Preconcentration Strategy for Pharmaceuticals in Wastewater with Liquid Chromatography UV Detection

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Introduction

- Pharmaceuticals in the aquatic environment, an emerging problem
- Not removed by regular wastewater treatment
- Residues found in the ng/L range
- Low risk for acute toxicity, but risk for chronic effects
- Most common method for quantification is SPE together with LC-MS

SPE = Solid-Phase Extraction
LC = Liquid Chromatography
MS = Mass Spectrometry

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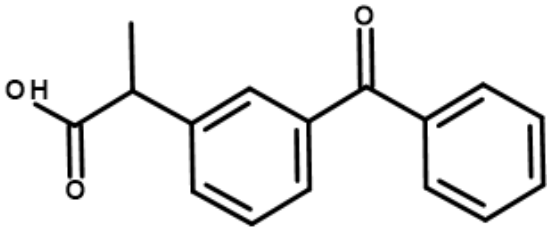
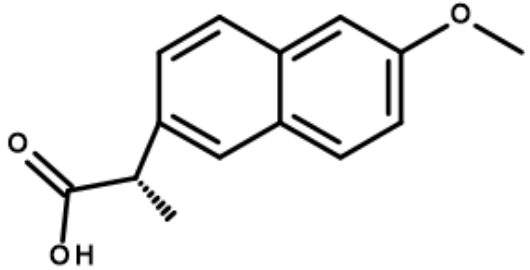
Aim

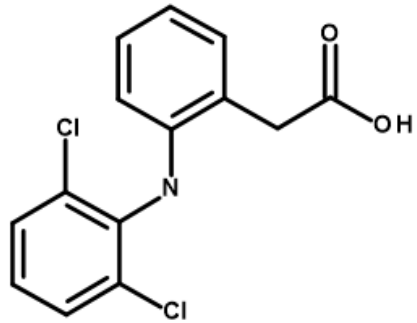
- Quantify Ketoprofen, Naproxen, Diclofenac and Ibruprofen from wastewater LC-DAD
- Is it possible to preconcentrate with rotary evaporation combined with SPE?



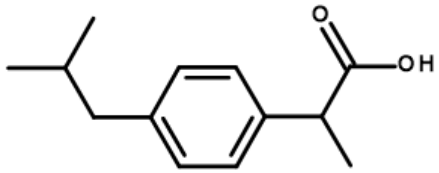
Ketoprofen



Naproxen



Diclofenac



Ibruprofen

LC = Liquid Chromatography
DAD = Diode Array Detection
SPE = Solid-Phase Extraction

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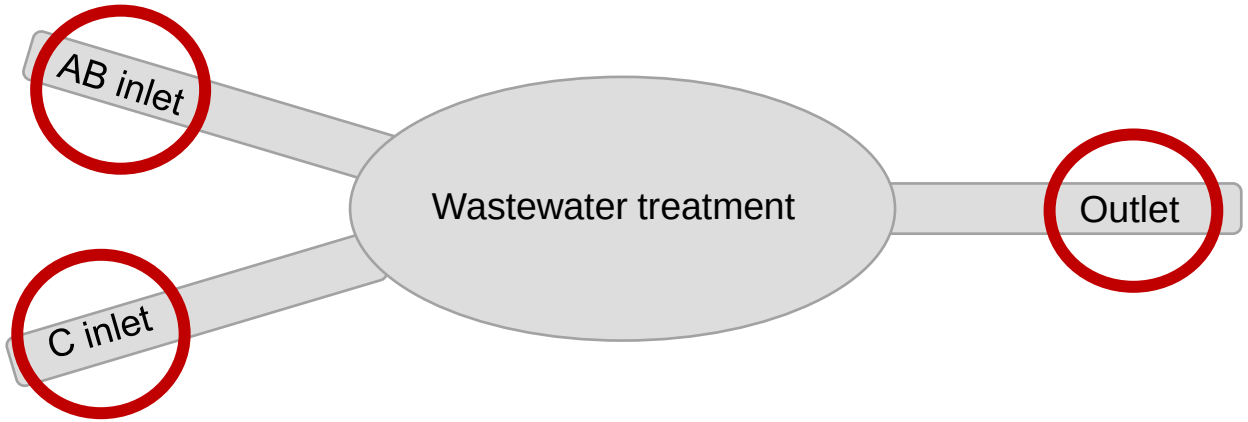
Structures drawn in Biovia Draw 2019

