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Determination of polar pharmaceutical residues in water using gas chromatography–mass spectrometry

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Introduction

Pharmaceuticals are released in the environment mainly through human wastes by excretion of unmetabolized parent compounds and metabolites. While in Europe, there is a tendency to implement monitoring programs for pharmaceutical contamination of the environment, in Romania, the EEA (European Environment Agency) recommendations, regarding the continue monitoring of such emerging contaminants, are not applied yet. New methods development for pharmaceutical residues detection is essential in exposure assessment.

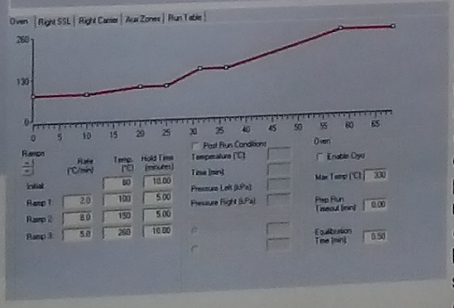
In this stuy, a gas chromatography/mass spectrometric screening method was developed for the determination of different clases of pharmaceutical residus in water. Antibiotics, non-steroidal anti-inflammatory drugs, analgesics, antiepileptic and psychiatric drugs, hormons were chosen as target substances, due to their relevance in terms of usage and toxicological behaviour.

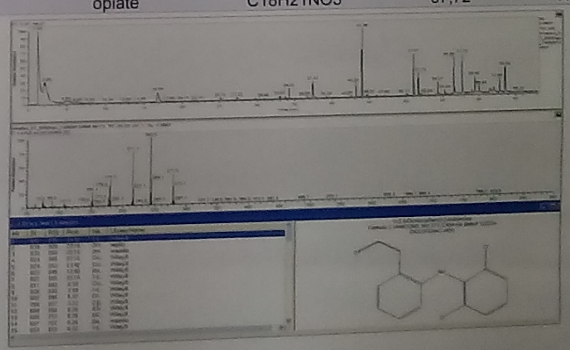
Solid phase extraction (C18) was used for sample extraction and concentration. Chemical derivatization using MSTFA reagent as well as pyridine/acetic anhydride reagent was tested in different experimental condition. Instrumental conditions were optimized. The developed methods are suitable for detection of selected pharmaceutical compounds in water in a concentration range of 10 to 50 ng/l.

Compound	Class	Formula	retention time / acetilation derivatization	retention time / sililation derivatization
amoxicilin trihidrate	pecililine	C16H19N3O5S	ND	ND
albendazole	benzimidazole	C12H15N3O2S	ND	ND
ampicilin trihidrate	peniciline	C16H19N3O4S	ND	ND
carbamazepine	anticonvulsant	C15H12N2O	54,38	ND
chloramphenicol	antibiotic	C14H19Cl2ON2	59,07	ND
flubendazole	benzimidazole	C16H12FN3O3	ND	ND
ivermectin	antiparasitic	C48H74O14	ND	ND
lincomycine HCl	lincosamide antibiotic	C18H35ClN2O6S	ND	ND
neomycin sulfate	aminoglycoside	C23H46N6O13	ND	ND
chloramphenicol	acetaminofen	C8H9NO2	42,54	ND
prednisolone	glucocorticoid	C21H28O5	51,1	ND
progesterone	steroid	C21H30O2	62,86	ND
oxitetracycline HCl	peniciline	C22H25ClN2O9	ND	ND
trimethroprim	chemotherapeutic	C14H18N4O3	ND	ND
acid salicilic	salicylate	C7H6O3	25,6	ND
diazepam	benzodiazepine	C16H13ClN2O	56,61	56,6
diclofenac	NSAID	C14H10Cl2NNaO2	52,1	52,08
secobarbital	barbiturate	C12H18N2O3	43,28	ND
ibuprofen	NSAID	C13H18O2	34,27	34,24
ketamina	anesthetic	C13H17C2NO	44,8	44,77
clorsulon	benzimidazole	C8H8Cl3N3O4S2	ND	ND
cafeina	stimulant (alkaloid)	C8H10N4O2	44,06	44,04
codeina	opiate	C18H21NO3	57,72	ND

Sample pre-treatment
Filtrate (150nm filter) 500 ml water
pH 3 (acetic acid)
SPE - Strata X, 200 mg, 6 cc
Precondition: 6 ml methanol followed by 6 ml water
Wash step: 6 ml water, followed by 6 ml methanol/water 30%
Elution: 6 ml methanol
Evaporate
Derivatization Method 1: 100 µl MSTFA + 30µl piridine heat at 60° C 30 min - injection Method 2: 300 µl piridine: acetic ahnydride reagent (2:3), heat at 60° C 30 min, evaporate, redisolve in MeOH - injection

GC-MS analysis
Trace GC Ultra. GC-Ions trap ITQ 900 MS. Thermo Scientific
Ionization voltage: 70eV
Full scan acquisition of m/z 100 – 1000
Column: 30 m x 2 5mm; df = 0,25 µm
Helium carrier gas flow: 1 ml/min
Temperature of transfer line, ion trap, and the manifold: 300° C, 210° C and 80 ° C.
Temperature gradient:





Conclusions

♦ Derivatization with pyridine/acetic anhydride reagent was found to be more sensitive and reproducible and also allowed the detection of more of selected compounds.

♦The level of detection was 50 ng l^{-1} for diclofenac, ibuprofen, secobarbital, codeine, diazepam; 100 ng l^{-1} for carbamazepine, ketamine, paracetamol, progesterone; and 150 ng l^{-1} for chloramphenicol, prednisolone, salicylic acid and methyl salicylate.

♦Antibiotics oxytetracycline, ampicillin, amoxicillin, lincomycin and benzimidazoles albendazole and flubendazole cannot be detected in water sample probably due to thermal decomposition.

♦The described method enabled the determination of the 13 relevant pharmaceutical compounds in contaminated water samples.

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