Hyphenation and automation of large-volume online-SPE with liquid chromatography mass spectrometry

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Overview

- **Development of automated online-SPE LC-MS/MS method for 85 micropollutants.**
- **Automated screening of different SPE materials.**
- **Optimization of complete analysis workflow by intelligent software algorithm.**

Introduction

Solid Phase Extraction (SPE) is a technique usually required to achieve an acceptable limit of detection for target analysis in environmental samples. A severe drawback of offline SPE is the time consuming sample preparation. Online SPE circumvents this and enables complete automating of the SPE-LC-MS/MS workflow. Innovative software algorithms help to perform SPE in parallel and can thus reduce the overall cycle time for sample preparation and analysis. For the highest degree of flexibility, the new autosampler platform in combination with an automated cartridge exchanger was used. Therefore, the injection volume can be varied from 10 µL up to 10 mL.

Methods

Figure 1: ACE (automated cartridge exchanger); HPD (high pressure dispenser); PAL RTC (Prep and load robotic tool change).

Online SPE unit: PAL RTC (CTC Analytics); ACE, HPD (Spark Holland)
HPLC pumps: Agilent 1100
SPE cartridges: Variable cartridges (see Figure 4)
Stationary phase: Merk Chromolith C18; 50 × 2 mm
Mobile phase A: Water + 0.1% formic acid
Mobile phase B: Methanol + 0.1% formic acid
Injection volumes: 1 mL, 5 mL or 10 mL; (50 µL LC-Mode)
Gradient: Linear solvent gradient within 10 minutes
Temperature: 40 °C
Flowrate: 0.5 mL min⁻¹
Detector: Sciex TripleQuad MS
Software: Chronos, controls autosampler, SPE enrichment processes and data acquisition
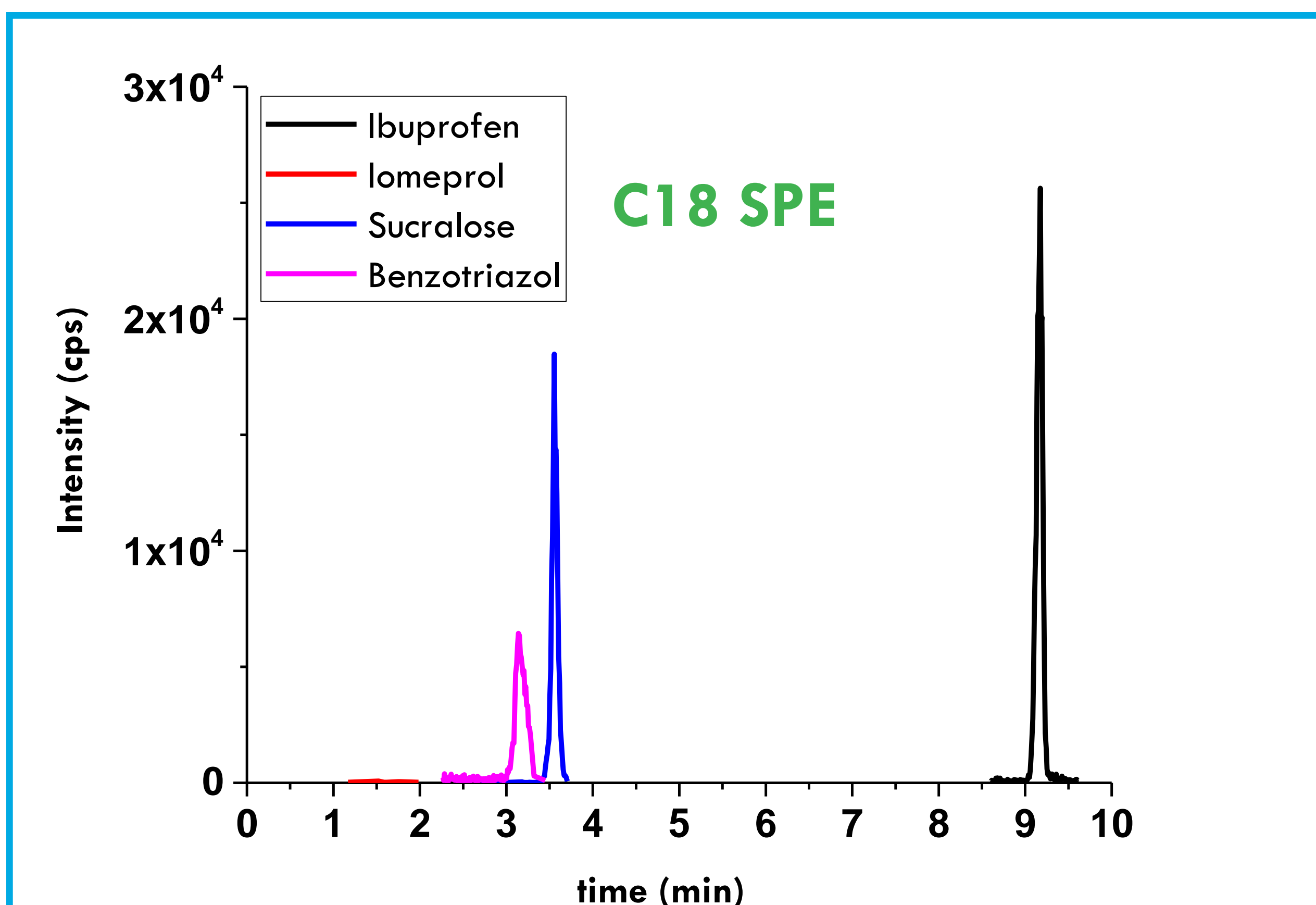
Results and discussion

