Novel microextraction capsule technique to extract personal care products from environmental water samples

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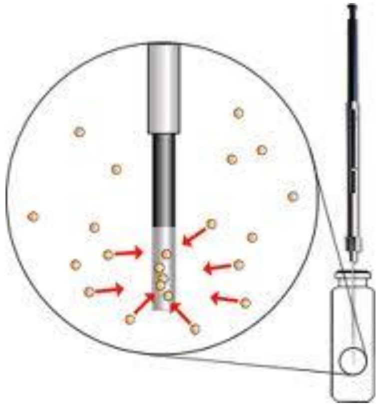
OUTLINE

- Introduction
- Aim
- Results
  - Optimisation
  - Evaluation
  - Application
- Conclusions

INTRODUCTION

EXTRACTION TECHNIQUES

SPME

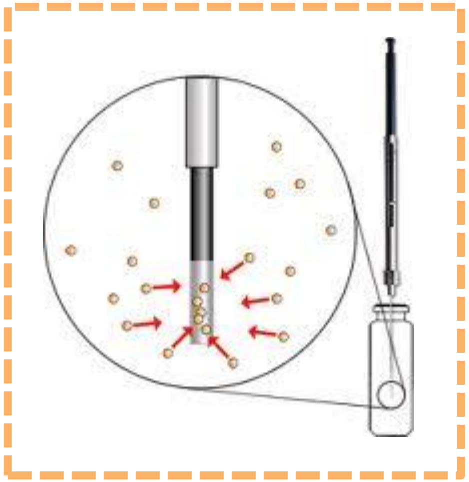


SBSE

INTRODUCTION

EXTRACTION TECHNIQUES

SPME



SBSE

- ✓ **Availability of different fibers.**
- ✓ **Less volume of extracting phase.**

INTRODUCTION

EXTRACTION TECHNIQUES

SPME

SBSE

- ✓ Larger extracting phase.
- ✓ Limitation of commercial available coatings.

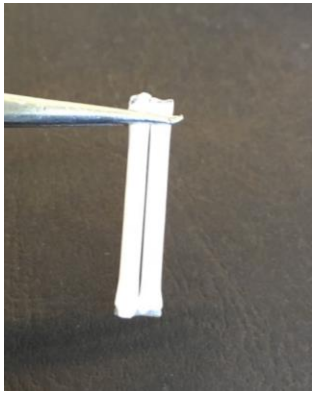
INTRODUCTION

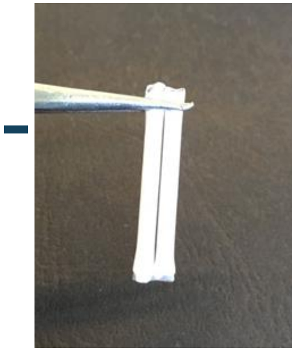
EXTRACTION TECHNIQUES

SPME

SBSE

CPME





INTRODUCTION

CAPSULE PHASE MICROEXTRACTION

Porous (0.2 µm) Tube

Cylindrical Magnet

Sol-gel Coated Fiber

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A. Kabir, K. G. Furton, Microextraction Capsule, US Patent application 14/806100, 2017.

