



Techniques for reduced ion suppression in negative mode LC/MS analysis of WWTP samples

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Introduction

Water samples from wastewater treatment plants constitute a highly complex matrix with hundreds of organic compounds at concentrations ranging from low ppt to ppm levels. The major organic fraction of the wastewater has a natural origin. However, recent years waste water trace constituents as pharmaceuticals and personal care products (PPCP) have received increased attention due to the potential as environmental hazards. As a consequence, chemical analytical methodology is needed in order to monitor the environmental fate of the PPCPs and LC/MS has become the leading analytical tool for a wide range of PPCP-applications. Due to the sample complexity of wastewater samples ion suppression is well known for LC/MS applications. In this work, analytical techniques to reduce ion suppression are presented.

Methodology

Sample preparation

Samples from WWTPs are challenging when analysing compounds by LC/MS in negative ionisation mode. Co-extracted humic acids present in the final extract will be ionised in ES-, resulting in highly suppressed analyte signals. By a modified ion exchange SPE clean-up, the amounts of humic acid in the final sample is significantly reduced.

The sample extract is sequentially cleaned by passing through Isolute Multi Mode adsorbent (904-0030-14) and then passing over activated Oasis Max adsorbent (186000370 from Waters).

Chemical Analysis

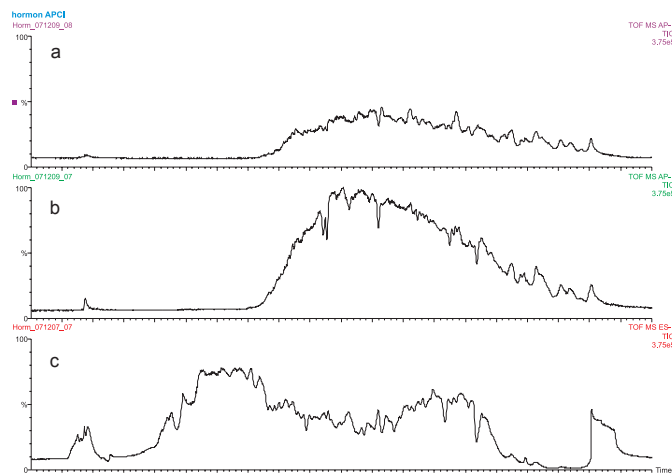
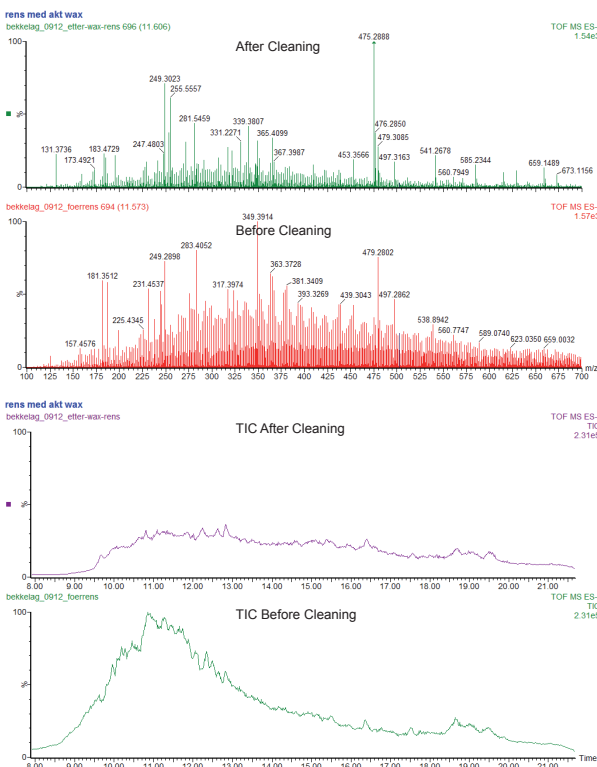
By using APCI- instead of ES- a wide range of compounds can be analysed at adequate sensitivity with less suppression from humic acids yielding cleaner chromatograms.

Instrumentation

Waters UPLC system combined with LCT Premier TOF high resolution mass detection. Chromatographic separation was performed on a Waters Acquity HSS T3 column, 100x2.1 mm i.d., 1.8 µm particle size, using 0.3 mL/min acetonitrile/water as the mobile phase. The injection volume was 5 µL.

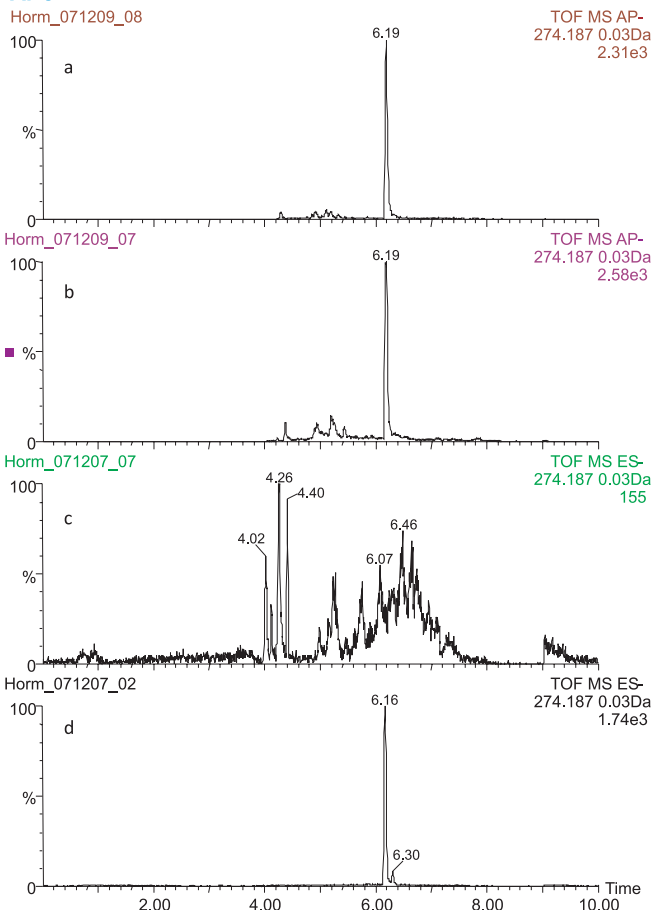
Compound	m/z
BPA	227.079
TBBPA	542.736
Triclosan	250.935
Octylphenol	205.155
Nonylphenol	219.172
Dodecylphenol	261.224
Sucralose	395.006
Estradiol	271.149
17- α -ethinylestradiol	295.155
Estriol	287.152
Estrone	269.138
Progesterone	313.162

Mode	Capillary/corona	Cone V	Desolv °C	Source °C	Desolv.gas L/h	Aperture V
ES-APCI-	2700 V 5 µA	50 50	350 350	150 150	750 200	5 5



a) TIC of rinsed extract of sewage sludge (APCI-)
b) TIC of raw extract (APCI-)
c) TIC of raw extract (ES-)

Hormones APCI



Trace of d3- β -estradiol (ISTD) at m/z 274.1865

a) Rinsed extract of sewage sludge, APCI-
b) Raw extract, APCI-
c) Raw extract, ES-
d) Methanol standard solution, 87 ng/mL, ES-

Conclusion

In negative ion LC/MS analysis of WWTP samples, high amounts of co-extracted organic compounds can lead to ion suppression and interfering peaks. By application of an extra clean-up step and using a soft ionisation technique, the sensitivity of the analysis is significantly enhanced.