Polar Organic Chemical Integrative Sampler (POCIS) Sampling and Analysis

Standard Operating Procedure

University of Washington Tacoma Laboratories at the Center for Urban Waters

Washington Department of Natural Resources

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1 FIELD SAMPLING

Deployment and retrieval from the sampling site will be performed by WDNR personnel according to published protocol (Alvarez 2010). Generally:

- Sample canisters should be sealed until deployment.
- Following retrieval samplers should be placed in their original containers and stored on ice for delivery to the laboratory.
- Samplers should be rinsed with DI water upon retrieval to remove any organic debris associated with the sampler.
- All field sample containers should be clearly labeled with
    - Site ID
    - Date of deployment
    - Date of retrieval
    - Personnel
- Field notes should record the same information and include notes on condition, etc.

1.1 Field Blank

A field blank should be prepared for each sampling event. A field blank is a POCIS exposed to air for the same duration as the deployed samples. One POCIS is designated as a field blank. The original container is then opened at the beginning of deployment and remain open until the deployment is complete.

Once the field blank container is resealed the POCIS is to be held on ice for transport to the laboratory.

Field blanks are stored in the dark at -20°C until extraction and analysis.

2 PREPARATION – SAMPLE CONTAINER WASHING AND GLASSWARE PREPARATION

2.1 General Information

POCIS samplers utilizing a chromatography column and methanol. The setup is shown in Figure 1. All glassware should be cleaned prior to use and between samples. Clean all glassware by rinsing 3x with methanol.

2.2 Extraction

The extraction protocol was adopted from Alvarez (2010), Li et al (2010), and Carlson et al (2013).

Prepare each chromatography column by adding clean glass wool plugs and approximately 3g of anhydrous sodium sulfate.

- Rinse POCIS samplers under DI water to remove any material adhering to the membrane surfaces.
- Optional step -placed in samplers in DI water for at least 15 min to wet the Oasis HLB phase. Wetting the Oasis HLB phase simplifies the extraction procedure by avoiding the fine, powdery nature of the Oasis HLB sorbent, which can be very vulnerable to air currents when dry.
- Disassemble the POCIS disks and carefully transfer sorbent powder into glass chromatography column.
- Rinse membranes with methanol to transfer any attached sorbent powder to the column.
- Add 10 µL of internal standard mixture onto the top of the sorbent.
- Elute compounds off sorbent with 50 mL methanol.
- Reduce the eluate was volume to near dryness with the turbovap at 40°C.
- Transfer eluant to autosampler vial in 1000 µL methanol.
- Store at -4°C for no longer than one week prior to analysis.

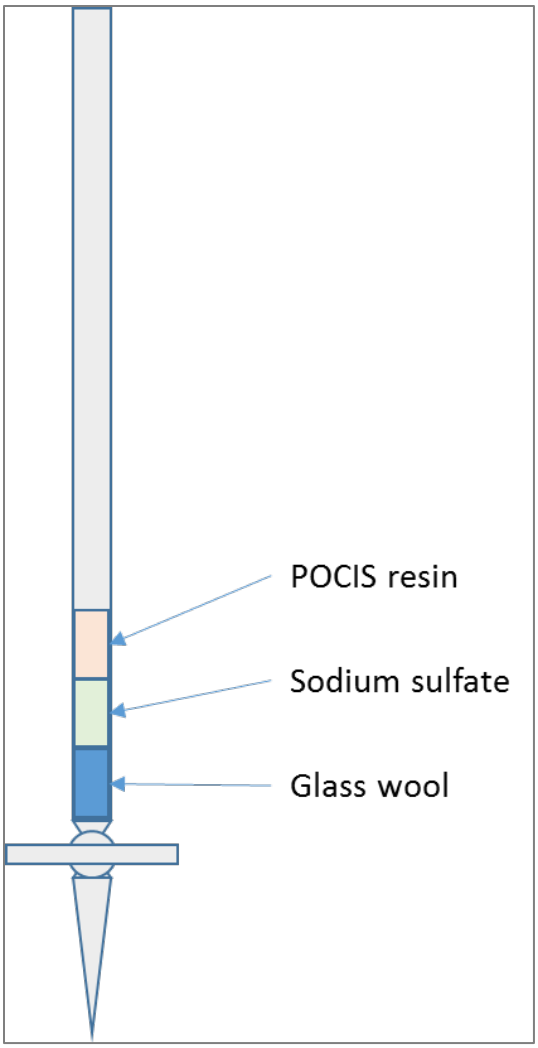

Figure 1. Chromatography column setup for POCIS extraction

2.3 QAQC Samples

2.3.1 Field Blanks

Field blanks account for potential exposure to anthropogenic compounds during the course of the deployment and sample handling process. As described above, a field blank should be collected with each deployment and extracted along with the field samples.

