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OFFICE OF
RESEARCH AND DEVELOPMENT

June 1, 2012

Samples received from Pavilion, WY

Received samples shipped on ice in coolers from Pavilion, WY on multiple dates. Each shipment of samples was shipped FedEx overnight. These samples were sampled under the Pavilion Groundwater Project, Task 23993, and Rick Wilkin is the Project Manager. Described below are the dates and contents of each shipment.

April 18, 2012: Received 14 1-L amber bottles at 1:00 pm. There were 2 1-L bottles for each sample, and there were 2 L each of 7 different samples in total. The samples consisted of field and equipment blanks in addition to 5 groundwater samples. One of the field blank bottles had broken during transit. Samples received included the following:

Field blank 1
Equipment blank 1
PGDW20-0412
PGDW20d-0412
EPAMW02-0412-1
PGDW23-0412
PGDW30-0412

April 19, 2012: Received 6 1-L amber bottles at 1:00 pm. There were 2 1-L bottles for each sample, and there were 2 L each of 3 different samples in total. The samples consisted of field and equipment blanks in addition to 1 groundwater sample. Samples received included the following:

Field blank 2
Equipment blank 2
PGDW05-0412

April 24, 2012: Received 10 1-L amber bottles at 12:53 pm. There were 2 1-L bottles for each sample, and there were 2 L each of 5 different samples in total. The samples consisted of field and equipment blanks in addition to 3 groundwater samples. Samples received included the following:

Field blank 3
Equipment blank 3
PGDW50-0412
PGPW02-0412
EPAMW02-0412-2

April 24, 2012: Received 10 1-L amber bottles at 12:53 pm. There were 2 1-L bottles for each sample, and there were 2 L each of 5 different samples in total. The samples consisted of field and equipment blanks in addition to 3 groundwater samples. Samples received included the following:

Field blank 3
Equipment blank 3
PGDW50-0412
PGPW02-0412
EPAMW02-0412-2

April 26, 2012: Received 14 1-L amber bottles at 11:30 am. There were 2 1-L bottles for each sample, and there were 2 L each of 7 different samples in total. The samples consisted of field and equipment blanks in addition to 5 groundwater samples. Samples received included the following:

Field blank 4
Equipment blank 4
EPAMW01-0412
EPAMW01d-0412
EPAMW01-0412-4
EPAMW01-0412-7
EPAMW01-0412-10

May 1, 2012: Received 2 1-L amber bottles at 1:45 pm, each containing the identical sample source. Samples received included the following:

"Riverton, WY Truck Water"

Methods Used for Sample Analysis

The samples were analyzed for ethoxylated alcohols, ethoxylated alkylphenols, alkylphenols, and acrylamide. Described below are the procedures used for each analysis.

Ethoxylated alcohols and ethoxylated alkylphenols:

Used solid-phase extraction (SPE) to extract for specific analytes. ASTM Method D 7458-09 [1] and USGS Method Number O1433-01 [2] were used as starting points for the method used here. These methods both enable the analysis of nonylphenol diethoxylate (NPEO2), in addition to alkylphenols, but there are currently no standard methods for the analysis of the full range of nonylphenol ethoxylate oligomers (EO3-EO20) or alcohol ethoxylate oligomers ($C_{12-15}EO_x$, where x = 2-20).

A total of 500 mL of each sample was extracted using an Autotrace SPE Workstation. The samples were extracted using Waters Oasis HLB SPE cartridges (200 mg, 6 cc). The cartridges were first conditioned with 5 mL methanol and 5 mL water. After conditioning, a 500 mL sample was loaded onto the cartridges. To ensure quantitative recovery, the sample flasks were then rinsed with 50 mL water, which was also loaded onto the cartridges. The SPE cartridges were then rinsed with 2 mL water before drying with N_2 for 30 min. The samples were eluted off the cartridge first with 5 mL 2:2:1 methanol/acetone/ethyl acetate and then with 5 mL 90:10 methyl t-butyl ether/methanol. The eluate was then concentrated and solvent exchanged with a TurboVap Concentrator to 0.5 mL in methanol. Seven different surrogates were added prior to the extraction, which included C_6EO_5, C_8EO_4, C_8EO_5, $C_{10}EO_4$, $C_{10}EO_6$, $C_{12}EO_3$, and $C_{12}EO_4$. It is difficult to obtain high-quality standards at higher alkyl chain lengths of ethoxylated alcohols, as they typically exist as technical mixtures of a range of different alkyl chain lengths and ethoxylate oligomers.