Figure 2: Chromatogram of selected analytes by 1 mL SPE with C18 cartridge. Polar analytes (Iomeprol, Benzotriazol) show partial or no enrichment.
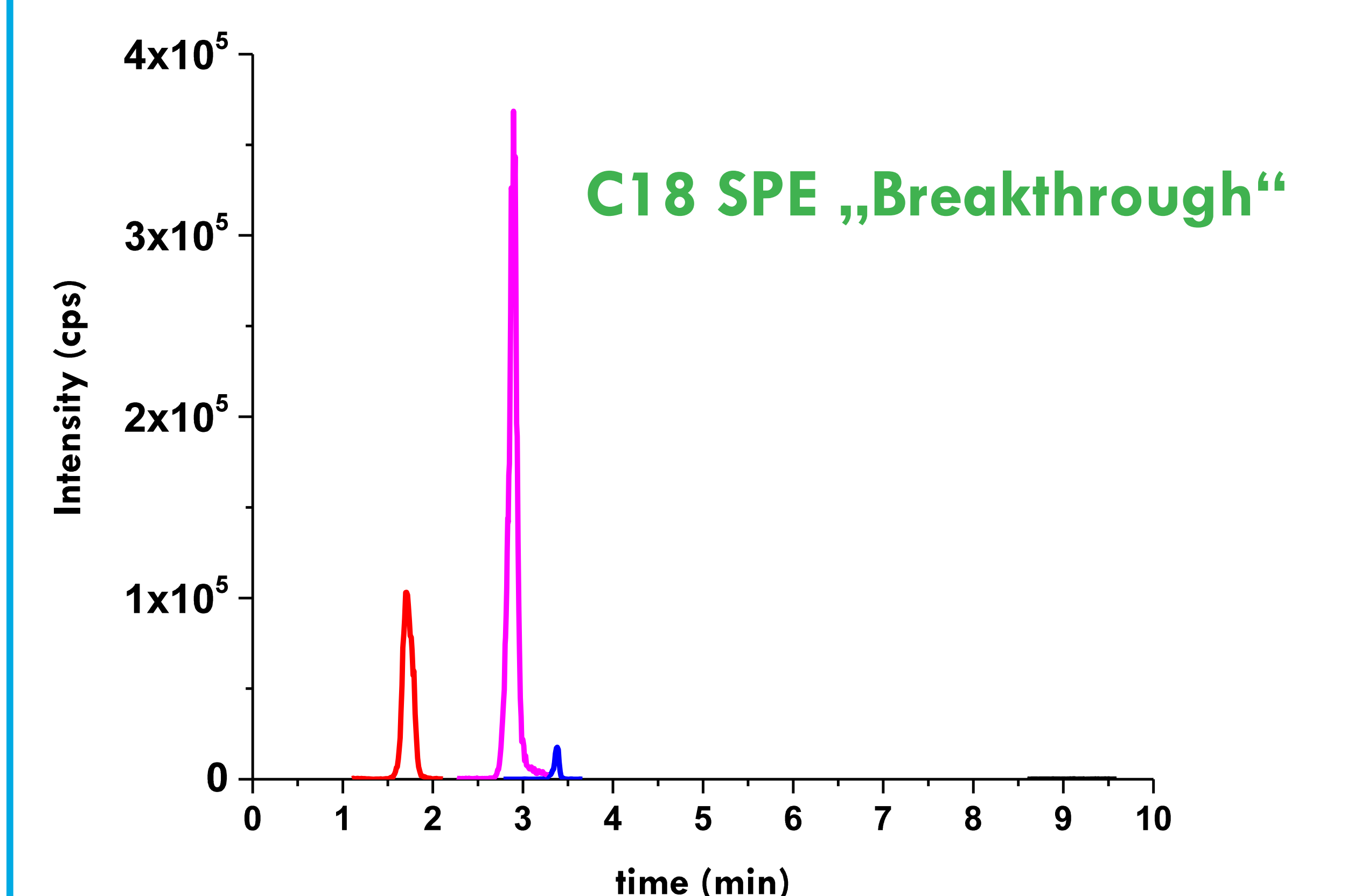

