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Determination of micropollutants in water samples from swimming pool systems

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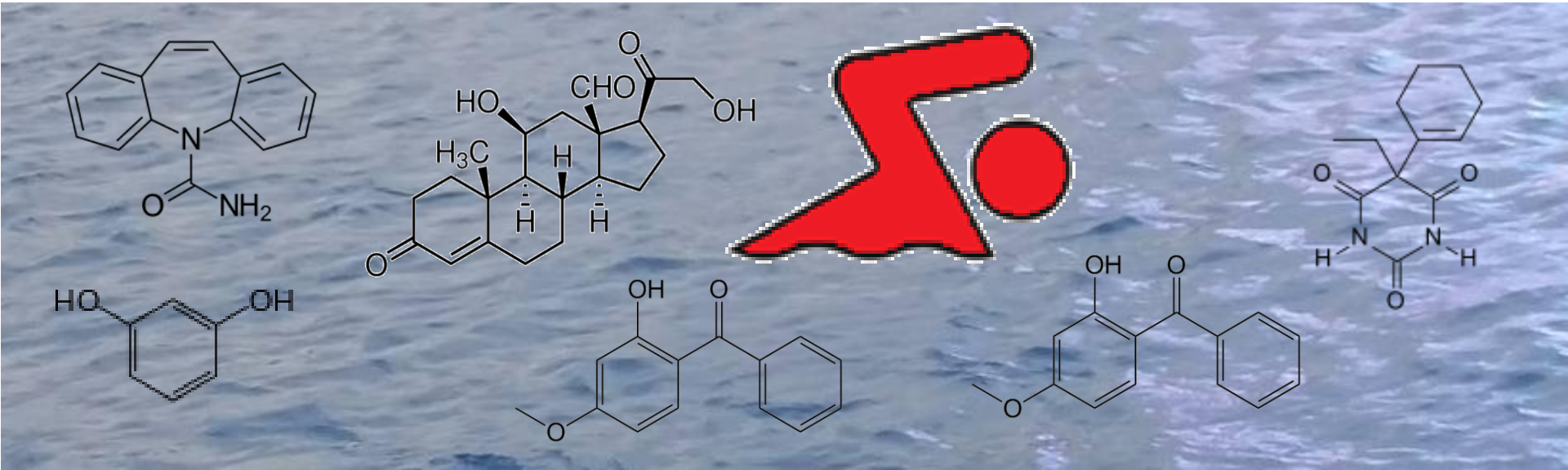
INTRODUCTON

- Research on PPCPs in swimming pools are still in their infancy and available data are limited.
- PPCPs are designed to be biologically active even at low concentrations.
- Long-term exposure to the PPCPs mixture may potentially cause negative health effects.
- PPCPs' degradation in swimming pool water treatment systems is possible and their by-products may be more relevance to the health of swimmers than their parent compound

INTRODUCTON

- Swimmers have direct contact with the compounds present in the swimming pool water and their by-products



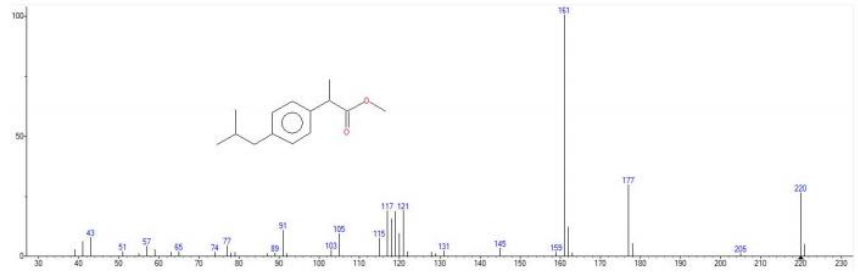
INTRODUCTON

- The determination of PPCPs requires very sensitive analytical methods that enables to confirm the presence of tested compounds in a complex organic extract.
- This study presents a selection of procedure for determining the concentration of three compounds from the macro-group of Pharmaceutical and Personal Care Products.

