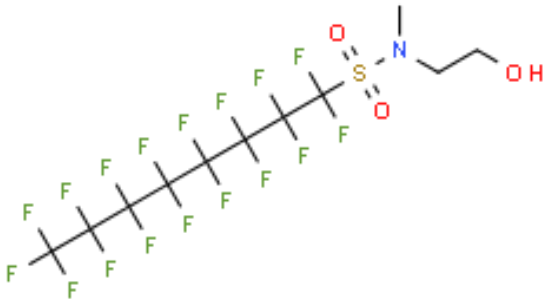
FTOH 6:2
(MW: 364.10)



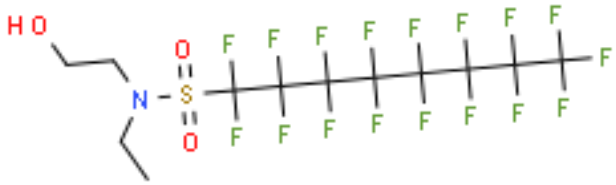
FTOH 10:2
(MW: 464.12)



N-MeFOSA
(MW: 513.17)



N-MeFOSE
(MW: 557.22)



N-EtFOSE
(MW: 571.25)

Analytical method (HS-GC-MS/MS)

- 0,3 g finely cut sample weighed in 20 mL vial and 2 isotopically labelled IS (M2FOET & dNMeFOSA) are added
- 8 mL H_2O and 0.6 g NaCl are introduced to the vial
- Analytes identified and measured by HS-GC-MS/MS analysis

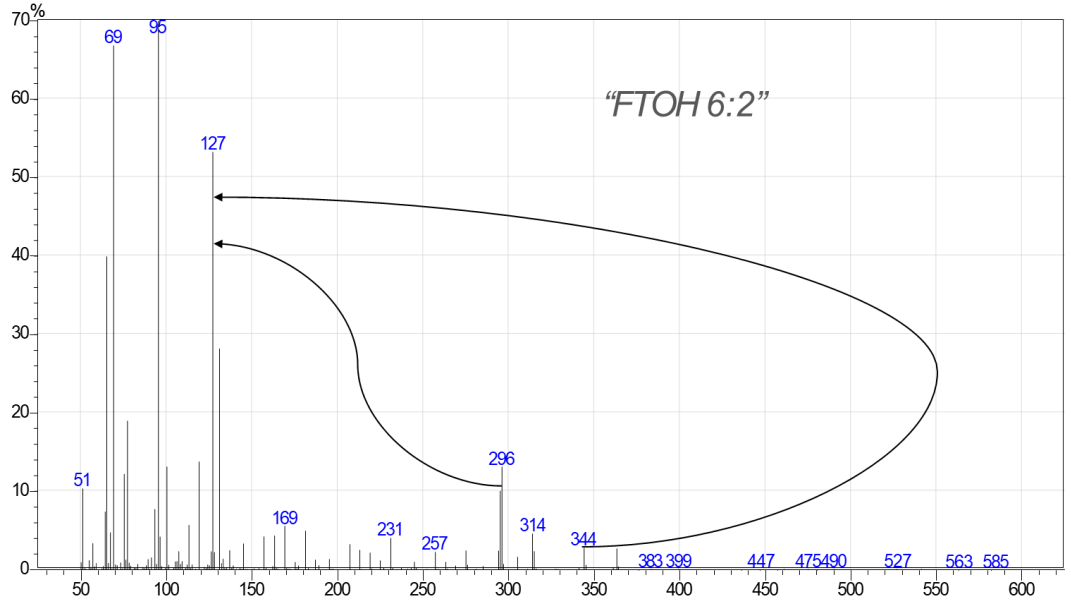
GC-MS/MS: Shimadzu TQ 8040,
Column: Mega–17MS (60 m x 0.25 x 0.25 µm)

SPME parameters	
Fiber	50/30 DVB/CAR/PDMS
Fiber pre-conditioning	250°C/10 min
Sample Equilibration	65°C/10 mim
Sample Extraction	65°C/30 min
Sample Desorption	240°C/10 min