Methodology

Sampling

- Random spot checking samples were taken
- No representative picture



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Methodology

SPE

- C18
- Washed with 25% organic phase (50 : 50 Methanol : Acetonitrile)
- Eluted with 75% organic phase (50 : 50 Methanol : Acetonitrile)

LC - DAD

- Isocratic elution with 25 : 25 : 50 Methanol : Acetonitrile : Buffer
- Three wavelengths for detection

SPE = Solid-Phase Extraction
LC = Liquid Chromatography
DAD = Diode Array Detection

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Figure drawn in BioRender.com

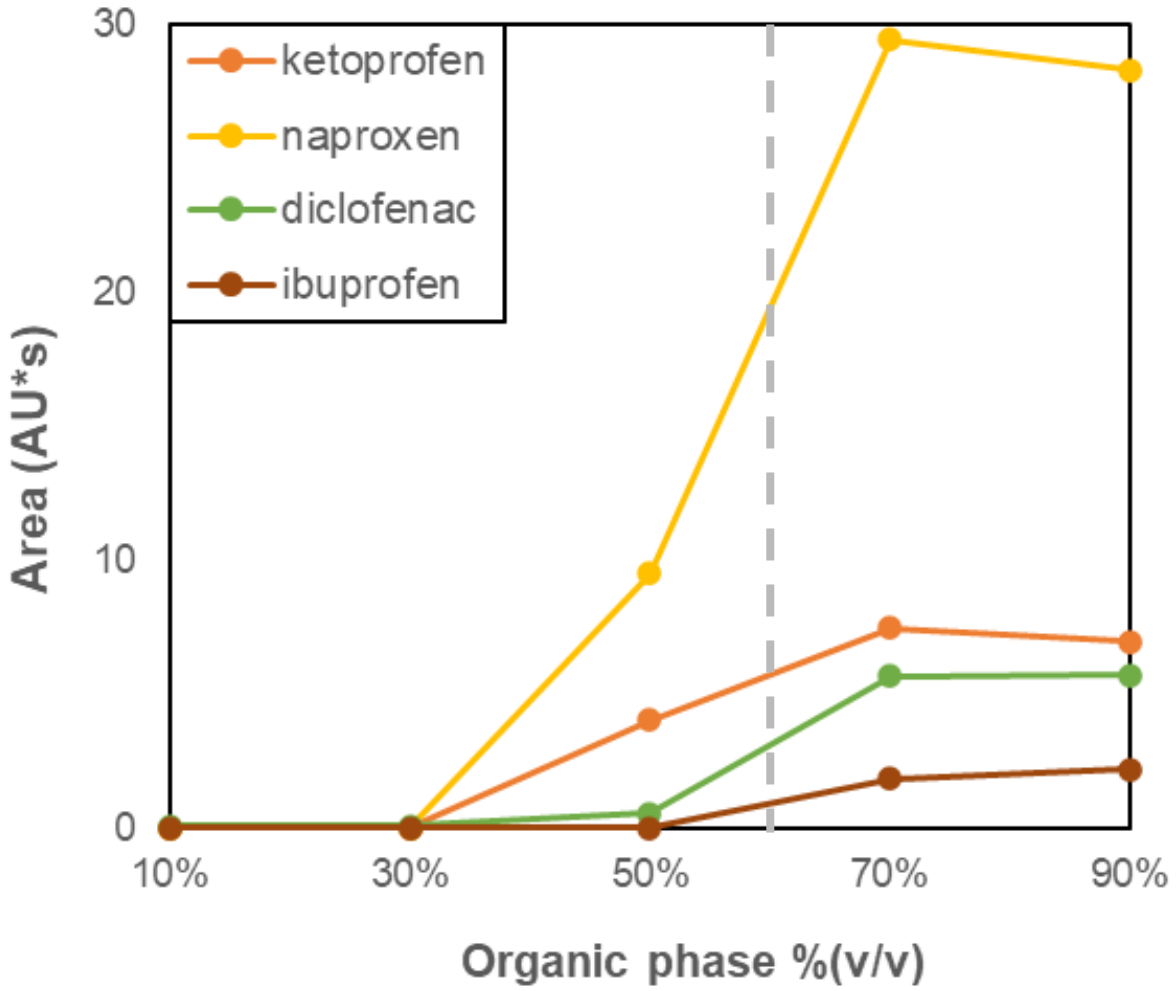
Results

Rotary evaporation

Time: 35 min
Concentration factor: 50

SPE

Washing: 25 % org.
Elution: 75 % org.



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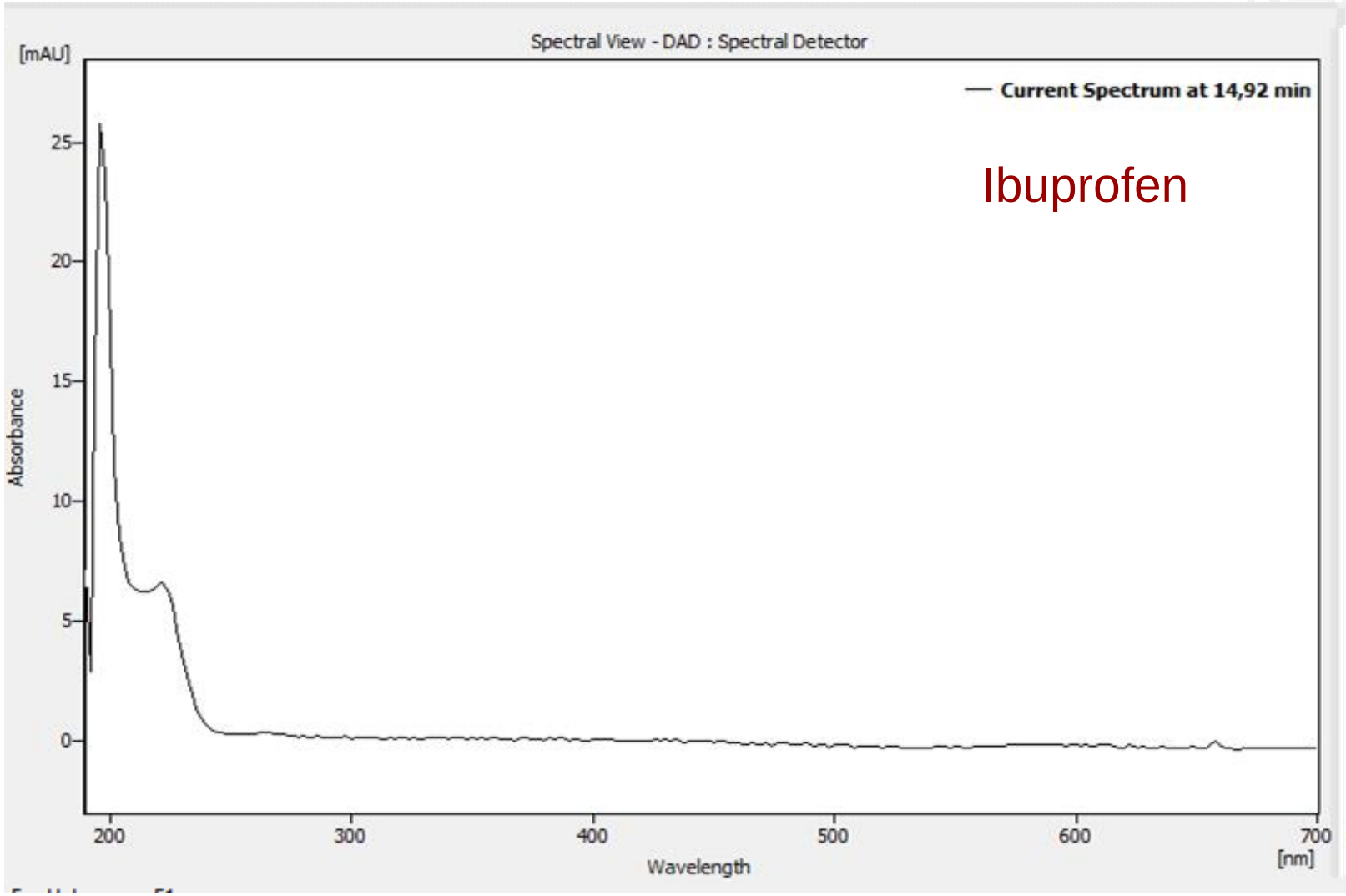
SPE = solid-phase extraction