Extraction conditions selection

SPE – Solid Phase Extraction

The operating parameters selection

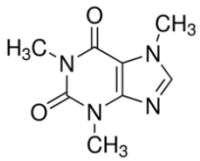
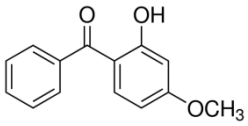
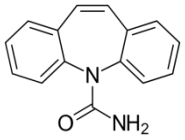


NIST 17 Mass Spectral Library

GC/MS - Gas Chromatograph with Mass Detector

MATERIALS AND METHODS

Table 1. Characteristics of tested compounds

Standard	Structural formula	Molecular formula	Molar Mass [g/mol]	CAS Number	Purity
Caffeine (CAF)		$C_8H_{10}N_4O_2$	194.19	58-08-2	> 99%
Benzophenone-3 (BP-3)		$C_{14}H_{12}O_3$	228.24	131-57-7	98%
Carbamazepine (CBZ)		$C_{16}H_{12}N_2O$	236.27	298-46-4	>99%

MATERIALS AND METHODS

Table 2. Characteristics of Supelclean™ Tubes applied to Solid Phase Extraction

Tube Type	Bed Weight [g]	Tube Volume [mL]	Carbon Loading [%]	Bed Type
ENVI-8	1	6	14	C8 (octyl)
ENVI-18	1	6	17	C18 (octadecyl)
LC-8	0.5	6	7	C8 (octyl)
LC-18	1	6	11.5	C18 (octadecyl)
LC-CN	0.5	6	7	Cyano
LC-Ph	0.5	3	5.5	Phenyl

RESULTS – The determined operating GC-MS (EI) parameters

Injector:
250 °C

Ion source:
230 °C

The support phase:
helium with a flow
of 1.1 mL/min

Ion trap:
150 °C

The oven
temperature
program:
80 °C (6 min),
5 °C/min to 260 °C,
20 °C/min to 300 °C