Analytical method (HS-GC-MS/MS)

Identity Confirmation:
2 MRMs and the MRM Intensity Ratio monitored, Retention time

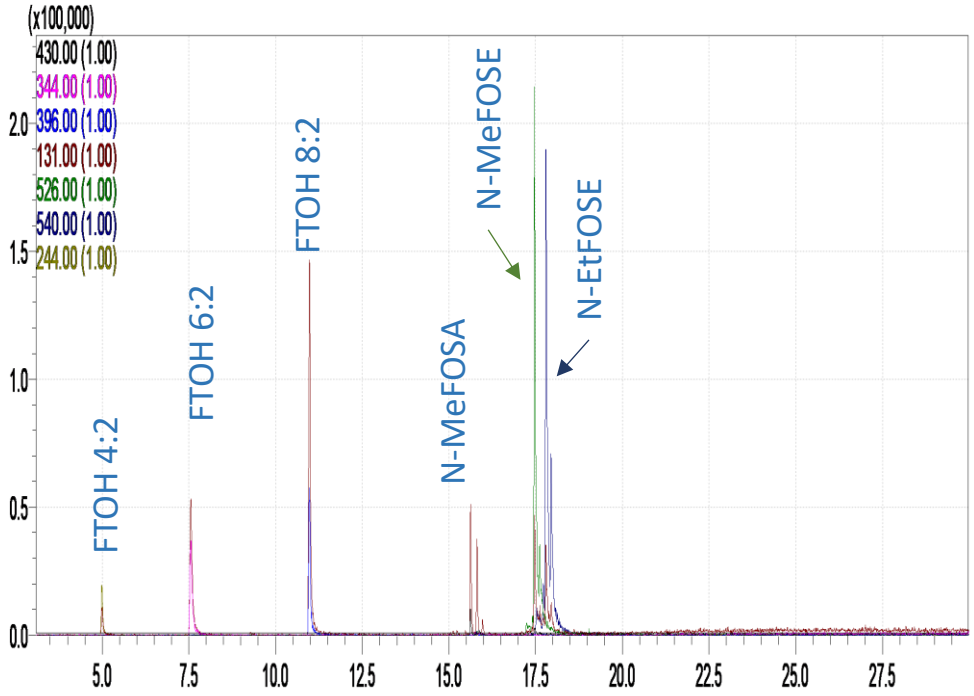
PFAS	MRM quant	CE (V)	MRM qual	CE (V)
FTOH 4:2	244 > 196	3	196 > 127	7
FTOH 6:2	344 > 127	9	296 > 127	6
FTOH 8:2	396 > 127	6	127 > 77	14
N-MeFOSA	131 > 69	18	430 > 11	28
N-MeFOSE	526 > 169	18	462 > 93	21
N-EtFOSE	540 > 169	21	448 > 69	24



Analytical method (HS-GC-MS/MS)

- Quantitation: Matrix-matched calibration standards, 2 isotopically labelled IS (M2FOET & dNMeFOSA)

- Method validated
  Recoveries 75-130 %
  RSDs ≤ 15%
  LOQ: 20 ng g^{-1}



P&B samples analysed

32 samples collected in 2020 from super-markets, fast-foods, bakeries, coffee shops, restaurants etc

- Paper takeaway food containers (food boxes, pastry boxes, pizza boxes)
- Paper plates, bowls, coffee cups, ice cream cups, paper straws
- Paper bags for bread and bakery products and food wrapping paper
- Biodegradable sugar cane food containers
- Baking paper
- Paper cup cake cases

Results

- ✓ 28% of the paper samples tested were positive for FTOH 6:2
- ✓ FTOH 6:2 concentrations up to 1020 ng g^{-1} were found(*)
- ✓ FTOH 4:2, FTOH 8:2, N-MeFOSA, N-MeFOSE, N-EtFOSE were not detected in the samples tested

Sample	FTOH 6: 2 (ng g^{-1})
Paper plate	1000
Paper food box	710
Paper bag for bakery products 1	998
Paper bag for bakery products 2	498
Burger wrap paper	685
Souvlaki wrap paper	795
Paper bag for hot food	80
Take away clam food container (sugar cane)	1020
Food tray (sugar cane)	70

