

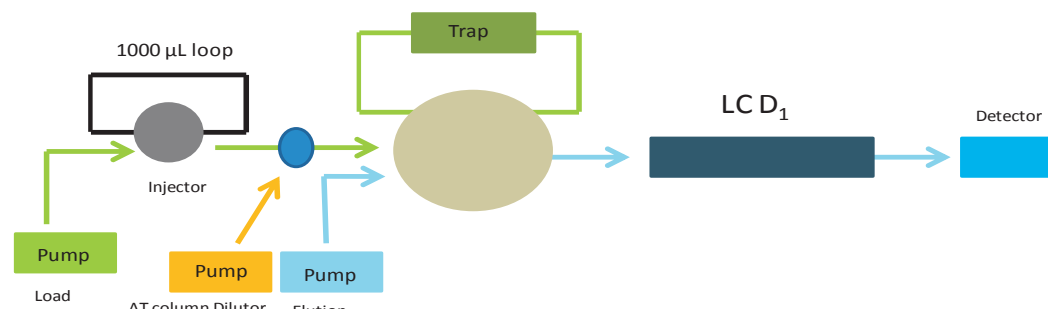
PPCP Analysis in Bottled, Tap and Surface Water using Time De-Coupled Chromatography

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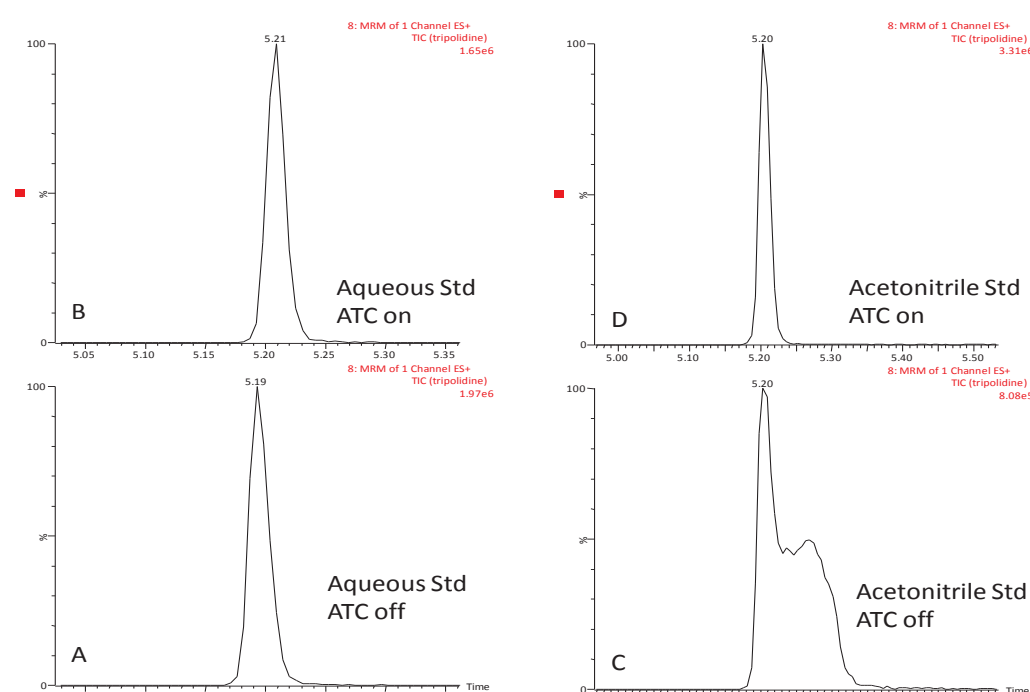
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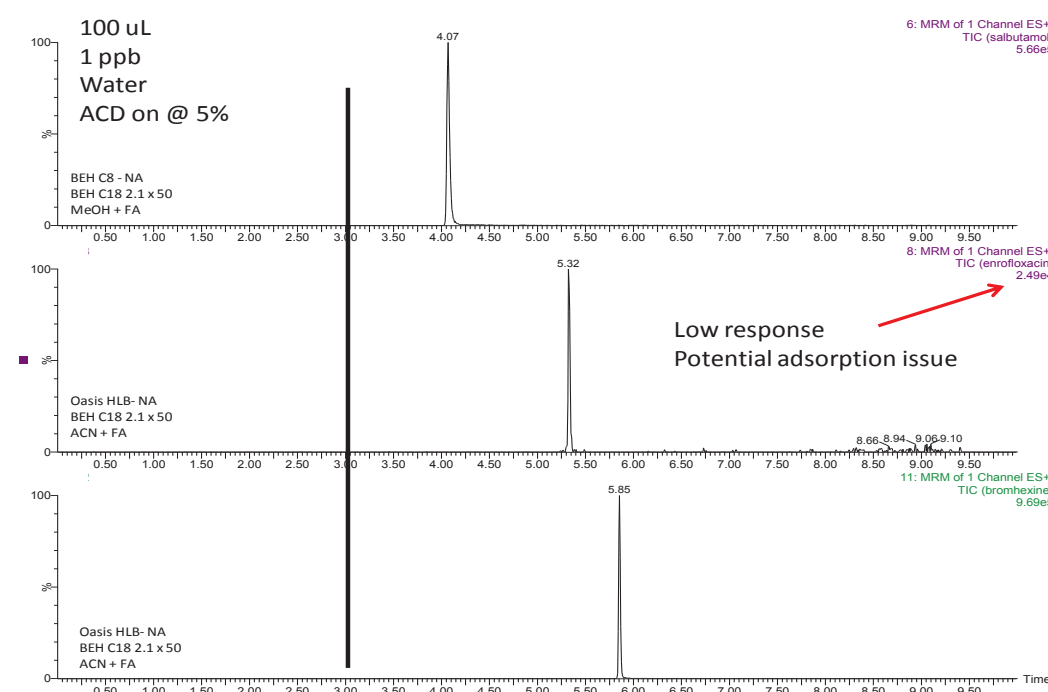
Time De-Coupled Chromatography (2D mode)



