

LC/MS Application Note



ENVIRONMENTAL

Determination of pharmaceuticals
in water and surface water using
online SPE coupled to liquid chroma-
tography mass spectrometry



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Determination of pharmaceuticals in water using online SPE coupled to liquid chromatography mass spectrometry

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Overview Results

- Monitoring of pharmaceuticals in surface and waste waters.
- conventional offline SPE LC-MS and online SPE LC-MS
- The challenging goal of 10 ng/L for monitoring was achieved by use of online SPE.
- Demonstration of a routine method for the online SPE LC-MS analysis of 24 pharmaceuticals in surface and wastewater.

Introduction

- The ubiquitous distribution of pharmaceuticals in different water bodies results in negative environmental effects. In Germany alone about 8'000 metric tons are drained into sewage systems every year. Roughly 90% of these compounds pass through treatment plants into different waterbodies.
- The low environmental concentrations require efficient enrichment and clean-up methods.
- Solid phase extraction (SPE) promises to achieve the monitoring target of 10 ng/L for each analyte.
- Automated enrichment and clean-up prior to liquid chromatography mass spectrometry (LC-MS) analysis using online SPE is demonstrated.

Methods

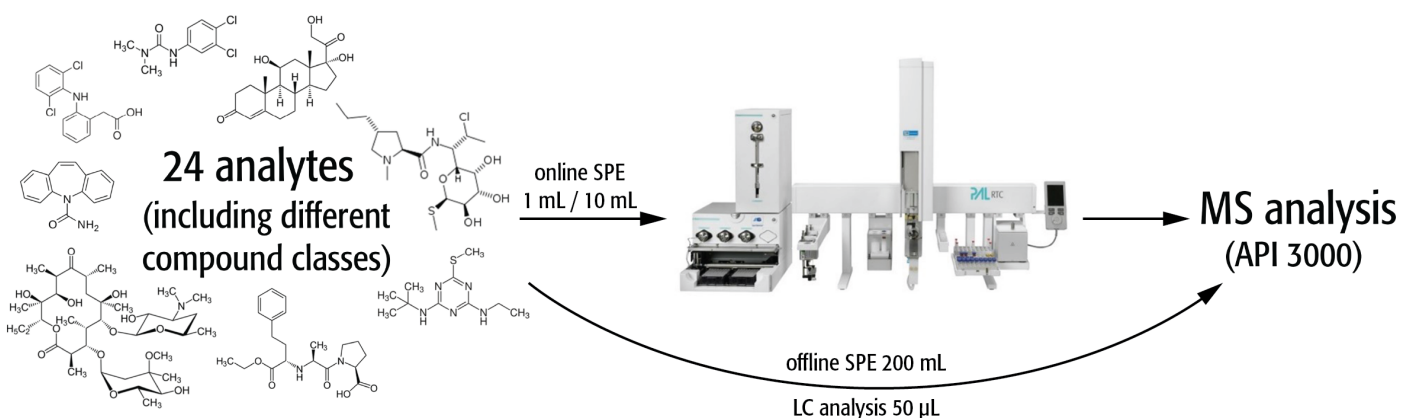


Figure 1: Instrument setup

Offline SPE

Cartridge Phenomenex, Strata-X (polymeric reversed phase)
 Sample volume 100 mL - 1 L

Drying under nitrogen, Resolution in 1 mL water + 0.1% formic acid

Instrumentation online SPE

Sample prep PAL RTC
 Automated SPE Axel Semrau CHRONECT μ SPE Exchange Module
 Cartridge type/format HySphere C18 10 x 2 mm
 LC Agilent 1100
 Column Chromolith FastGradient Rp 18e 50-2 mm (Merck)
 MS Sciex API 3000 under Analyst 1.6.2
 Control software Chronos v. 4.4

Results

- C18 material was the best compromise between enrichment capability and peak shape for the analysis of the pharmaceuticals analyzed here.
- Enrichment factors of up to 200 (equal to 10 mL injection) resulted in good recovery rates.
- The recovery for conventional offline SPE and online SPE was comparable. The recovery of most analytes is between 80 and 120% (fig. 2)