Mass spectrometry (MS) analysis was performed on a Waters LC-TOF Premier instrument in full scan positive ionization mode. The TOF was coupled to a Waters Acquity UPLC system. The ethoxylated alcohols were separated on a Waters Acquity UPLC BEH C18 column (1.7 µm, 2.1 x 100 mm). The ammonium adducts of the individual oligomers were used for quantitation.

Alkylphenols

Octylphenol (OP) and nonylphenol (NP) were extracted simultaneously with the ethoxylated compounds using the SPE protocol described above. Deuterated surrogate standards (4-tert-OP-3,5-d_2 and *n*-NP-2,3,5,6-d_4) were added prior to extraction.

MS analysis was performed on an AB SCIEX 4000 Q TRA P that was coupled to a Shimadzu HPLC system. The alkylphenols were separated on a Waters Acquity UPLC BEH C18 column (1.7 µm, 2.1 x 100 mm). The alkylphenols were analyzed in negative ionization multiple reaction monitoring (MRM) mode.

Acrylamide

EPA methods 8032A and 8316 are suitable for the analysis of acrylamide (AA). Method 8316 involves analysis by HPLC-UV at 195 nm, but the detection level is 10 µg/L. This short wavelength is not very selective for acrylamide, i.e. interferences are likely, and the sensitivity is not adequate for water. Method 8032A involves the bromination of AA, followed by GC-MS analysis. This method is much more selective for acrylamide, and detection limits are much lower, 0.03 ug/L. However, in complex matrixes, the acrylamide may suffer from interferences and poor extraction efficiency. To avoid derivatization reactions that may react with other compounds present in environmental matrixes and to lower the detection limit, ESD-Las Vegas was tasked with developing a new analytical method for the determination of AA.

Acrylamide is not retained by conventional SPE media because it is a small, highly polar molecule. Activated carbon SPE cartridges (500 mg, 6 cc) from Biotage were used to capture the AA from water, following a similar method of Lucentini et al.[3] Additionally, Rosén et al.[4] described a tandem extraction, the first acting as a chemical filter and the second retaining AA, which was implemented here. The HLB cartridge flowthrough from the ethoxylate/alkylphenol extraction was collected and then passed over the Biotage activated carbon cartridges (AA is not retained at all by the HLB cartridges). The cartridges were rinsed with water, and AA was eluted with 10 mL methanol. The eluate was then concentrated to 0.5 mL using the TurboVap Concentrator. Deuterated AA (AA-d3) was added to the samples prior to extraction.

MS analysis of AA was performed in positive ionization MRM mode on a Thermo Finnigan TSQ Quantum Ultra that was coupled to a Dionex Ultimate 3000 HPLC system. A Dionex IonPac ICE-AS1 ion exclusion column (4 x 250 mm, 7.5 µm) was used for the LC separation of AA. The 72 > 55 transition ($[M+H]^+$) was used for quantitation.

Results

Ethoxylated alcohols and ethoxylate alkylphenols:

Because no standards exist for $C_{12-15}EO_x$ ethoxylated alcohols, we obtained a technical mixture of these alcohols from Shell (Neodol 25-9), which were used in the quantitation of the ethoxylated alcohols. However, the purity of the Neodol 25-9 and the exact composition are unknown. The composition was determined to be approximately 20% $C_{12}EO_x$, 30% $C_{13}EO_x$, 25% $C_{14}EO_x$, and 25% $C_{15}EO_x$ based on the integration of the extracted ion chromatograms. Additionally, quantitation was performed from an external calibration curve, as no deuterated standards are commercially available. Deuterated standards were previously synthesized and used by Evans et al. for a more accurate quantification.[5] A technical mixture of nonylphenol ethoxylate (NPEO) was used for the quantitation of NPEO. In USGS Method O1433-01[2], because technical mixtures were used as standards for alkylphenols and NPEO2, octylphenol monoethoxylate (OPEO1), and octylphenol diethoxylate (OPEO2), all values were reported as estimated values. Therefore, the quantitation of all ethoxylated alcohols and ethoxylated alkylphenols should be considered an estimate of the analyte concentrations.