2.3.2 Laboratory Blank

A laboratory blank can account for potential contamination because of the processing of the samplers. An evaluation of the laboratory process should be performed over the course of the experiment by analyzing a set of three POCIS blanks.

2.3.3 Matrix Spikes

Matrix spikes are POCIS prepared with a known quantity of targeted chemicals. This type of spike is carried throughout the whole processing scheme to determine the percent recovery of the targeted chemicals at the laboratory during analysis and to establish control limits for the analytical process. A matrix spike can help determine if ion suppression of the target chemicals will occur because of the passive sampler matrix.

A set of matrix spike will be prepared at the beginning of the project period prior to deployment.

2.4 Analytical

Prepared samples can be run either on a liquid chromatograph (LC) triple quadrupole dual mass spectrometer system (QqQ-MS/MS) or an LC quadrupole time of flight mass spectrometer system (QToF-MS/MS). The University of Washington Tacoma laboratories at the Center for Urban Waters utilizes an Agilent 1290 Infinity LC coupled with an Agilent 6430 QqQ-MS/MS and/or and Agilent 1290 Infinity LC coupled with and Agilent 6530 QToF-MS/MS. Analytical approach is described below.

2.4.1 LC-QqQ-MS/MS

Analysis for the compounds of interest (Table 1) is based on the approach described in Parikh et al. (2014). The transitions are shown in Table 1. The LC settings are:

Mobile phase A: 5µM ammonium acetate + 0.1% acetic acid in H_2O.

Mobile Phase B: 5µM ammonium acetate + 0.1% acetic acid in methanol

Mobile Phase Gradient:

Time	%A	%B
0	95	5
1	95	5
4	50	50
17	0	100
20.1	95	5
22	95	5

Flow: 0.3 mL/min

Column Temp: 45°C

Column: Agilent Zorbas Eclipse C18. 2.1 x 100 mm. 1.8 µm. (P/N 959704-902)

2.4.2 LC-QToF-MS/MS

The general approach to sample and data analysis are outlined in the SOP titled, “Quadrupole Time of Flight Liquid Chromatography Dual Mass Spectrometry (QTOF-LC-MS/MS) Setup, Operation, and Data Analysis - Non Targeted Analysis of Trace Organic Contaminants”

The initial analysis for the compounds of interest is performed with MS Only positive ionization mode. The basic TOF settings are shown below.