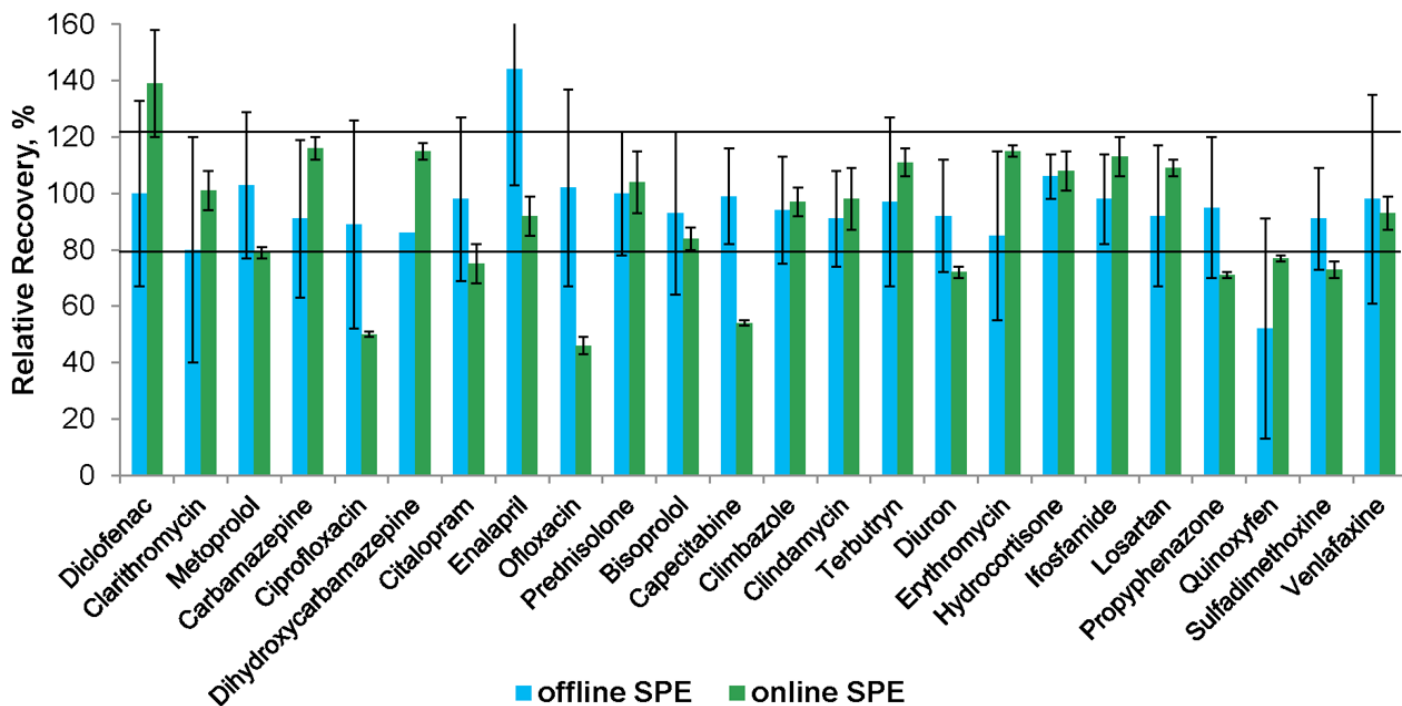


Fig.2: Relative recovery and reproducibility for the 24 compounds analyzed.

- The average reproducibility for online SPE (5.1%) is better than for offline SPE (27%, see error bars in fig. 2)
- The analysis time/sample was minimized by efficient overlapping of tasks with an intelligent software algorithm (Chronos)