Results

UV Spectra



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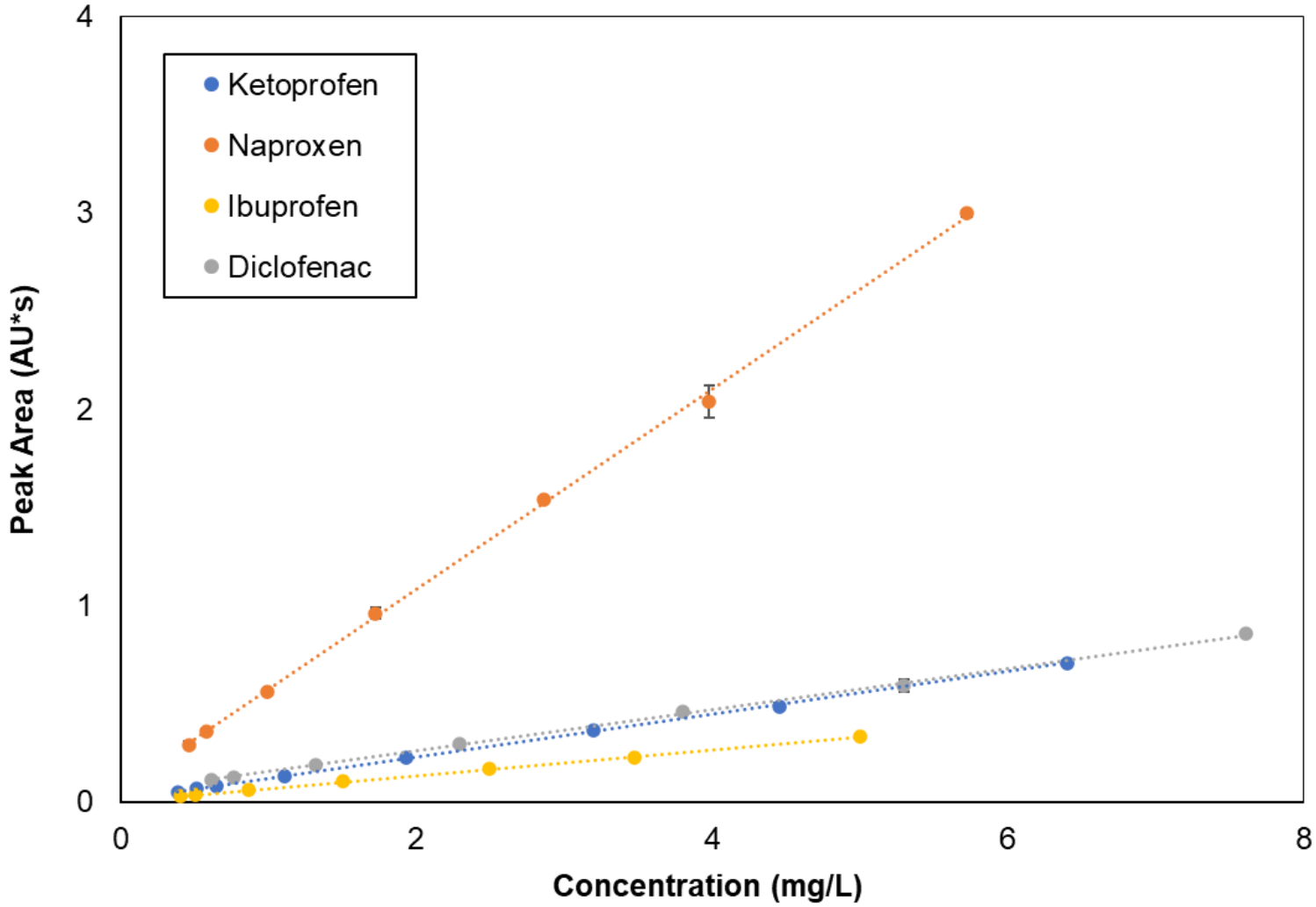
Results

