Development of a Drinking Water Method for the Measurement of Select Organic Contaminants in Drinking Water Using Hydrophilic-Modified Polymeric SPE and GC/MS

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Background

- In October 2009, the USEPA's Office of Ground Water and Drinking Water (OGWDW) published Drinking Water Contaminant Candidate List 3 (CCL 3).
- CCL 3 contains potential contaminants that the agency may consider for regulation. One of the key pieces of information necessary to make a regulatory determination for a contaminant is its nationwide occurrence.
- OGWDW collects the necessary occurrence data under its Unregulated Contaminant Monitoring Regulations (UCMRs).
- In order for a contaminant to be included in a UCMR, a standardized analytical method for its measurement in drinking water must be available.
- A group of compounds from CCL 3, which were not amenable to any current EPA method, were evaluated for grouping into a new method.
- The group consists of two industrial compounds (***o*-toluidine** and **quinoline**), the pesticide **dimethipin**, and the food additive **butylated hydroxyanisole** (BHA).

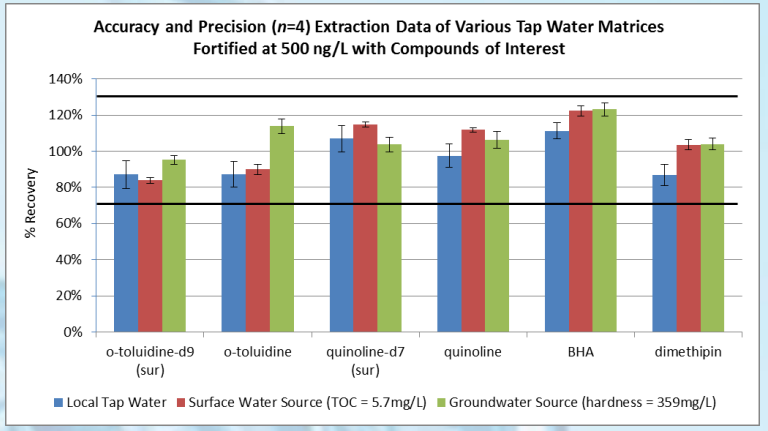
Instrumentation: GC/MS

Column: J&W DB-1701, 30m x 0.25mm x 0.25µm
Injector: 275°C (splitless mode), 20 psi pulse
Inj. vol: 1 µL
Flow: 1 mL/min, helium carrier gas
Oven: 60°C for 1 min, to 300°C at 10°C/min, hold 2 min.
Total time = 27 min.
MS Transfer Line: 275°C

MS Full Scan Option: scan 50-350 *m/z*

MS SIM Option: 6 windows, ion (as *m/z*), dwell time (in msec)
WIN1, 5.00 min: (106.10, 25) (107.10, 25)
(112.10, 25)(114.10, 25)
WIN2, 7.64 min: (102.00, 25) (108.10, 25)
(129.10, 25)(136.10, 25)
WIN3, 10.62 min: (137.10, 25) (162.10, 25)
(164.10, 25)(180.10, 25)
WIN4, 13.76 min: (54.10, 75) (118.00, 75) (188.10, 25)
WIN5, 17.16 min: (79.00, 75) (149.00, 75)
WIN6, 20.37 min: (236.20, 25) (240.20, 25)

Results- Quality Control Data from Matrix Extracts at High Level Fortification (GC/MS-SIM)



Lower and upper limit bars are set at 70% and 130%, respectively, to represent Data Quality Objectives (DQOs).

Extraction Procedure

Cartridge: 500mg Oasis HLB (Waters), Strata-X (Phenomenex), or Bond Elut Plexa (Agilent)

Sample: 1 L water, add preservatives: ascorbic acid, Trizma buffer (pH 7.0), EDTA trisodium salt, and diazolidinyl urea (DZU); add surrogates: ***o*-toluidine-d_9** and **quinoline-d_7**

Cartridge Conditioning: 5 mL dichloromethane (DCM)
10 mL methanol
10 mL lab reagent water (LRW)

Sample Load Rate: ≤10 mL/min

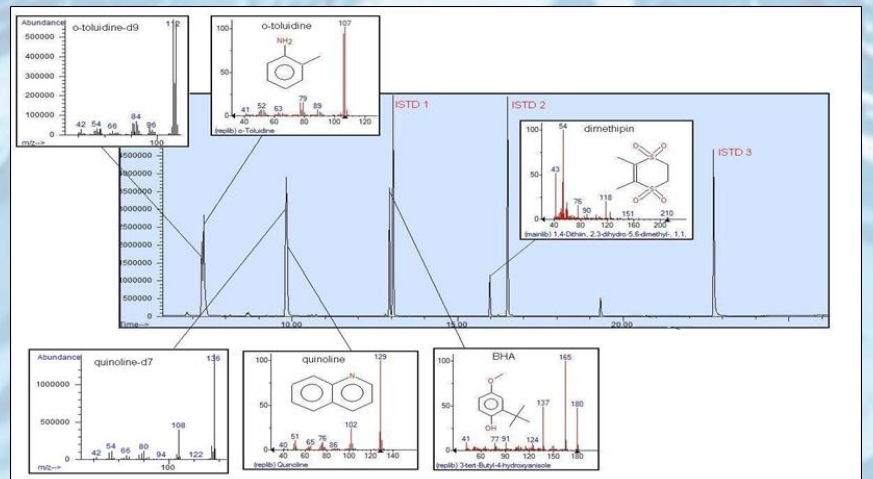
Sorbent Dry Time: 10 min

Elution: DCM (2 x 5mL)

Extract Dry: 8g sodium sulfate

Concentration: 1mL by water bath/nitrogen evaporation, add internal standards (**acenaphthene-d_{10}**, **phenanthrene-d_{10}**, and **chrysene-d_{12}**)

Example Full Scan Total Ion Chromatogram, 5 ug/mL with Mass Spectra



Internal Standards acenaphthene-d_{10}, phenanthrene-d_{10}, and chrysene-d_{12} (5 µg/mL each) labeled as ISTD 1, ISTD 2, and ISTD 3, respectively.

Detection Limits Compared to Health Reference Levels (HRLs)

DLs and LCMRLs (µg/L) Calculated from Replicate Analyses of Fortified Reagent Water Samples, Compared to Current HRL*

Full Scan GC/MS

Analytes	DL	LCMRL	HRL
o-toluidine	0.007	0.011	0.194
quinoline	0.036	0.084	0.010
BHA	0.044	0.062	0.581
dimethipin	0.037	0.075	153

SIM GC/MS

Analytes	DL	LCMRL	HRL
o-toluidine	0.001	0.003	0.194
quinoline	0.003	0.005	0.010
BHA	0.003	0.013	0.581
dimethipin	0.001	0.003	153

* Contaminant Information Sheets for the Final CCL 3 Chemicals, Office of Water (4607M) EPA 815-R-09-012, August 2009

Conclusions and Future Work

- A method has been developed for occurrence monitoring that meets EPA's requirements for accuracy, precision, and sensitivity.
- The method allows for full scan and selected ion monitoring (SIM) options, along with multiple sorbent options.
- The method is currently being evaluated in a multi-lab study.