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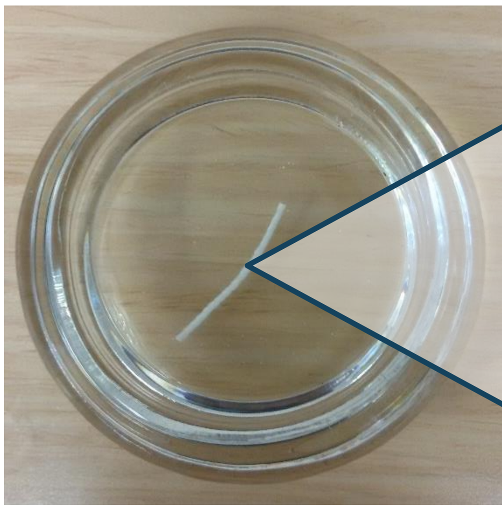
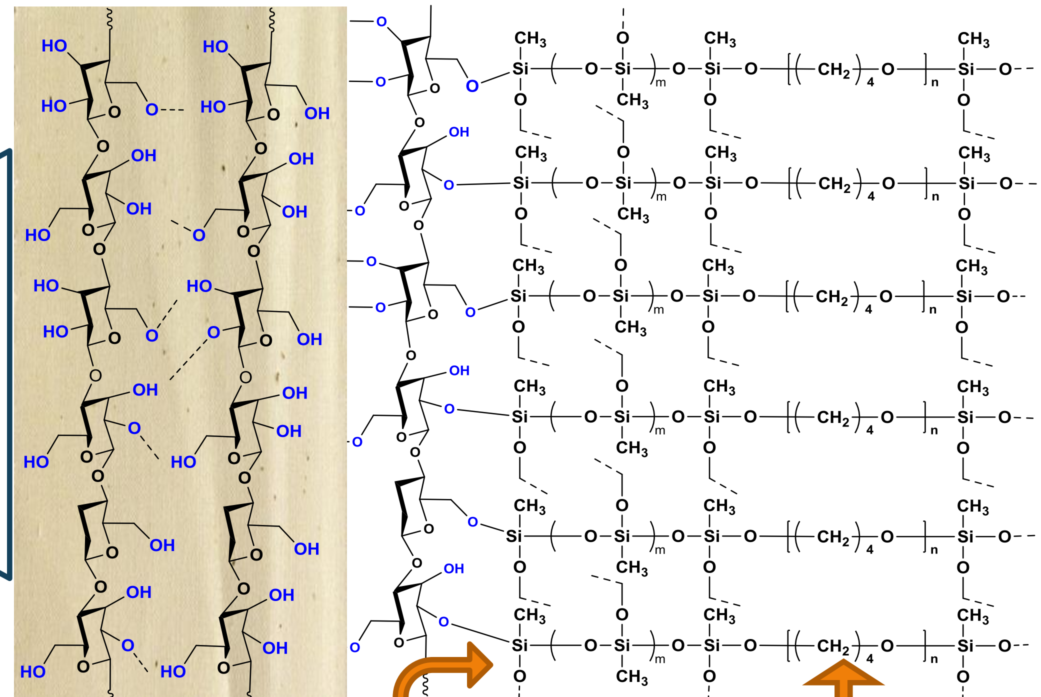
INTRODUCTION

CAPSULE PHASE MICROEXTRACTION



Sol-Gel coating



Inorganic Polymer Network

Organic Polymer integrated into Sol-Gel Network

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INTRODUCTION

CAPSULE PHASE MICROEXTRACTION

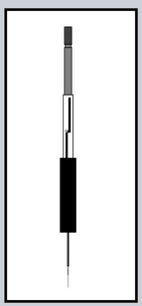
- ✓ Material 0,2 µm porous protected.
- ✓ High volume of sorbent in form of ultra-thin porous film.
- ✓ Primary contact surface area (220 mm^2).
- ✓ Strong covalent bonding between the fiber substrate and the sol-gel coating

Some material available:

- ✓ poly (dimethylsiloxane)
- ✓ poly (dilethyldiphenylsiloxane)
- ✓ C_{18}
- ✓ C_8
- ✓ poly (tetrahydrofuran) (THF)
- ✓ poly (UCON)
- ✓ poly (PCAP-DMS-CAP)
- ✓ poly (ethylenglycol) (PEG)
- ✓ poly Carbowax 20M

INTRODUCTION

CAPSULE PHASE MICROEXTRACTION

SPME	SBSE	CPME
 (20 mm x 0.305 mm o.d.)	 (10 mm x 3.2 mm o.d.)	 (30 mm x 2.25 mm o.d.)
10-20 mm^2	100 mm^2	220 mm^2

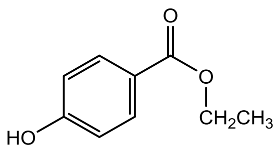
AIM

- ✓ **Optimisation** of the conditions of **CPME.**
- ✓ **Evaluation** of **CPME** in terms of recoveries and matrix effects
- ✓ **Application** in **CPME**/LC-MS/MS to determine PCPs in **surface** and **sewage** water samples