Calibration



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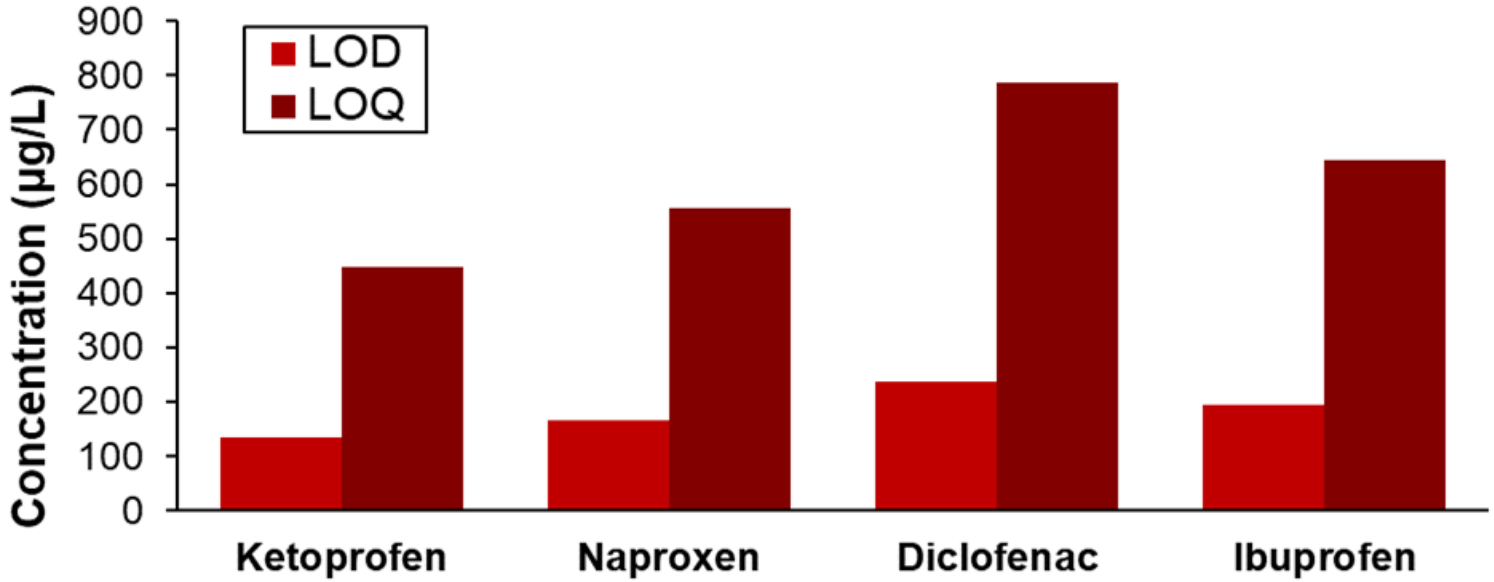
Results