Ion recording
mode:
50 ÷ 700 m/s

RESULTS - The linearity of mass detector response

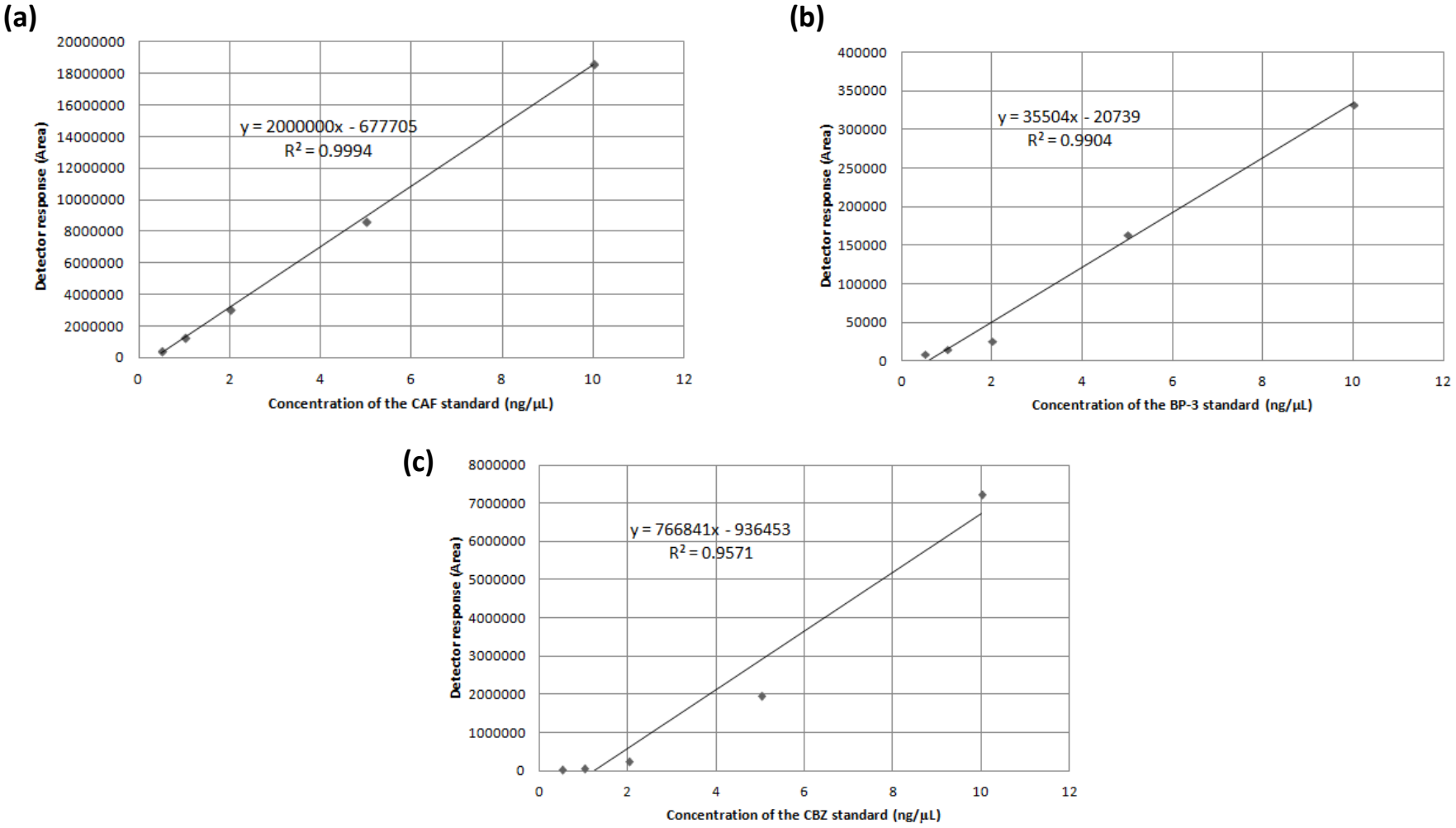


Figure 1. Calibration curve by GC-MS for (a) CAF, (b) BP-3, (c) CBZ

RESULTS - The linearity of mass detector response

Table 3. The parameters of calibration curves for determining micropollutants by GC-MS

Standard	$t_R \pm SD$	R^2	a	S_a	b	S_b
CAF	19.37 ± 0.01	0.99	2 000 000	316 802	-677 705	459 921
BP-3	22.46 ± 0.02	0.99	35 504	2 019	-20 739	2 931
CBZ	24.19 ± 0.02	0.95	766 841	295 337	936 453	428 759

- **The obtained values of R2 coefficient show the linearity of the detector's response.**
- **Retention times of compounds allow for proper separation and appropriate identification in complex water matrices.**
- **The standard deviations of t_R are acceptable.**

RESULTS - The repeatability of the measurements

Table 4. Coefficient of Variation (CV) for five concentration levels of tested micropollutants

Standard	CV [%]					LOD [ng/L]
	0.5 ng/µl	1.0 ng/µl	2.0 ng/µl	5.0 ng/µl	10.0 ng/µl	
CAF	0.66	1.39	1.81	1.67	2.25	0.02
BP-3	1.32	1.41	2.28	2.08	0.95	0.02
CBZ	2.81	2.89	2.68	1.59	1.66	0.10

- **The LOD determines the lowest quantity of a substance that can be distinguished from the absence of that substance within a stated confidence limit**
- **The obtained values of CV do not exceed 3% that confirm the high repeatability of conducted measurements.**

