MIXED-MODE LIQUID CHROMATOGRAPHY-HIGH RESOLUTION MASS SPECTROMETRY SCREENING FOR POLAR CHEMICALS IN WATER

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I. INTRODUCTION & OBJECTIVES

The rise of liquid chromatography-high resolution mass spectrometry (LC-HRMS) combining its high mass accuracy and resolution capacities allows to screen for a large set of organic pollutants without the need of having pure standards and chemical-classes targeted methods. However, most LC-HRMS screening methods rely on reversed-phase LC (RPLC), which is quite limited for the detection of very polar chemicals [1]. Thus, the goal of this study was to improve the analytical detectability of very polar chemicals by using mixed-mode LC (MMLC), which combines ion exchange and reversed-phase mechanisms, hyphenated to HRMS, for screening purposes. The MMLC-HRMS approach was developed with a series of model polar chemicals (including neutral, acidic and basic chemicals) and then applied to suspect and non-target screening studies.

II. MATERIALS & METHODS

Water samples (100 mL)

Concentration step (Freeze-drying)

0.2 mL extracts

LC

Mixed Mode Column
Acclaim Trinity P1 (2.6 µm; 3 mm × 50 mm)

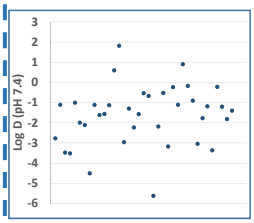
HRMS

QTOF 6520 Agilent Technologies
ESI (+) and ESI (-) at 4GHz

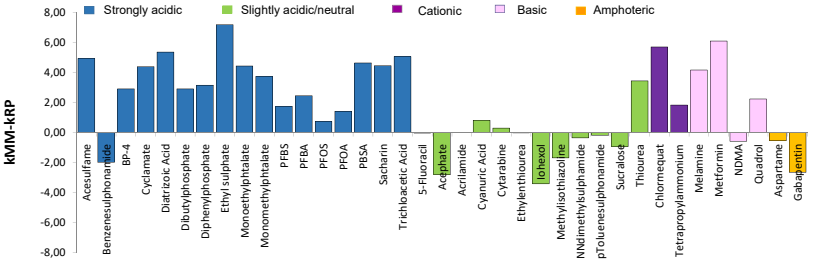
III. RESULTS

LC method development

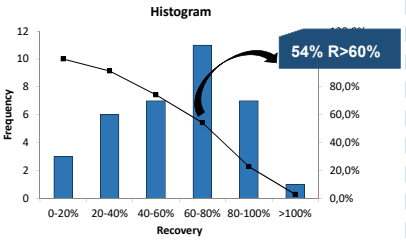
37 model polar analytes
(logD<2)



Separation MMLC vs. RPLC



Apparent recovery evaluation



Screening method

17 water samples (PROMOTE sampling campaing) [2]

Screening lists:
- Extracted from Wode et al. [3] ≈2000 common water pollutants
- PROMOTE consortium [2] ≈1000 PMOCs from REACH

↓ LC-MS injection

Software:Masshunter
Algorithm: Find by Formula (FBF)
Maximum mass error (±5 ppm)
Score > 80
Minimum peak height (1000 counts)
Manual filtering by peak shape

↓ **127 suspects**

↓ LC-MS/MS injection

Comparison with spectra libraries:
Massbank, MzCloud, Metlin and Agilent

↓ **25 tentatively identified compounds**

↓ Blank injection (Ratio sample/blank > 10)
Standard injection (if available)

↓ **22 identified compounds**

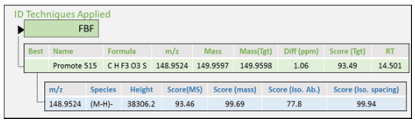
21 identified by analytical standard (Rt and >2 common product ions)

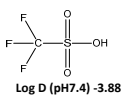
1 identified by MS/MS spectra interpretation (metabolite)

Example : Trifluoromethane sulfonic acid (barely described in literature) [4]

Example: Trifluoromethane sulfonic acid identification

(a) Compound identified by FBF algorithm: Database PROMOTE [2]

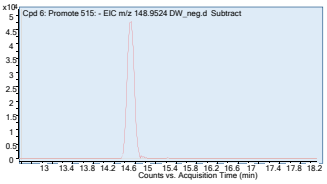




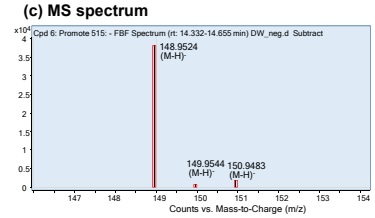
Detected in 40% of samples

Log D (pH7.4) -3.88

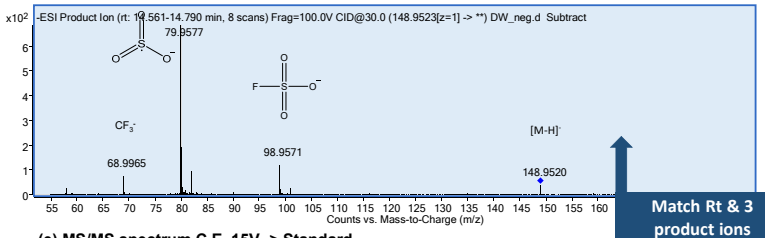
(b) Chromatographic peak



(c) MS spectrum

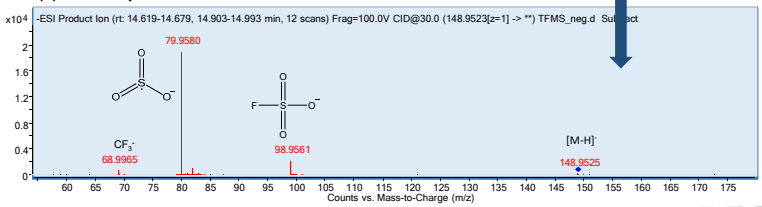


(d) MS/MS spectrum C.E. 15V -> Sample



Match Rt & 3 product ions

(e) MS/MS spectrum C.E. 15V -> Standard



IV. CONCLUSIONS

MMLC-HRMS is a new alternative for the determination of very polar chemicals, which also can turn useful for medium polarity contaminants. Its application to water samples has shown that it is capable of detecting novel very polar compounds, not previously reported in the literature.

Bibliography

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[2] PROMOTE project - PROtecting Water Resources from MObile TracE Chemicals http://www.promote-water.eu
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[4] D. Zahn, T. Frömel, T. Knepper. Water Res 101, 292 (2016)

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