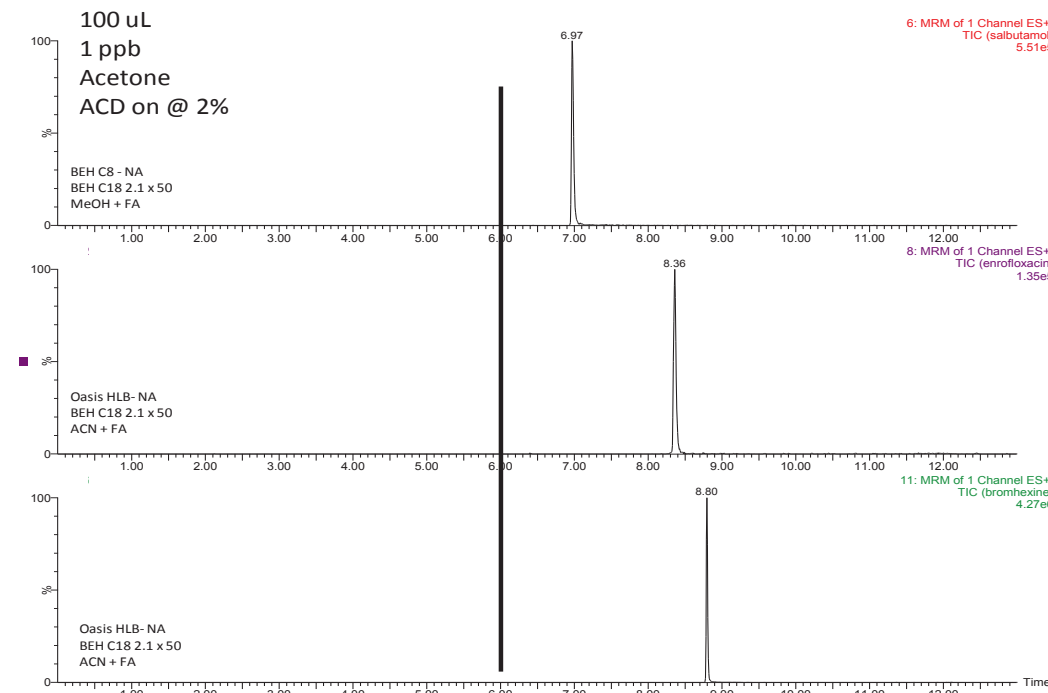
AT-column dilution principle



AT-column dilution – water extract

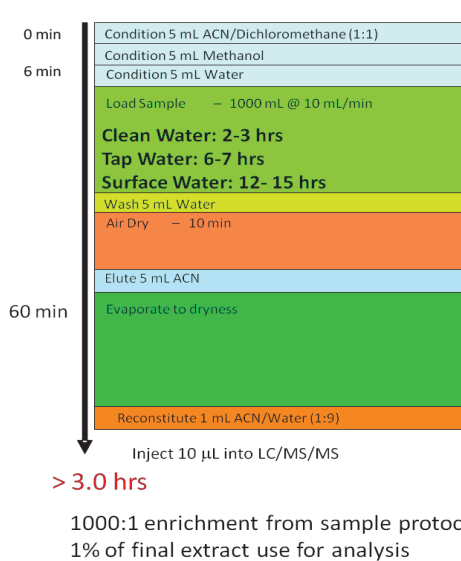


AT-column dilution – acetone extract

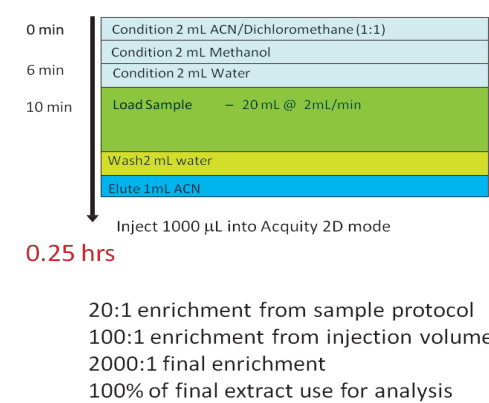


Extraction protocols for LC/MS/MS platforms are optimized to reach target recovery levels at trace levels (sub ppb); which often time are below detection capabilities with current detectors (optical or destructive). Therefore, a sample enrichment step is usually included in the macro-extraction protocol to reach acceptable quantification limits. However, it comes at a price, hour long extraction process, large sample amount and resources. Time De-Coupled Chromatography

Macro Extraction Protocol



Micro Extraction Protocol



Method Development

MAX Wash 1
MAX Wash 2
MAX Elute
MCX Wash 2
MCX Wash 2
MCX Elute

	A	B	C	D	E	F
MAX Wash 1	4	0	3	0	0	4
MAX Wash 2	7	90	9	1	0	7
MAX Elute	1	12	2	92	91	94
MCX Wash 2	3	0	4	0	0	0
MCX Wash 2	4	0	9	0	1	2
MCX Elute	26	0	20	0	1	7

MCX Wash 2
MCX Wash 2
MCX Elute
MAX Wash 1
MAX Wash 2
MAX Elute
STD un-extracted

MCX Wash 2	0	0	0	0	0	0
MCX Wash 2	0	95	0	12	9	3
MCX Elute	93	13	90	0	1	34
MAX Wash 1	13	1	6	0	1	4
MAX Wash 2	2	3	3	0	0	10
MAX Elute	0	1	1	1	1	10
STD un-extracted	7366	35780	18028	3437	5090	249

Legend: A-Levamisole, B-Diethylcarbamazine, C- Procaine, D- Sulfamethoxazole
E-sulfadimethoxine, F- Enrofloxacin

Results calculated as percentage from an un-extracted standard

Final Method

15 mL 15 mL



Anion Exchanger (MAX)
Wash 1: 1.5 mL water + 1% NH₄OH
Wash 2: 1.5 mL MeOH
Elute: 1.6 mL MeOH + 1% FA