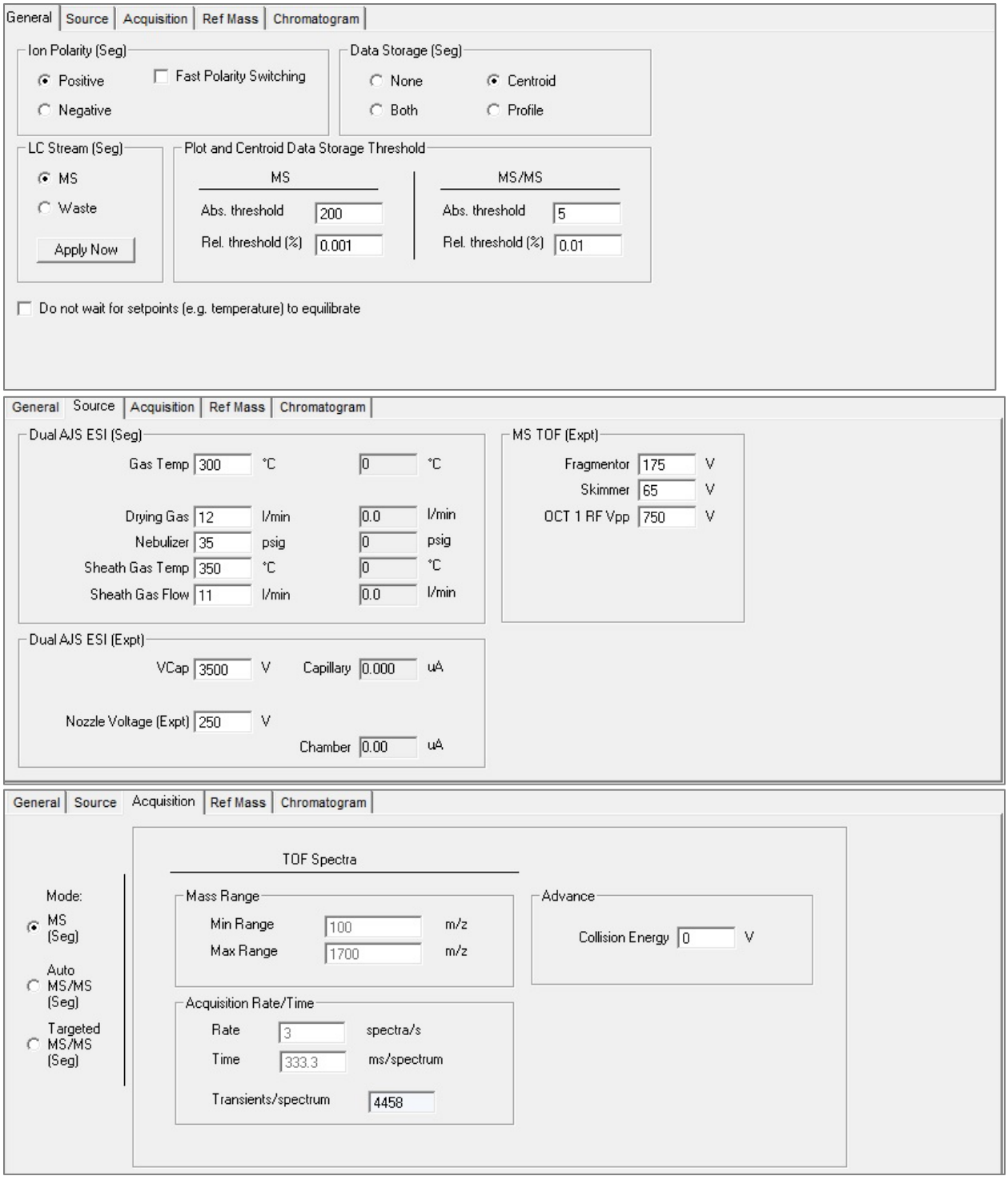

Figure 2. Summary of TOF settings for MS only, positive ionization mode analysis.

The LC settings are the same as section 2.4.1 except where otherwise noted:

Flow: 0.4 mL/min

Column: Agilent Zorbax Eclipse Plus C18. 2.1 x 100 mm. 1.8 µm. (P/N 959758-902)

3 ANALYTES

Table 1 describes the analytes of interest in this study. An inclusion list should be included into the MSMS analytical run to ensure they are captured

Table 1. Selected SSRIs, ionization mode, and transitions for LC-QqQ-MS/MS analysis

Compound	Ionization	Transition (m/z)		Reference
Fluoxetine	+	310.3	148.0	(Alvarez et al. 2014, Bringolf et al. 2010)
	+	310.2	44.1	(Ferrer and Thurman 2013)
	+	310.2	43.9	(Li et al. 2010)
Fluoxetine – Qual	+	310.2	148	
Norfluoxetine	+	296.1	133.7	(Alvarez et al. 2014, Li et al. 2010)
Sertraline	+	306.1	274.8	(Alvarez et al. 2014, Dodder et al. 2014)
	+	306.2	158.9	(Li et al. 2010)
Norsertraline (N-desmethylsetraline)	+	292.1	158.9	(Li et al. 2010, Parikh et al. 2014)
Citalopram	+	325.2	109	(Alvarez et al. 2014, Li et al. 2010, Liscio et al. 2014, Parikh et al. 2014)
Citalopram – Qual	+	325.2	262	(Parikh et al. 2014)
N-Desmethyl citalopram	+	311.2	262.1	(Parikh et al. 2014)
	+	311.2	108.9	(Li et al. 2010)
N-Desmethyl citalopram - Qual	+	311.2	234	(Schultzt and Furlong 2008)
Escitalopram	+	325.1	109.0	(Liscio et al. 2014)
Venlafaxine	+	278	260	(Alvarez et al. 2014, Liscio et al. 2014, Schultzt and Furlong 2008)
	+	264.2	43.9	(Li et al. 2010)
Desvenlafaxine (O-desmethylvenlafaxine)	+	264.2	58	(Ferrer and Thurman 2013)
Duloxetine	+	298	44	(Alvarez et al. 2014, Schultzt and Furlong 2008)
Bupropion	+	240	184	(Alvarez et al. 2014, Schultzt and Furlong 2008)
Hydroxybupropion	+	256	130	
Bupropion-D9	+	249	203	
Paroxetine	+	330.2	192.1	