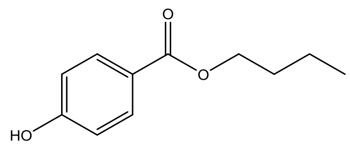
RESULTS - Optimization

TARGETS

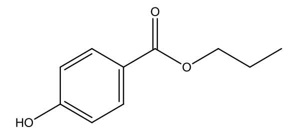
Personal Care Products



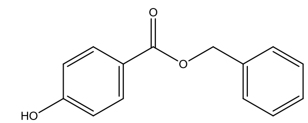
Ethylparaben (EPB)



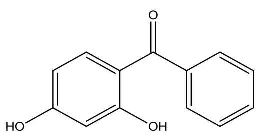
Buthylparaben (BPB)



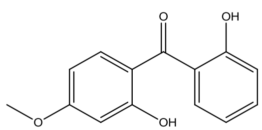
Propylparaben (PrPB)



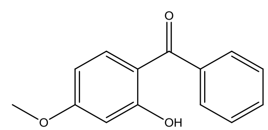
Benzylparaben (BzPB)



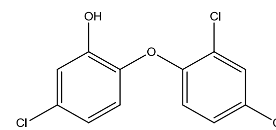
Dihydroxybenzophenone (DHB)



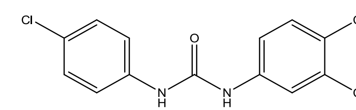
Dihydroxymethoxybenzophenone (DHMB)



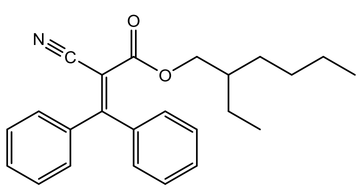
3-benzophenone (BP-3)



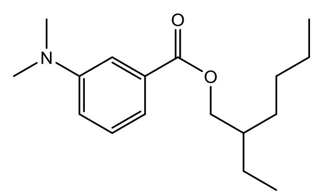
Triclosan (TCS)



Triclocarban (TCC)



Octocrylene (OC)



Octyldimethyl-p-aminobenzoic acid (OD-PABA)

RESULTS - Optimisation

METHOD OPTIMISATION

CPME

Extraction	Liquid Desorption
pH	Solvent
Agitation speed	Volume
Ionic strength	Time
Sample volume	
Extraction Time	

LC-(ESI)-MS/MS

Chromatographic separation

MS/MS parameters

RESULTS - Optimisation

METHOD OPTIMISATION LC-MS/MS

LC CONDITIONS

Column	Kromasil C_{18} (150x4.6 mm, 5 µm)
Mobile phase	A: H_2O, pH 3 (HCOOH) B: ACN
Gradient	see table below
Flow-rate	600 µL/min
Temp.	40 ^{0}C
Inj.	50 µL

Gradient:

T (min)	% B
0	15
12	90
20	100
22	100
25	15
30	15

MS/MS CONDITIONS

Capillary voltage	4000 V
Neb. Pressure (N_2)	45 psi
N_2 flow	12 L/min
Source Temp.	350 ^{0}C

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RESULTS - Optimization

METHOD OPTIMISATION LC-MS/MS

Analyte	t_R min	Ioniz. mode	Precursor Ion (m/z)	Cone Vol. (V)	Quantifier		Qualifier	
					Product Ion (m/z)	C.E. (eV)	Product Ion (m/z)	C.E. (eV)
EPB	10.39	-	165	100	92	15	136	10
PrPB	11.59	-	179	100	92	15	136	10
DHB	12.05	-	213	130	135	15	169	10
BzPB	12.53	-	227	100	92	20	136	10
BuPB	12.69	-	193	100	92	15	137	10
DHMB	13.03	-	243	80	93	15	123	15
BP-3	14.79	+	229	100	151	15	105	15
TCC	15.41	-	313	130	160	10	126	15
TCS	15.62	-	287/289	18	35	5	35	5
OC	16.37	+	384	130	272	5	228	5
OD-PABA	19.94	+	278	130	166	20	151	20