The primary ethoxylated alcohols that were observed in the Pavilion samples were NPEOx, OPEOx, and C12-15EOx. Also detected in many samples at very low sensitivity were C16 and C17 ethoxylates; however, the signal was very low for these compounds, much too low to be quantified. The concentrations of ethoxylates in the various samples are shown in Table 1.

The NPEOx technical mixture standard that was used for calibration consists of mainly $NPEO_{8-17}$. However, in all of the samples beginning with the letters "EPAMW", the values given for NPEOx are artificially low because the distribution of NPEO oligomers was shifted predominantly towards the lower end, mainly 3-9 EO units. This phenomenon was only observed for the "EPAMW" samples, and it was seen in all of the "EPAMW" samples. NPEOx was observed in all samples, including field and equipment blanks at low levels (except field blank 1, in which higher concentrations of C12-15EOx and NPEOx were observed).

For OPEOx, no calibration standard was available. However, low levels of OPEOx were observed in all samples. The lab at ESD-LV used to use a dish detergent whose active ingredient was OPEOx, and so it is unclear whether the nearly constant low levels seen in all samples is left over from the dish detergent. The only sample in which OPEOx exhibited a large signal was in EPAMW01-0412. If the calibration curve for NPEOx were used to provide an estimate of the OPEOx levels in EPAMW01-0412, OPEOx would measure between 1-2 µg/L.

Many QC criteria were not met for ethoxylated alcohols, including laboratory blanks (C12EO, C14EO, and NPEO present in some of the samples), and lab fortified blanks and lab fortified matrixes usually had low recoveries (<50%). As such, and for the reasons listed above, the quantitation values for the ethoxylated alcohols should not be considered more than estimates of the actual values. Extraction recoveries of higher alkyl chain ethoxylates (i.e., C14 and C15) were lower than the lower chain ethoxylates. This phenomenon has been previously observed [6], and the use of more nonpolar solvents to elute off the SPE cartridges should aid in higher recoveries.

Alkylphenols

Both 4-tert-OP-3,5-d_2 (OP-d2)and *n*-NP-2,3,5,6-d_4 (NP-d4) were added as surrogate standards. However, only the OP-d2 was used because the NP-d4 was *n*-NP, i.e., the nonyl chain was not branched but was linear. Therefore, the recoveries of the NP-d4 were much different than those of the actual OP or NP, which are typically branched isomers.

All QC criteria were met for alkylphenols except for one instance of low spike recovery in a lab fortified matrix for nonylphenol. When this sample was re-extracted, it met QC criteria. Also, extraction recoveries were low in many samples, as judged by isotopically labeled surrogates. Extraction recoveries (average of 44%) were comparable to USGS Method O1433-01, which reported a recovery of NP of 36.8%.

The "EPAMW" samples were generally the only samples that contained quantifiable levels of alkylphenols; however, PGDW50-0412 contained low levels of nonylphenol (~0.1 µg/L). EPAMW02-0412-1 had the highest levels of OP and NP at 2.9 and 28 µg/L, respectively.

For EPAMW02-0412-2, no OP-d2 was added prior to extraction. Therefore, accurate quantitation was not possible. This sample was, however, a sample that was chosen as a laboratory fortified matrix. The spike recoveries in the lab fortified matrixes for OP and NP ranged from 105-127% and 56-107%, respectively; therefore, the adjusted concentrations of OP and NP in EPAMW02-0412-2 were estimated to range from 0.5-0.7 and 7.4-7.9 µg/L, respectively.