Methanol	ENVI-8	Recovery [%]	88.6	100	100
		LOQ [ng/L]	0.63	2.78	1.51
	ENVI-18	Recovery [%]	100	100	100
		LOQ [ng/L]	0.57	2.07	1.18
	LC-8	Recovery [%]	79.8	83.5	66.2
		LOQ [ng/L]	0.66	2.40	1.77
	LC-18	Recovery [%]	95.4	75.3	100
		LOQ [ng/L]	0.91	4.07	2.08
	LC-CN	Recovery [%]	40.6	100	100
		LOQ [ng/L]	3.23	3.39	1.69
	LC-Ph	Recovery [%]	100	100	72
		LOQ [ng/L]	0.81	2.56	2.03
Acetonitrile	ENVI-8	Recovery [%]	82.7	100	93
		LOQ [ng/L]	0.37	1.82	1.26
	ENVI-18	Recovery [%]	85.1	82.2	100
		LOQ [ng/L]	0.43	2.31	1.18
	LC-8	Recovery [%]	100	100	94.2
		LOQ [ng/L]	1.27	7.19	4.29
	LC-18	Recovery [%]	99.3	78.6	100
		LOQ [ng/L]	1.12	8.06	3.62
	LC-CN	Recovery [%]	27.6	100	82.5
		LOQ [ng/L]	1.14	1.52	1.06
	LC-Ph	Recovery [%]	100	73.7	92.5
		LOQ [ng/L]	0.25	2.04	1.04
Methanol + Acetonitrile	ENVI-8	Recovery [%]	97	100	85
		LOQ [ng/L]	2.40	3.68	3.31
	ENVI-18	Recovery [%]	100	100	100
		LOQ [ng/L]	0.84	0.95	0.87
	LC-8	Recovery [%]	86.2	100	90
		LOQ [ng/L]	0.77	1.10	1.24
	LC-18	Recovery [%]	100	100	100
		LOQ [ng/L]	0.82	2.62	2.51
	LC-CN	Recovery [%]	36.7	85.7	77.7
		LOQ [ng/L]	7.58	9.52	10.64
	LC-Ph	Recovery [%]	100	100	100
		LOQ [ng/L]	2.92	7.35	9.52

RESULTS

- Recovery and LOQ for various combinations of SPE Tube types and the solvents

Chosen as the most optimal methodology

RESULTS – Recoveries in different matrices

Table 6. Recoveries obtained in the most optimal Solid Phase Extraction methodology (Methanol + Acetonitrile and ENVI-18 Tube) for different matrices

Matrix	Recovery ± SD [%]		
	CAF	BP-3	CBZ
Deionized water	100 ± 2.4	100 ± 9.9	100 ± 10.0
Tap water	92.5 ± 2.8	95.7 ± 1.2	98.4 ± 8.2
Swimming pool water	100 ± 2.2	100 ± 5.9	100 ± 5.4

- **Based on the calculated recovery factors, the accuracy of the results obtained from the chosen analytical method was very good.**
- **The repeatability of the results measured as the standard deviation was satisfactory, its value was in the range from 1 to 10%.**

RESULTS - the recoveries of the selected as the best conditions of Solid Phase Extraction for the various matrices

Table7. Limits of Quantification obtained in the most optimal Solid Phase Extraction methodology (Methanol+Acetonitrile and ENVI-18) for different matrices

Matrix	LOQ [ng/L]		
	CAF	BP-3	CBZ
Deionized water	0.84	0.95	0.87
Tap water	0.78	0.88	0.83
Swimming pool water	0.69	0.75	0.71

- **The lowest LOQs were obtained for swimming pool water, while the highest were observed for deionized water.**
- **The observed differences show the influence of the organic and inorganic substances presence in the water matrix on the LOQ value.**

CONCLUSIONS

- The presented analytical procedure enables the quantification of caffeine, carbamazepine and benzophenone-3 with satisfactory repeatability and accuracy.
- The obtained recovery values ensure the possibility of full quantitative control of the tested micropollutants in samples collected from swimming pool waster systems.
- The developed methodology can be used for analytical control of swimming pool water treatment processes from selected Pharmaceuticals and Personal Care Products.
- The different physicochemical composition of water affect on LOQ. The values of LOQ obtained for swimming pool water were lower than for deionized and tap water.