RESULTS - Optimisation

SELECTION of the CPME material

Initial conditions

5 mL MeOH
5 mL water
Stirred 5 min each

Conditioning

25 mL water at pH 3
Stirred 600 rpm 60 min

Extraction

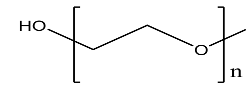
5 mL MeOH:ACN (1:1, v/v)
Ultrasonic bath 10 min

Liquid desorption

Evaporation to 100 µL
Redissolution with 1 mL MP

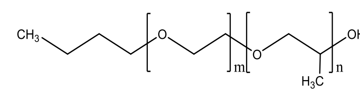
LC-MS/MS

CARBOWAX 20M



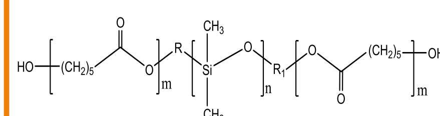
polar

UCON



medium polar

PCAP-DMS-CAP



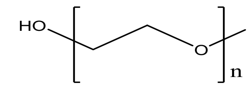
Block polar-apolar

RESULTS - Optimisation

SELECTION of CPME material

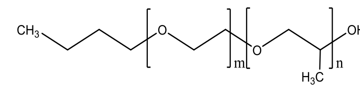
Analyte	CW-20M	UCON	PCAP-DMS-CAP
EPB	7	8	8
PrPB	13	10	9
DHB	24	22	20
BzPB	36	27	24
BuPB	29	29	29
DHMB	40	37	34
BP-3	58	47	44
TCC	60	22	28
TCS	74	62	62
OC	81	20	17
OD-PABA	89	39	42

CARBOWAX 20M



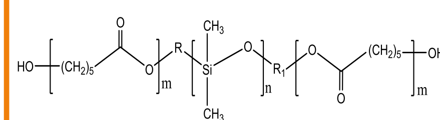
polar

UCON



medium polar

PCAP-DMS-CAP



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RESULTS - Optimisation

METHOD OPTIMISATION - CPME

	CPME parameters	Range	Optimised conditions
EXTRACTION	Sample pH	3 – 5 – 7	
EXTRACTION	Agitation speed (rpm)	300 – 600 – 900	
EXTRACTION	Ionic strenght (% NaCl)	0 – 5 – 10 – 15 – 20	
EXTRACTION	Sample volume (mL)	25 – 50 – 100	
EXTRACTION	Extraction time (min)	30 – 60 – 120 – 180 – 240 – 300	
LD	Solvent volume (mL)	5 – 10	
LD	Desorption solvent	MeOH – ACN – MeOH/ACN	
LD	Desorption time (min)	5 – 10 – 15	

