Validation and Development of an optical detection microfluidic device for the determination of antibiotics in environmental waters

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INTRODUCTION

Very little attention has been directed towards the implementation of supported liquid membranes (SLMs) into the microfluidic chip format[1-3]. Up to date, fluoroquinolones have been quantified using traditional LPME by our group resulting in longer extraction times and higher sample consumption. Compared with the conventional LMPE, in this work, we focus on sample miniaturization technique and this new system has been down-scaled resulting in a very high extraction efficiency in only 5 minutes extraction and 10 µL of sample. This system improves the advantages of the existing techniques by decreasing the organic solvent consumption and decrease significantly the sample volume required for the analysis (2000x times).

This work consists of the development and calibration of a microfluidic device for direct fluorescence detection. First, the microchip was evaluated and tested using fluorescein, a substance of high fluorescence, soluble in methanol, and widely used as a marker in methods of measuring other non-fluorescent substances. This microfluidic device was applied to the determination of an antibiotic commonly used for people and animals: norfloxacine. The measurements were carried out using two optical fibers, spectrometers and optical potentiometers at a wavelength of 278 y 445 nm.

Finally, the microfluidic device was calibrated for norfloxacine with dection limits and quantitation limits of 0.07 mg/L and 0.24 mg/L, respectively. This device was satisfactory applied in environmental samples, specifically to waters from the Llobregat River passing through Manresa, Barcelona. This has been demonstrated to be a low-cost device offering short time of analysis and low detection and quantification limits. Additionally, this device is reusable and easy sampling to use.

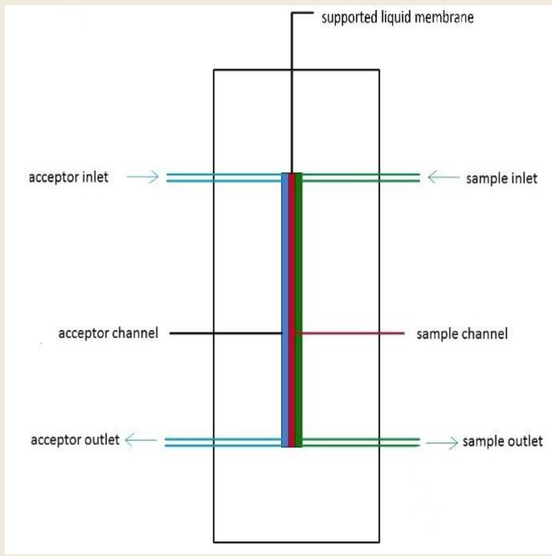


Figure 1. Schematic of liquid phase microextraction on a microfluidic-µLPME.

METHODOLOGY

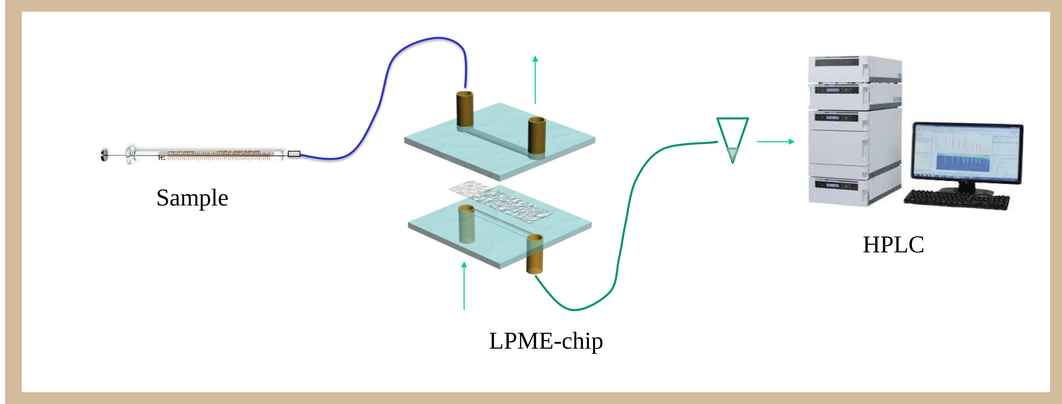


Table 1. µLPME optimization

Parameters	Conditions
Length of membrane	13 mm
Organic solvent	Dihexylether
Extraction time	5 minutes
Acceptor phase	pH 12
Donor phase	pH 3.5
Acceptor and donor flow rate	1 µL/min

Table 2. Gradient optimization by HPLC

Column
LiChroCART® 75-4 Purosphere® STAR RP-18e 3 µm (75 x 4.0 mm i.d.)

Time	A (0.1% Formic acid)	B (Methanol)	Flow (mL/min)
0	75	25	0,8
13	0	100	0,8
14	0	100	0,8

RESULTS

Real sample treatment

Adjust pH 3,5

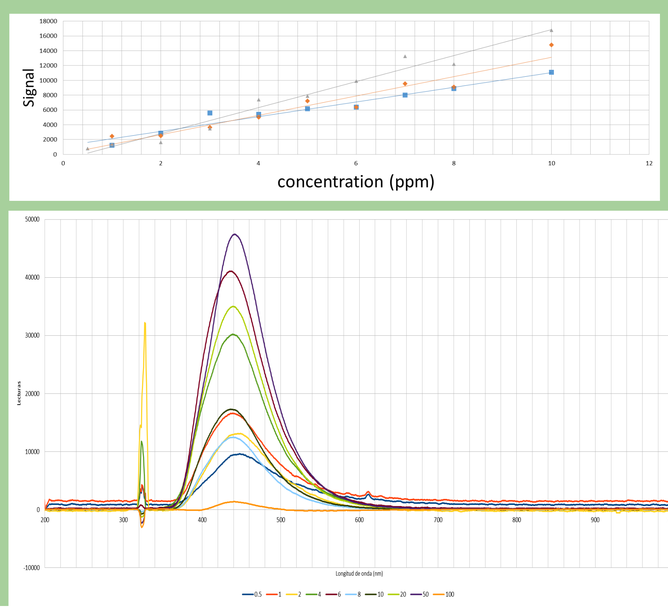
LPME-Chip

Analysis (photonic chip)

Table 3. µLPME/HPLC recoveries (average of three determinations ± standard deviation) from non-diluted spiked environmental samples *at 0.5 µg mL^{-1}.*

	RIVER RUBÍ	RIVER SEC	LAC PETTITE
Norfloxacin	85.6 ± 1.2	83.0 ± 0.2	95.2 ± 0.1

Calibration curve at different concentrations of norfloxacin



CONCLUSIONS

This work presents for the first time the microfluidic µLPME reusable for the determination of acid drugs and its successfully application in environmental samples. This new geometry for µLPME offer higher recoveries over 83% % for all drugs in environmental samples. The new geometry of this µLPME allows replacing the membrane after extractions decreasing the cost instrumentation. This device has been demonstrated to be suitable for environmental samples (river and lake water) with excellent clean-up and baselines.

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