200 µL injection

Acidic PPCP

Sulfamethoxazole
Sulfamerazine
Sulfadimethoxine
Enrofloxacin
Bromhexine

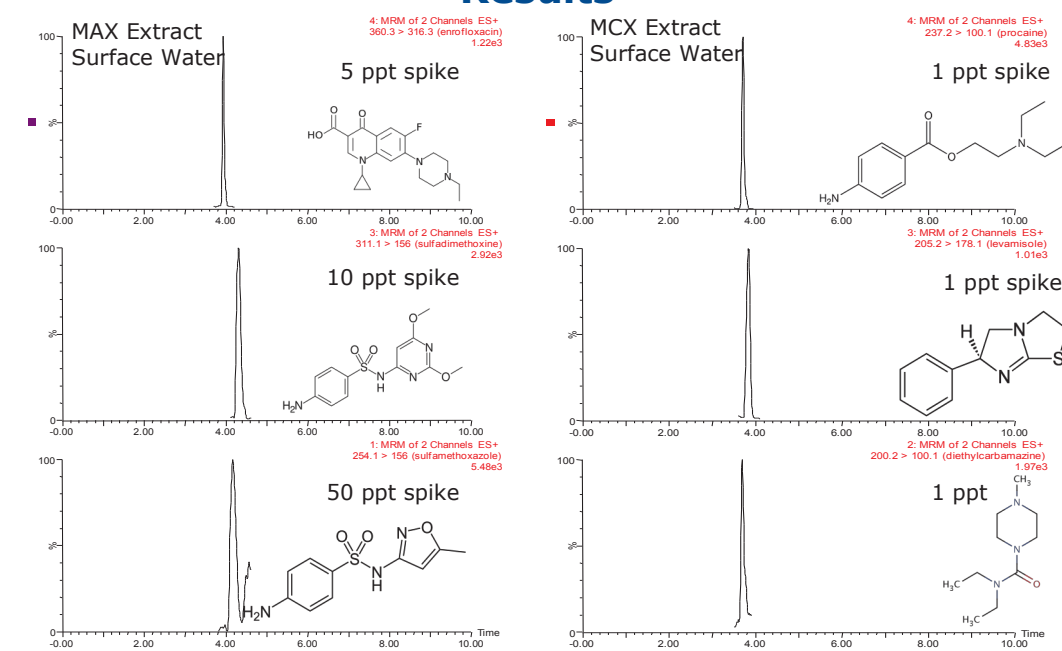
Cation Exchanger (MCX)
Wash 1: 1.5 mL water + 1% FA
Wash 2: 1.5 mL MeOH
Elute: 1.6 mL MeOH/ACN + 1% NH₄OH

200 µL injection

Basic PPCP

Benzocaine
Diethylcarbamazine
Levamisole
Procaine
Salbutamol
Cimetidine
Triprolidine
Trimethoprim
Buflomedil
Diltiazem
Miconazole

Results



Time De-Coupled Chromatography offers options of large volume injections capabilities (aqueous & organic extracts). The analytical process showed time reduction for hour-long method reduced to less than 15 minutes. This research showed detection limit at 1 ppt for PPCP's in bottled, tap and surface water sample using a 15 mL volume. The solution has the capability to inject up to 1 mL methanol and acetonitrile for SPE extracts (10x enrichment), thus eliminating the time consuming evaporation to dryness and reconstitution step.

Detection Limit & Recoveries

Pharmaceuticals	MAX	LOD ppt	Linearity (r ²)	Bottled	Tap	Surface
Recoveries @ 10 ppt						
Sulfamethoxazole		50	0.991	na	na	na
Sulfamerazine		5	0.993	73.7	70.3	112.4
Sulfadimethoxine		10	0.994	80.5	79.2	75.6
Enrofloxacin		10	0.993	92.7	85.0	84.5
Bromhexine		1	0.991	101.0	87.4	80.4
Pharmaceuticals MCX						
Recoveries @ 10 ppt						
Benzocaine		2	0.991	88.5	90.9	92.6
Diethylcarbamazine		1	0.997	90.1	99.7	105.1
Levamisole		1	0.997	102.6	104.9	114.2
Procaine		1	0.990	84.7	87.2	95.8
Salbutamol		10	0.990	88.9	89.1	81.3
Cimetidine		1	0.992	90.6	81.0	102.4
Triprolidine		1	0.994	103.0	88.4	113.9
Trimethoprim		1	0.993	94.3	99.8	97.6
Buflomedil		1	0.992	97.5	95.0	101.6
Diltiazem		1	0.994	96.2	103.2	91.5
Miconazole		1	0.998	99.1	89.9	79.3

Conclusions

- Trace level detection (ppt)
- Minimum sample preparation (> 15 min)
- High reduction of manual labor (80%)
- Wide pH range SPE & LC sorbents
- Rapid method development
- High level of reproducibility and robustness
- Better precision & accuracy (< 10 %)
- Reduce field sample volume by 50 times

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