RESULTS - Optimisation

METHOD OPTIMISATION - CPME

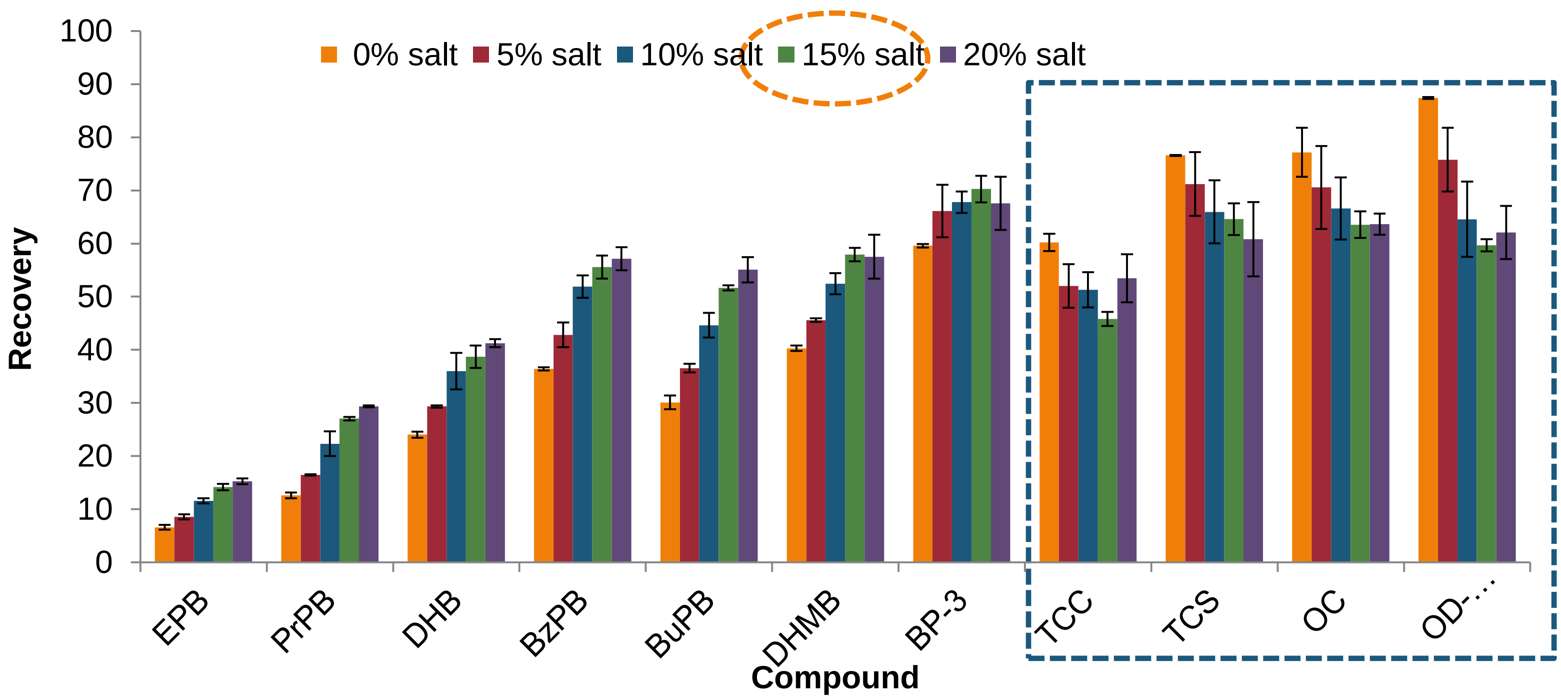
	CPME parameters	Range	Optimised conditions
EXTRACTION	Sample pH	3 – 5 – 7	
	Agitation speed (rpm)	300 – 600 – 900	
	Ionic strenght (% NaCl)	0 – 5 – 10 – 15 – 20	
	Sample volume (mL)	25 – 50 – 100	
	Extraction time (min)	30 – 60 – 120 – 180 – 240 – 300	
LD	Solvent volume (mL)	5 – 10	5 mL
	Desorption solvent	MeOH – ACN – MeOH/ACN	MeOH/ACN
	Desorption time (min)	5 – 10 – 15	10 min

RESULTS - Optimisation

METHOD OPTIMISATION - CPME

CPME parameters	Range	Optimised conditions
Ionic strength (% NaCl)	0 – 5 – 10 – 15 – 20	