Figure 3: Breakthrough sample of 1 mL SPE shows detection of polar analytes. Non polar compounds like Ibuprofen are completely enriched on SPE-cartridge.
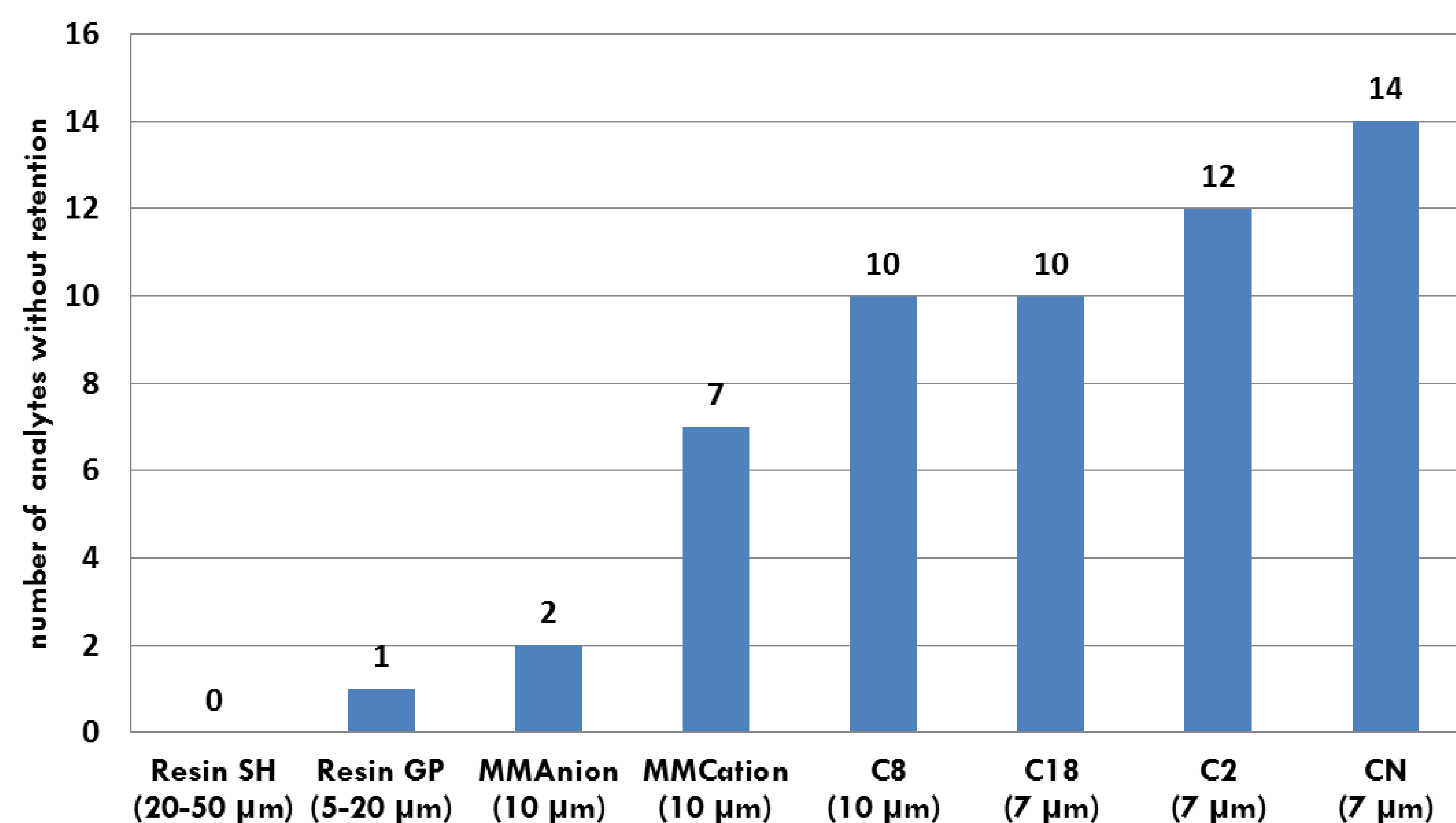