$$LOD = 3 \times \frac{S}{m} \qquad LOD = 10 \times \frac{S}{m}$$

S, standard deviation of calibration residuals
m, slope

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Wastewater samples

- Naproxen and ibuprofen detected in influents
  - Ibuprofen <LOQ

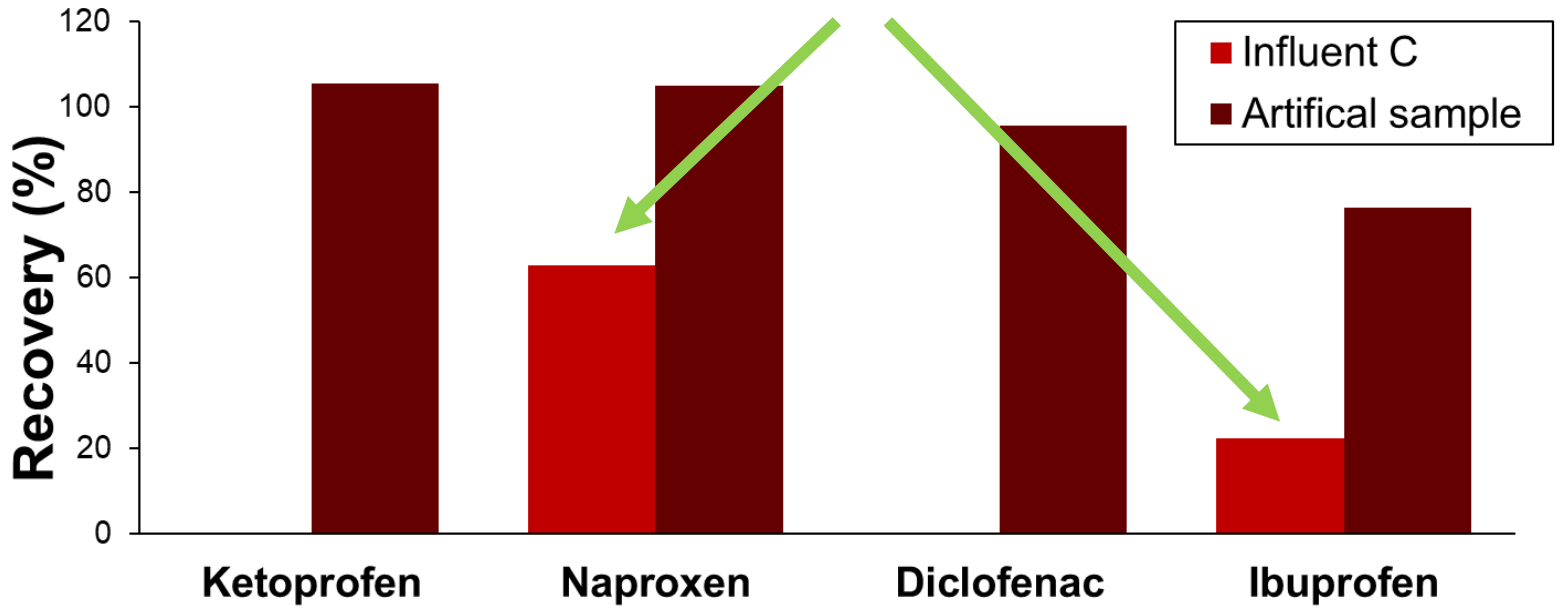
- No significant difference between influent AB and C for naproxen
  - Extra unknown peaks

- No compounds detected above LOD for effluent

LOQ = limit of quantitation
LOD = limit of detection

Recovery of wastewater

- Recovery only for influent C
  - Limited sample amounts – repetition not possible
- Lower recovery in sample compared to artificial sample



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Recovery of wastewater

- Reasons:
  - heat degradation – to good recovery in artificial sample
  - solubility of compound in water
  - overloading the SPE

→ Matrix effects

SPE = solid-phase extraction

Recovery of wastewater

- The method works in principle
- Needs more optimization
  - better filters
  - use mass spectrometer with internal standards

- Faster method than only using SPE:
  - Rotary evaporation + SPE ~ 55 minutes
  - Only SPE > 100 minutes

SPE = solid-phase extraction

Conclusion

- Rotary evaporation and SPE combined as sample preparation method
- Provides a faster sample preparation method
- Could detect naproxen and ibuprofen in influent samples
- Low recovery in wastewater sample
  - needs more optimization

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SPE = solid-phase extraction

Thanks for listening!