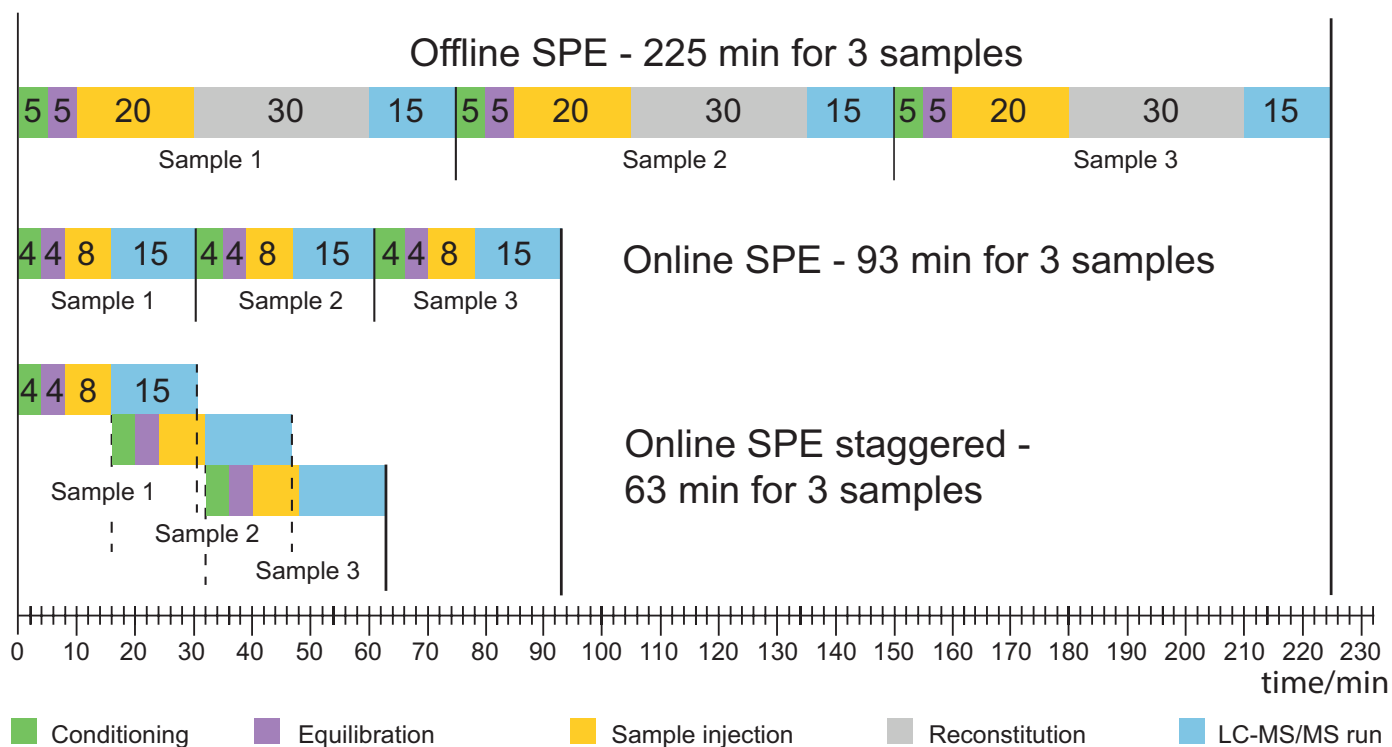
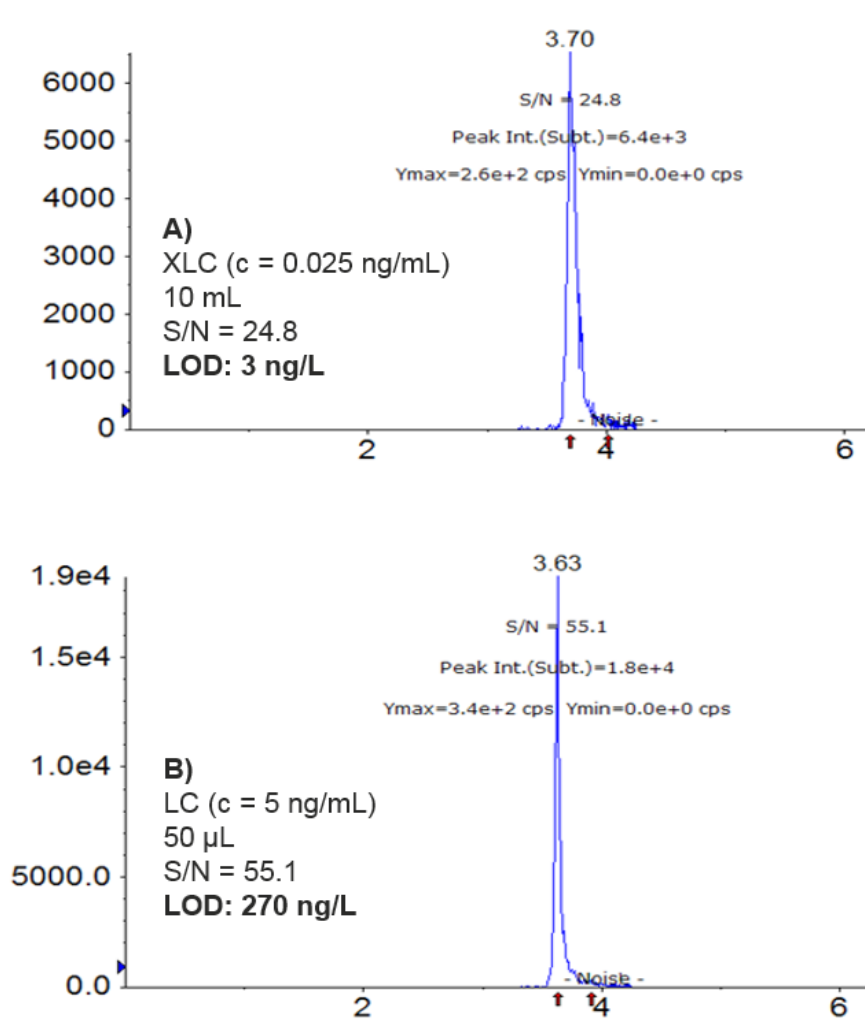