E X T R A C T I O N

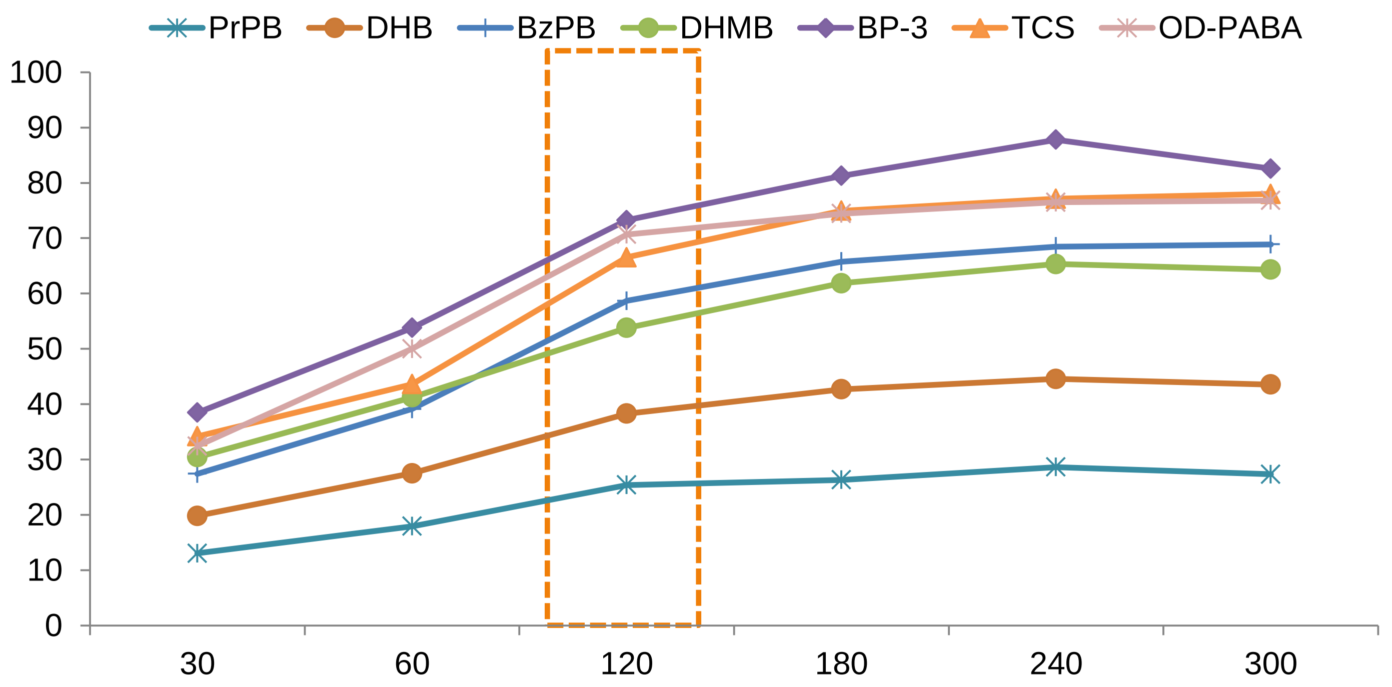


RESULTS - Optimisation

METHOD OPTIMISATION - CPME

CPME parameters	Range	Optimised conditions
Extraction time (min)	30 – 60 – 120 – 180 – 240 – 300	

EXTRACTION



RESULTS - Optimisation

METHOD OPTIMISATION - CPME

	CPME parameters	Range	Optimised conditions
EXTRACTION	Sample pH	3 – 5 – 7	3
	Agitation speed (rpm)	300 – 600 – 900	600 rpm
	Ionic strenght (% NaCl)	0 – 5 – 10 – 15 – 20	15% NaCl
	Sample volume (mL)	25 – 50 – 100	50 mL
	Extraction time (min)	30 – 60 – 120 – 180 – 240 – 300	120 min
LD	Solvent volume (mL)	5 – 10	5 mL
	Desorption solvent	MeOH – ACN – MeOH/ACN	MeOH/ACN
	Desorption time (min)	5 – 10 – 15	10 min

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RESULTS - Evaluation

% RECOVERY – ULTRAPURE WATER

Analyte	CW-20M CPME
EPB	26
PrPB	47
DHB	56
BzPB	73
BuPB	71
DHMB	85
BP-3	90
TCC	64
TCS	67
OC	73
OD-PABA	77

RESULTS - Evaluation

% RECOVERY – ULTRAPURE WATER

Analyte	CW-20M CPME	SBSE Acrylate	SBSE EG-Silicone
EPB	26	n.a.	n.a.
PrPB	47	2	10
DHB	56	9	24
BzPB	73	14	39
BuPB	71	n.a.	n.a.
DHMB	85	9	26
BP-3	90	10	45
TCC	64	43	59
TCS	67	42	80
OC	73	n.a.	n.a.
OD-PABA	77	n.a.	n.a.