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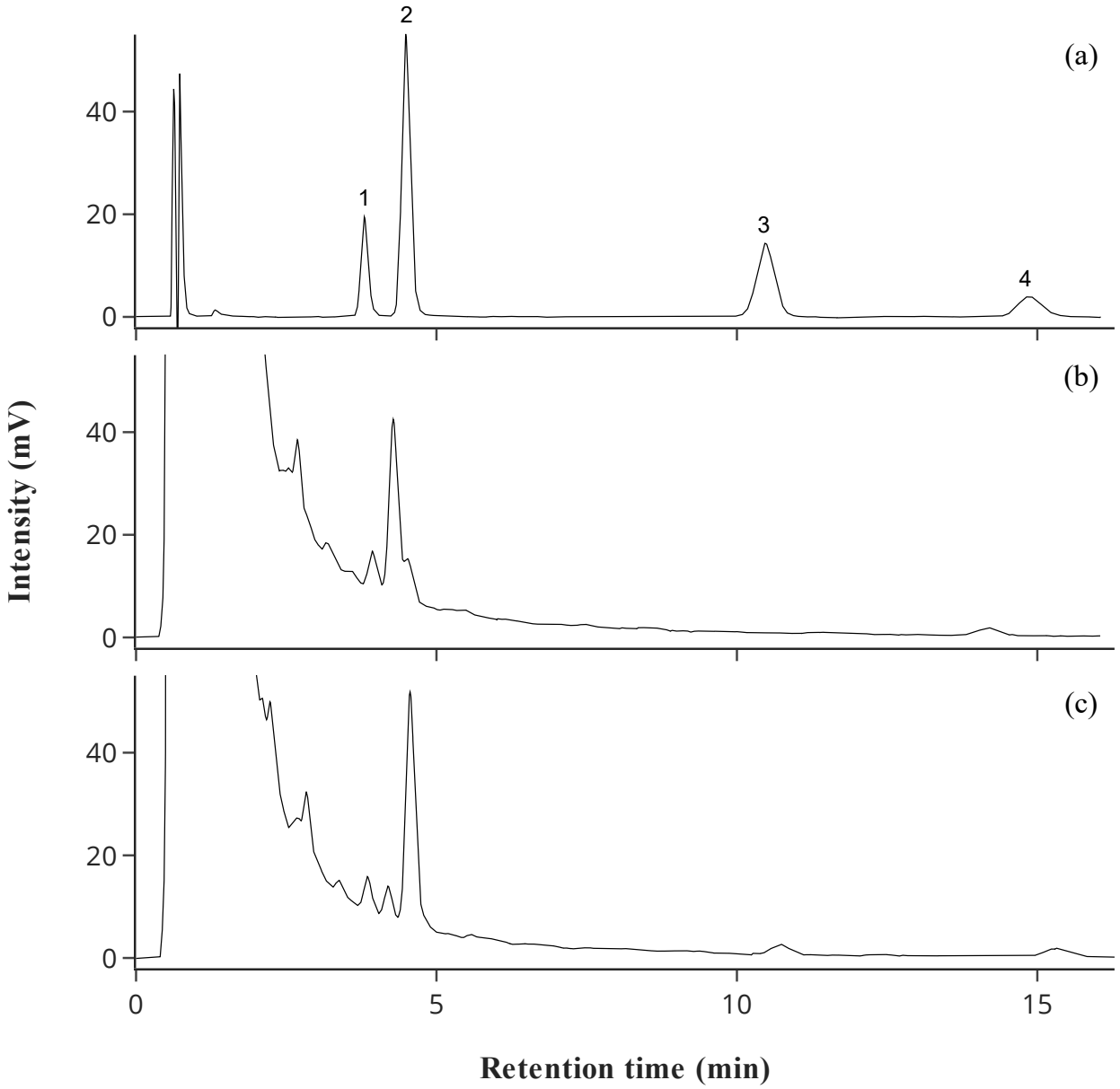

Figure 2: *Chromatograms for (a) calibration solution of (1) ketoprofen 646 µg/L, (2) naproxen 577 µg/L, (3) diclofenac 768 µg/L, and (4) ibuprofen 505 µg/L; (b) influent C sample; and (c) spiked influent C sample. Wavelenght: 220 nm.*

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