Fig.3: Comparison of time consumption for processing of 3 samples using offline SPE, online SPE and staggered online SPE.

- Applying online SPE the limit of detection (LOD) improved for example from 270 ng/mL to 3 ng/mL for metoprolol (fig. 4)



(Data from Sciex API 3000.)

Fig.4: A: Extracted ion chromatogram of a 10 mL online SPE sample of metoprolol (0.025 ng/mL)
 B: Extracted ion chromatogram of a 50 µL direct injection sample of metoprolol (5 ng/mL)

- The limit of detection is improved by a factor of 66 on average by enrichment via online SPE.
- For most pharmaceuticals the LOD is below the monitoring target of 10 ng/L (fig. 4) even though an older MS system was used.

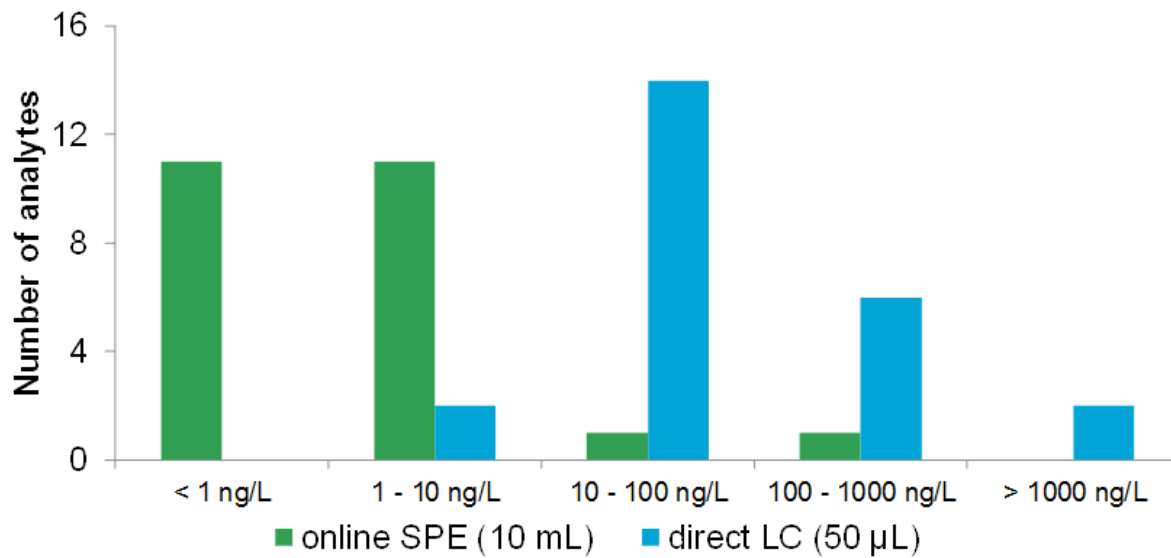


Fig.5: Comparison of the limits of detection (LOD) for the compounds analyzed between online SPE (green) and direct injection (blue). For 22 of the 24 compounds the desired LOD < 10 ng/L was achieved with online SPE.

Conclusions

- Online SPE is a suitable routine tool for the automated enrichment of pharmaceuticals from wastewater.
- Recovery and reproducibility of online SPE are comparable to or better than conventional offline SPE.
- The monitoring target of 10 ng/L is achieved for 22 of 24 pharmaceuticals, even with an older MS system.
- Chronos as control software allows to overlap SPE process and MS-analysis, resulting in a runtime of only 162 min for 10 samples.
- The automated process improves process safety and minimizes labor cost.

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