Figure 4: Detected analytes without retention on selected cartridge material.

- Resin material is highly efficient for enrichment of the selected analytes (Fig. 4).
- Peaks are very broad, because of large particle diameter (Fig. 5 + 6).
- Resin SH cartridge shows larger peak widths than Resin GP.
- SPE cartridges should be filled with 5 µm particles.
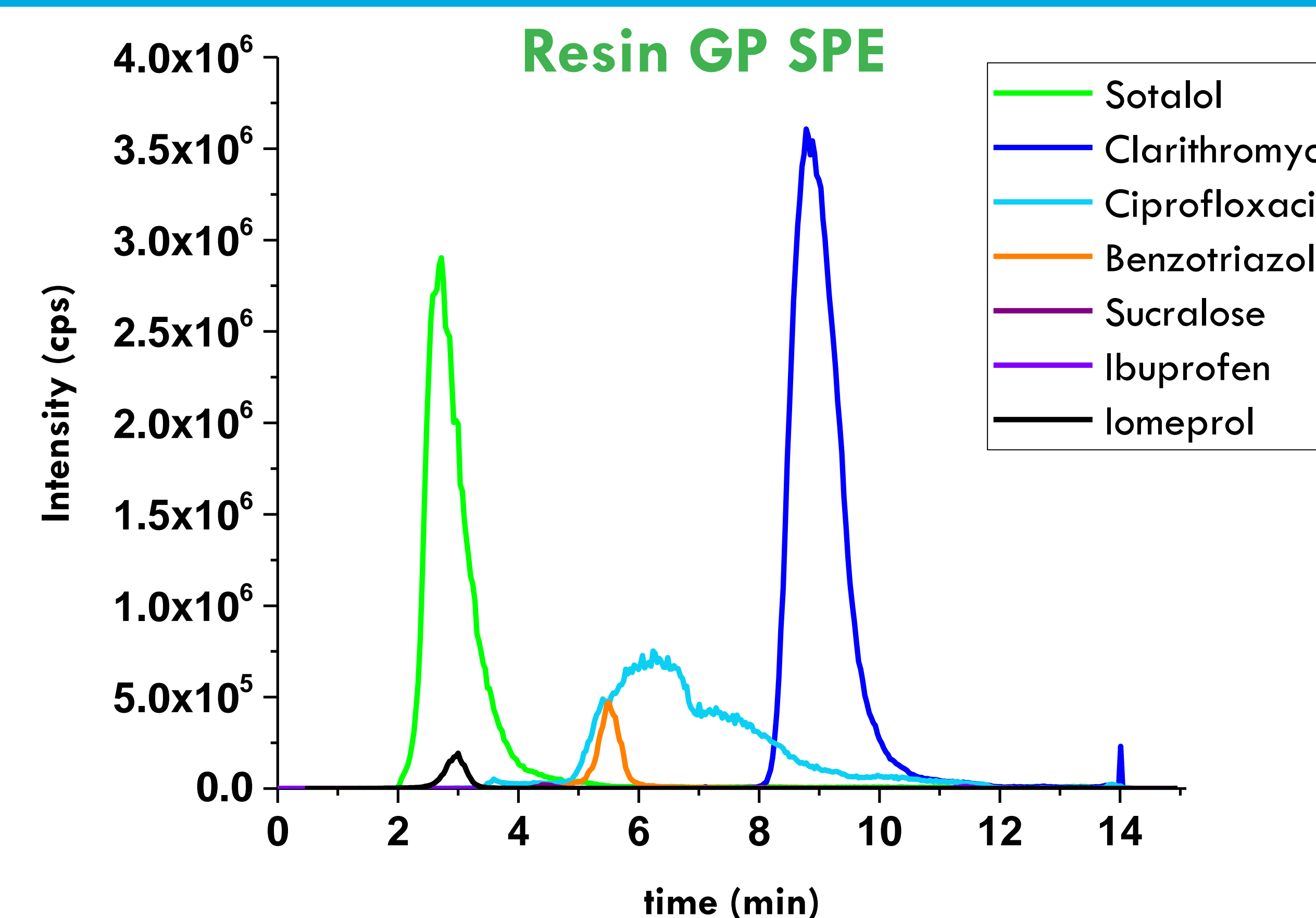- Alternatively, sample can be eluted by HPD focusing mode.