(*) Corresponds to a maximum theoretical migration of 23 ng g^{-1} (for 6 dm^2/kg)

Considerations on the findings

- These results indicate the prevalence of 6:2 FTOH over the 8:2 FTOH in paper & board FCMs in the Greek and by extension in the EU market (*).
- In 2020, the US FDA announced the voluntary phase-out, beginning in 2021, of the short-chain PFAS that contain 6:2 FTOH, following concerns about the biopersistence potential of 6:2 FTOH.
- Up to now, 6:2 FTOH has not been assessed by EFSA.

(*) It has been reported that 6:2 FTOH was dominant in paper & board FCMs produced in USA, as US industry replaced C8-PFAS with C6 –PFAS, whereas the 8:2 FTOH and other long-chain FTOHs were dominant in paper FCMs produced in China (Yuan et al., 2016, DOI: 10.1021/acs.est.5b03806)

Targeted and suspect screening analysis of paper & board FCMs by UHPLC-qTOF (on-going project)

- Aqueous and 95% EtOH extracts of paper & board FCM samples are analysed by UHPLC-qTOF using SWATH data acquisition mode (Sequential Window Acquisition of all Theoretical Mass Spectra)
- The analytical strategy includes:
  - Sample extracts analysed in both ESI (+) and ESI (-) ionization mode using 4 mobile phases : 2 for ESI(+) and 2 for ESI(-)
  - Targeted quantification of certain PFAS, PAAS, PIs, bisphenols in the sample extracts
  - Suspect screening analysis based on the construction of an in-house database (~200 compounds: PAAS, PIs, phthalates, BPA/alternatives/derivatives, biocides etc)

Sample preparation

A

2 g sample
+
40 mL H_2O

→ 23 ^{0}C/24 h → 3000 rpm 10 min → Nylon filter 0,22 µm

→

B

2 g sample
+
40 mL 95 % EtOH

→ 60 ^{0}C/2 h MW → 3000 rpm 10 min → 1:1 dilution with H_2O

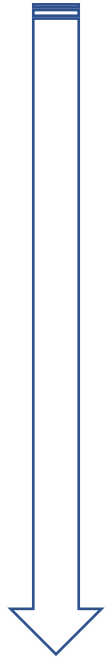
qTOF : SCIEX X500R (SWATH mode)
LC: Sciex ExionLC™ AD
Software: SCIEX OS 2.1.
Column: Kinetex EVO C18 Core-Shell, (2.6 µm x 100 x 2.1 mm)

[A] based on EN 645

Suspect screening

Criteria for the identification of suspect compounds:

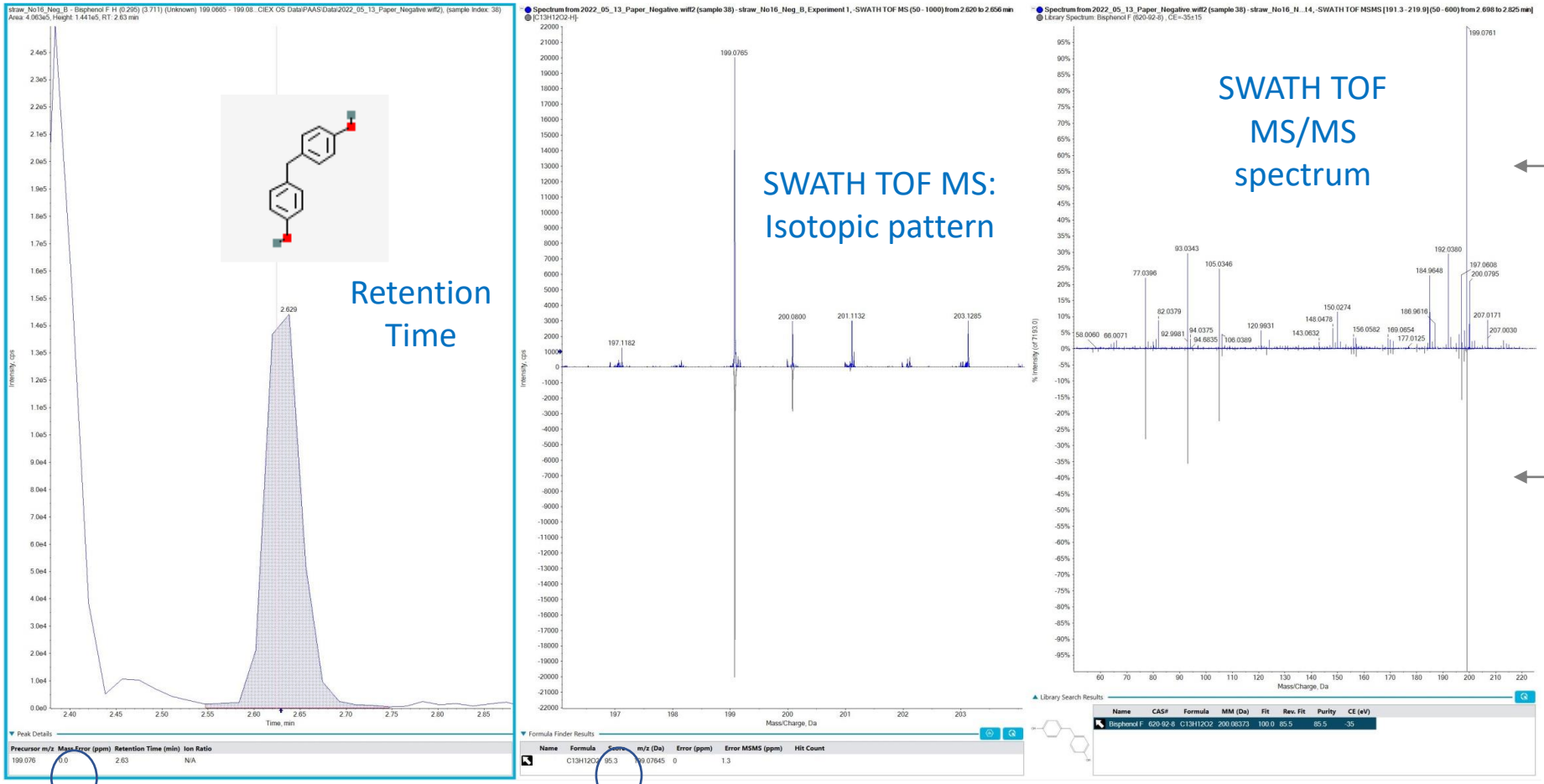
- Mass error of the precursor ion in the TOF MS spectra and the isotopic pattern fit are < 5ppm and > 85%, respectively
- Fragment ions in the TOF MS/MS spectra match to a high degree those predicted by the in-silico fragmentation of the corresponding suspect compound
- Fragment ions in the TOF MS/MS spectra match those of the corresponding suspect compound according to literature data, mass spectra libraries (e.g. Mass Bank)
- Retention Time and TOF MS/MS spectrum of the reference standard and the unknown peak - obtained in the same experimental conditions- coincide



Different levels of identification.

Identity confirmed when the analytical standard is available.

Example: Identity confirmation
BPF in a paper straw sample



PFAS: Analysis by UHPLC-qTOF

PFAS: Preliminary results (UHPLC-qTOF)

CONFIDENTIAL

PAAS, PIs, bisphenols & chemicals in the in-house suspect list - Analysis by UHPLC-qTOF

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Bisphenols: Preliminary results (UHPLC-qTOF)

Targeted and suspect screening analysis of paper & board FCMs by UHPLC-qTOF

On-going and future work

- Analysis of samples and data processing is still in progress.
- Tentatively identified chemicals of concern will be confirmed by reference standards and included in targeted monitoring.
- Examination of the SWATH data for potential identification of unexpected substances using chemical databases (e.g. ChemSpider) will follow.

➢ High Resolution mass spectra libraries specific for paper & board FCMs are needed

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