4 MATERIALS:

Compound	Supplier	Item Number	Notes
N-desmethylcetalopram HCL	Cerillant	D-047	1 mg/mL in methanol
(+) Bupropion-D9 HCl	Cerillant	B-052	100 µg/mL in methanol
(+) Hydroxybupropion HCL	Cerillant	H-066	1 mg/mL in Acetonitrile
(+) O-desmethylvenlafaxine (desvenlafaxine)	Cerillant	V-007	100 µg/mL in methanol
Carbamazepine	Fluka	94496-100mg	100 mg
Norfluoxetine HCl	Fluka	40724-1mg	1 mg
Sertraline HCl	Sigma	S6319-10mg	10 mg
R-(-)-Fluoxetine HCl	Fluka	94644-5mg	5 mg
Venlafaxine HCl	Sigma	V7264-10mg	10 mg
Paroxetine HCl hemihydrate	Sigma	P9623-10mg	10 mg
Norsertraline HCl (N-desmethylsetraline)	Cerillant	N-049	100 µg/mL in methanol
Citalopram HBr	Sigma-Aldrich	C7861-10mg	10 mg
Escitalopram oxalate	Sigma-Aldrich	E4786-10mg	10 mg
(S) - Duloxetine HCl	Sigma-Aldrich	SML0474-10mg	10 mg
Bupropion HCl	Cerillant	B-034	1 mg/mL in methanol

REFERENCES

Alvarez, D.A. (2010) Guidelines for the use of the semipermeable membrane device (SPMD) and the polar organic chemical integrative sampler (POCIS) in environmental monitoring studies, U.S. Geological Survey, Reston, VA.

Alvarez, D.A., Maruya, K.A., Dodder, N.G., Lao, W.J., Furlong, E.T. and Smalling, K.L. (2014) Occurrence of contaminants of emerging concern along the California coast (2009-10) using passive sampling devices. Marine Pollution Bulletin 81(2), 347-354.

Bringolf, R.B., Heltsley, R.M., Newton, T.J., Eads, C.B., Fraley, S.J., Shea, D. and Cope, W.G. (2010) Environmental Occurrence and Reproductive Effects of the Pharmaceutical Fluoxetine in Native Freshwater Mussels. Environmental Toxicology and Chemistry 29(6), 1311-1318.

Carlson, J.C., Challis, J.K., Hanson, M.L. and Wong, C.S. (2013) Stability of pharmaceuticals and other polar organic compounds stored on polar organic chemical integrative samplers and solid-phase extraction cartridges. Environmental Toxicology and Chemistry 32(2), 337-344.

Dodder, N.G., Maruya, K.A., Ferguson, P.L., Grace, R., Kiosterhaus, S., La Guardia, M.J., Lauenstein, G.G. and Ramirez, J. (2014) Occurrence of contaminants of emerging concern in mussels (Mytilus spp.) along the California coast and the influence of land use, storm water discharge, and treated wastewater effluent. Marine Pollution Bulletin 81(2), 340-346.

Ferrer, I. and Thurman, E.M. (2013) High Resolution Mass Spectrometry (LC/Q-TOF/MS) for the Detection of Pharmaceuticals in Water. Technologies, A. (ed).

Li, H.X., Helm, P.A. and Metcalfe, C.D. (2010) SAMPLING IN THE GREAT LAKES FOR PHARMACEUTICALS, PERSONAL CARE PRODUCTS, AND ENDOCRINE-DISRUPTING SUBSTANCES USING THE PASSIVE POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER. Environmental Toxicology and Chemistry 29(4), 751-762.

Liscio, C., Abdul-Sada, A., Al-Salhi, R., Ramsey, M.H. and Hill, E.M. (2014) Methodology for profiling anti-androgen mixtures in river water using multiple passive samplers and bioassay-directed analyses. Water Research 57, 258-269.

Parikh, N.R., Romm, M. and Miller, V.P. (2014) Ultrafast Analysis of Selective Serotonin Reuptake Inhibitors (SSRIs) in Human Serum by the Agilent RapidFire High-Throughput Triple Quadrupole Mass Spectrometry System. Technologies, A. (ed).

Schultzt, M.M. and Furlong, E.T. (2008) Trace analysis of antidepressant pharmaceuticals and their select degradates in aquatic matrixes by LC/ESI/MS/MS. Analytical Chemistry 80(5), 1756-1762.