Figure 5: XLC Chromatogram with Resin GP cartridge. Sucralose and Ibuprofen show low intensity.
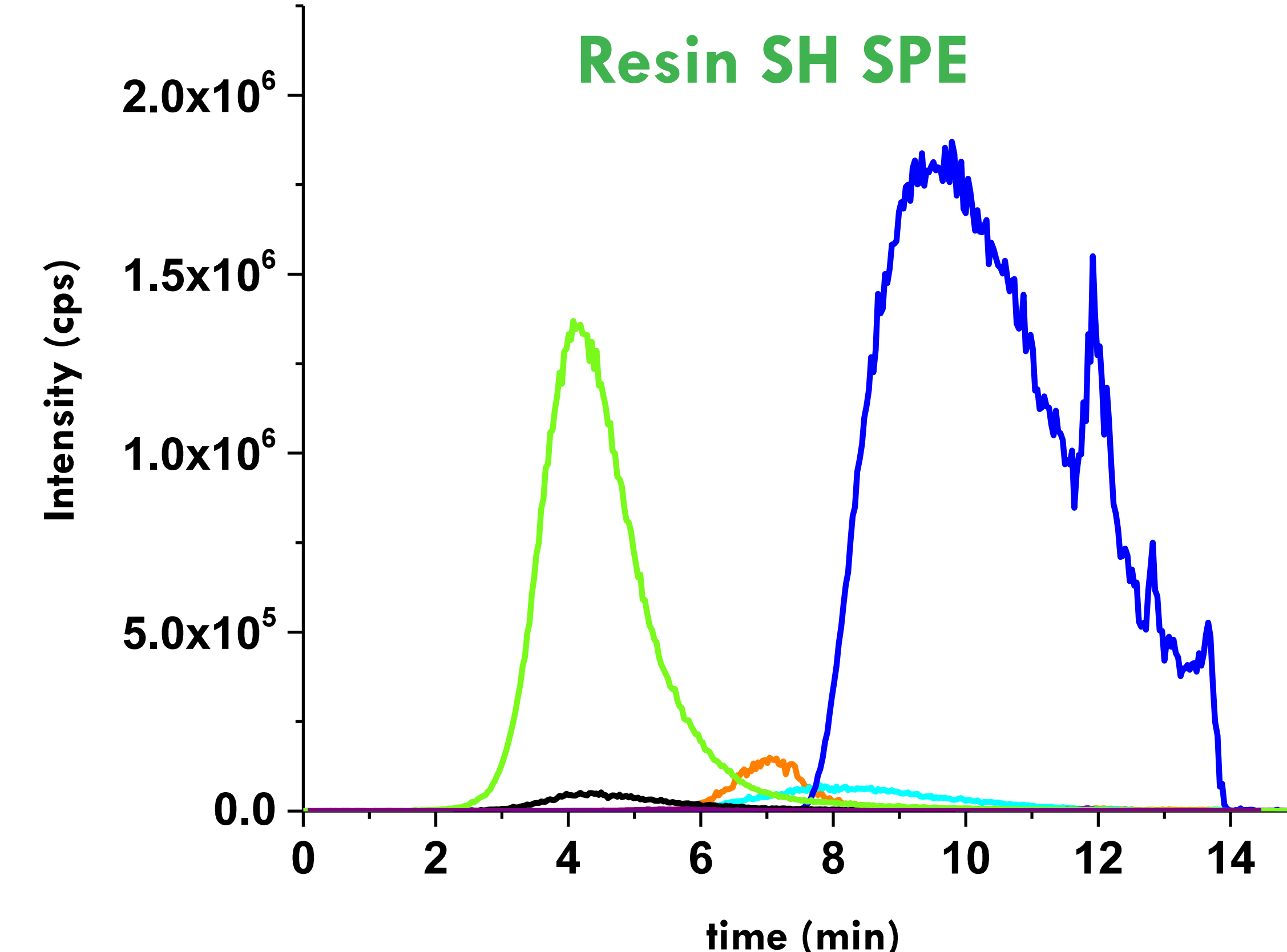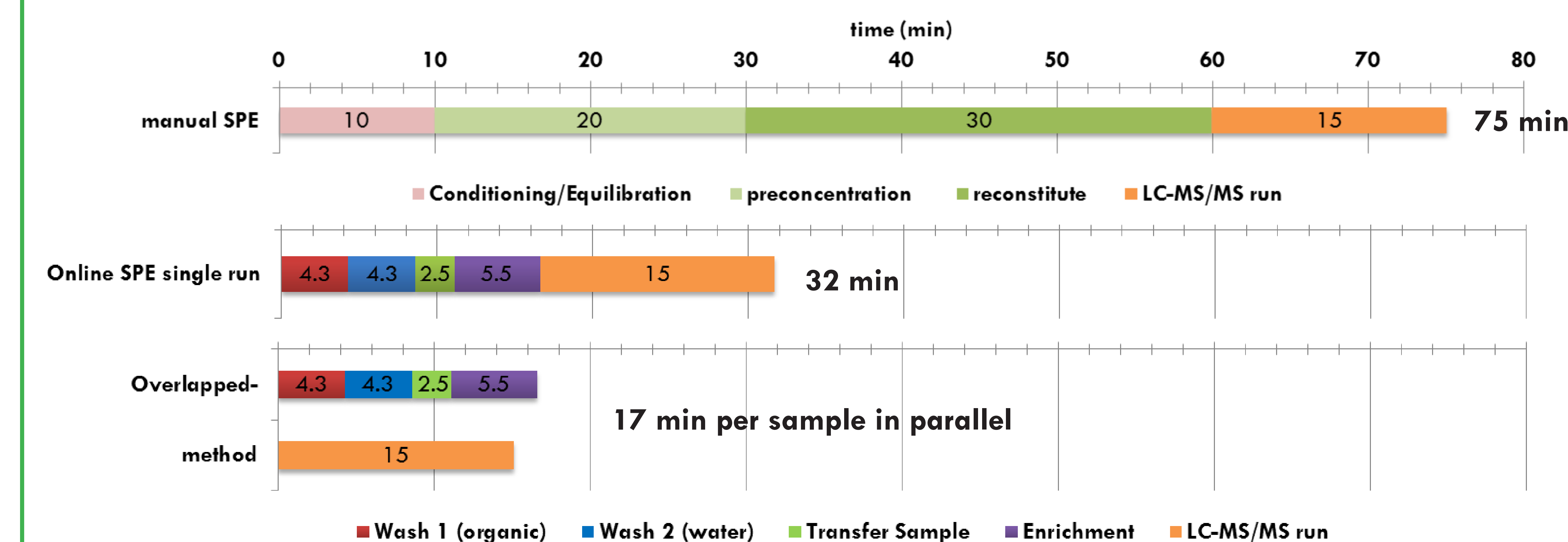

Figure 6: XLC Chromatogram with Resin SH cartridge. Sucralose and Ibuprofen show low intensity.

Length of different SPE methods (for 10 mL samples):

Conclusions/Outlook

- For sample enrichment C18 phase is not suitable for polar and moderately polar analytes.
- Polymeric materials like Resin SH and GP very suitable for enrichment of polar and non polar analytes.
- In order to obtain small peak widths small particle packed SPE cartridges (< 5 µm) are preferred.
- Different elution mode (HPD focusing) could be used in combination with large particle packed SPE cartridges
- Innovative software algorithm (Chronos) is a useful tool for interlacing and automation of complete workflow.

Acknowledgement