Acrylamide

No acrylamide was detected in any of the samples. All QC checks met data quality indicator criteria (instrument and laboratory blanks, laboratory fortified matrix, replicates, CCVs), except laboratory fortified blanks had low recoveries.

Table 1. Concentrations of Analytes (µg/L)

	AA	OP	NP	$C_{12}EO_{7-16}$	$C_{13}EO_{7-16}$	$C_{14}EO_{7-16}$	$C_{15}EO_{6-15}$	NPEOx
fieldblk1	ND	<0.05	0.42	0.30	0.58	0.38	ND	0.37
equipblk1	ND	<0.05	0.05	0.10	0.15	0.14	0.06	0.17
PGDW20-0412	ND	<0.05	<0.05	<0.05	ND	<0.05	<0.05	0.08
PGDW20d-0412	ND	<0.05	<0.05	<0.05	<0.05	<0.05	ND	0.06
EPAMW02-0412-1	ND	2.9	28	0.13	ND	0.34	ND	0.17
PGDW23-0412	ND	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.07
PGDW30-0412	ND	<0.05	<0.05	<0.05	ND	0.08	ND	0.11
fieldblk2	ND	<0.05	0.057	0.24	ND	0.65	ND	0.09
equipblk2	ND	<0.05	0.063	0.44	ND	1.16	ND	0.09
PGDW05-0412	ND	<0.05	0.11	<0.05	ND	<0.05	ND	0.13
fieldblk3	ND	<0.05	<0.05	<0.05	0.05	0.06	<0.05	0.07
equipblk3	ND	<0.05	0.068	0.12	0.17	0.12	0.07	0.23
PGDW50-0412	ND	<0.05	0.099	0.06	0.19	0.10	0.06	0.18
PGPW02-0412	ND	<0.05	0.058	<0.05	0.08	0.05	<0.05	0.11
EPAMW02-0412-2	ND	0.5-0.7[a]	7.4-7.9[a]	0.07	0.11	<0.05	<0.05	0.23
fieldblk4	ND	<0.05	0.074	0.08	0.06	0.24	<0.05	0.09
equipblk4	ND	<0.05	<0.05	0.05	0.09	0.11	<0.05	0.16
EPAMW01-0412	ND	0.14	0.60	<0.05	0.51	0.06	<0.05	0.84
EPAMW01d-0412	ND	0.13	0.57	<0.05	0.06	0.05	<0.05	0.06
EPAMW01-0412-4	ND	0.16	0.65	0.41	0.25	1.7	0.06	0.13
EPAMW01-0412-7	ND	0.098	0.65	1.4	0.11	5.0	<0.05	0.08
EPAMW01-0412-10	ND	0.051	0.24	0.18	0.07	0.62	<0.05	0.07
Riverton WY truck water	ND	<0.05	0.34	<0.05	0.09	<0.05	<0.05	0.17

[a] OP-d2 not added to sample. Values estimated from spiked sample concentration. See text.

References

1. ASTM D 7485-09, Standard Test Method for Determination of Nonylphenol, p-tert-Octylphenol, Nonylphenol Monoethoxylate, an Nonylphenol Diethoxylate in Environmental Waters by Liquid Chromatography/Tandem Mass Spectrometry, 2009.

2. USGS Method O-1433-01, Determination of Wastewater Compounds by Polystyrene-Divinylbenzene Solid-Phase Extraction and Capillary-Column Gas Chromatography/Mass Spectrometry, 2001.

3. Lucentini, L. et al., Determination of Low-Level Acrylamide in Drinking Water by Liquid Chromatography/Tandem Mass Spectrometry, J. AOAC Int., 92, 2009, 263-270.

4. Rosén, J. et al., Retention studies of acrylamide for the design of a robust liquid chromatography-tandem mass spectrometry method for food analysis, J. Chrom. A, 1172, 2007, 19-24.

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6. Lara-Martín, P.A. et al., Development of a method of the simultaneous analysis of anionic and non-ionic surfactants and their carboxylated metabolites in environmental samples by mixed-mode liquid chromatography-mass spectrometry, J. Chrom. A, 1137, 2006, 188-197.