CW-20M MEC

EG based

Acrylate Twister®

PA with a proportion of PEG

EG-Silicone Twister®

EG modified silicone

RESULTS - Evaluation

% RECOVERY & MATRIX EFFECT – SEWAGE WATER

	RIVER		EFFLUENT	
Analyte	% $R_{overall}$	% ME	% $R_{overall}$	% ME
EPB	19	-26	11	-49
PrPB	27	-36	21	-42
DHB	30	-33	23	-38
BzPB	39	-38	29	-39
BuPB	39	-32	28	-40
DHMB	33	-28	27	-32
BP-3	40	-23	33	-28
TCC	60	-22	56	-14
TCS	57	-24	34	-32
OC	43	-33	54	-17
OD-PABA	37	-44	28	-33

RESULTS - Application

METHOD VALIDATION – SEWAGE WATER

Analyte	EFFLUENT SEWAGE			
	LODs (ng/L)	Linear range (ng/L)	Repeatability (%RSD, n=5)*	Reproducibility (%RSD, n=5)*
EPB	5	20 – 5000	9	11
PrPB	7	20 – 5000	5	12
DHB	7	20 – 5000	5	7
BzPB	5	20 – 5000	4	8
BuPB	5	20 – 5000	6	6
DHMB	7	40 – 5000	8	13
BP-3	7	20 – 5000	10	17
TCC	2	20 – 5000	7	10
TCS	10	200 – 5000	6	9
OC	5	20 – 5000	12	15
OD-PABA	5	20 – 5000	9	11

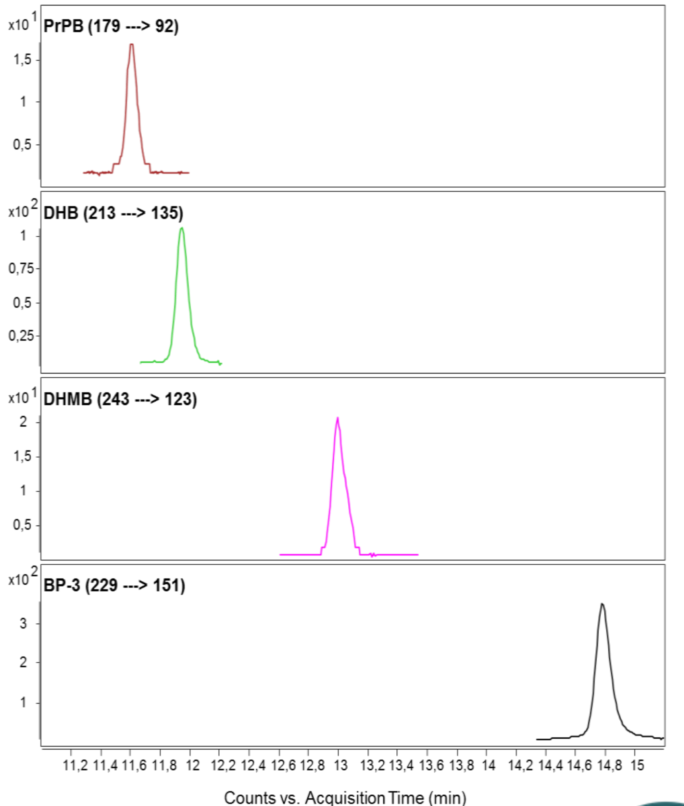
*at 20 ng/L

RESULTS - Application

ANALYSIS OF SAMPLES

Analyte	Concentration (ng/L) RIVER	EFFLUENT
EPB	n.d.	n.d
PrPB	n.d	26 - 43
DHB	< LOQ	< LOQ
BzPB	n.d	n.d
BuPB	n.d	n.d
DHMB	14 - 90	18 - 122
BP-3	36 - 93	95 - 142
TCC	n.d	n.d
TCS	n.d	n.d
OC	n.d	n.d
OD-PABA	n.d	n.d

EFFLUENT SEWAGE SAMPLE



CONCLUSIONS

- A novel sorptive extraction technique, capsule phase microextraction CPME have been proposed and successfully evaluated.
- The CW 20M material provided the best results for the extraction of PCPs.
- CPME provided better results than the commercially available SBSE with polar coatings.
- The CPME followed by liquid desorption with LC-ESI-MS/MS provided an efficient, simple and sensitive method for determination of PCPs.
- The analysis of river and effluent sewage samples revealed the presence of some PPCs.
- The proposed CPME technique might be extended to extract other target compounds in different sample matrices in future.

ACKNOWLEDGEMENTS

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Kenneth G. Furton

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Sameer Lakade

Rosa M. Marcé

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Project CTQ2014-52617-P

THANK YOU FOR YOUR ATTENTION !!!

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