

WASTEWATER ANALYSIS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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ABSTRACT

The U.S. Geological Survey National Water Quality Laboratory and National Research Program have developed a custom analytical method for the determination of compounds typically found in domestic and industrial wastewater. The method was developed in response to increasing concern over the impact of endocrine disrupting chemicals in wastewater on aquatic organisms. Compounds were isolated by continuous liquid-liquid extraction with methylene chloride and determined by capillary-column gas chromatography/mass spectrometry using selected-ion monitoring. The method focuses on the analysis of the alkylphenolethoxylate nonionic surfactant compounds that are persistent indicators of wastewater. Other compounds are representative of food additives, antioxidants, fire retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, polycyclic aromatic hydrocarbons, and high-use domestic pesticides. The method detection limits range from 0.05 to 0.2 microgram per liter for single compounds and about 0.2 microgram per liter for the sum of the isomeric compounds, such as nylphenol and nylphenolethoxylates.

INTRODUCTION

Industrial and domestic waste must be managed effectively to meet the challenges of increasing population, stringent regulatory requirements, and aging water treatment facilities. To meet these challenges, specific analytical methods are available to monitor chemical compounds in wastewater. However, because of the complexity of the sample matrix, several analytical methods are required to determine polar and non-polar organic compounds in the dissolved and suspended phases that may impact water quality. Several compounds are regulated by the U.S. Environmental Protection Agency (USEPA), and appropriate analytical methods are generally available (USEPA, 1995) to monitor for them in industrial wastes or in discharge from wastewater-treatment facilities. Other compounds known to be toxic to aquatic life are currently unregulated even though many, such as nylphenolethoxylates (NPEO's) are on the USEPA Toxic Substance Control Act Priority Testing List (USEPA, 1996). To improve the measurement of the impact of wastewater discharge practices on water quality, the U. S. Geological Survey (USGS) National Water

Quality Laboratory (NWQL) and National Research Program (NRP) have developed a custom analytical method. This method uses representative compounds from several compound classes, to monitor unregulated and regulated contaminants.

METHODS

The custom method is suitable for analysis of complex water samples such as wastewater effluents. One-liter samples, collected in amber glass bottles and stored at 4 °C, are necessary to achieve the low level of detection. Because many of the target compounds are common food additives (caffeine, butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT)), or found in detergents and plasticizers (nylphenol-NP, NPEO), care must be taken to avoid sample contamination. Field processing blanks and method blanks are used to monitor low-level contamination of samples.

To meet the needs of USGS projects, the NWQL has included several sewage indicators such as pesticides, caffeine, and alkylphenols to select USEPA targeted compounds and developed

a custom wastewater method. Other semi-volatile organic compounds that have been detected frequently in samples at the NWQL since 1995 were also added to the method even though many are currently unregulated.

Samples are extracted by continuous liquid-liquid extraction (CLLE) using methylene chloride as the extraction solvent. The unique design of the extractor (fig. 1) uses a porous glass frit that disperses methylene chloride solvent in micro-droplets, improving extraction efficiency compared to conventional designs. Extraction of whole-waters samples by this technique has been in use at the NWQL since 1994, and CLLE has become the extraction method of choice for a wide range of polar and non-polar organic compounds.

Once extracted, the CLLE sample volumes are reduced to 500 microliters prior to analysis by gas chromatography/mass spectrometry (GC/MS). Operation of the mass spectrometer in the selected-ion-monitoring (SIM) mode is necessary to achieve detection levels ranging from 0.05 to 0.20 micrograms per liter, which are required for most environmental samples.



Figure 1. Continuous liquid-liquid extractors with solvent-dispersing frits.

RESULTS

In 1998, 10 USGS projects submitted 126 samples for analysis by this method. Table 1 lists the detection frequency for the industrial and

domestic compounds used to identify potential sources of contamination in wastewater samples.

Table 1. Wastewater, method compounds, their use, and percent frequency of detection in 126 samples from diverse sources.

Compound	Use/Source	%
tetrachloroethylene	solvent	11
2-(2-butoxyethoxy) ethylacetate	solvent	8
phenol	disinfectant	15
trichlosan	antibacterial	17
4-cresol	preservative	9
benzaldehyde	flavor	12
acetophenone	fragrance	19
caffeine	stimulant	22
butylated hydroxyanisole	antioxidant	11
butylated hydroxytoluene	antioxidant	8
2,6-di- <i>t</i> -butylbenzoquinone	antioxidant	14
2,6-di- <i>t</i> -butylphenol	antioxidant	3
4-nonylphenol	detergent	25
4-nonylphenol monoethoxylate	detergent	21
4-nonylphenol diethoxylate	detergent	13
4-octylphenol monoethoxylate	detergent	17
4-octylphenol diethoxylate	detergent	6
1,4-dichlorobenzene	fumigant	12
1,3-dichlorobenzene	fumigant	4
naphthalene	fumigant	18
2,6-dimethylnaphthalene	gasoline	5
phenanthrene	hydrocarbon	19
anthracene	hydrocarbon	11
fluoranthene	hydrocarbon	18
pyrene	hydrocarbon	17
benzo(a)pyrene	hydrocarbon	4
tri-(dichloroisopropyl) phosphate	fire retardant	12
tri-(2-chloroethyl) phosphate	fire retardant	10
lindane	pesticide	1
<i>cis</i> -chlordane	pesticide	4
dieldrin	pesticide	5
methyl parathion	pesticide	1
diazinon	pesticide	11
chlorpyrifos	pesticide	3
carbaryl	pesticide	3
17- <i>beta</i> -estradiol	estrogen	2
cholesterol	fecal sterol	21
3- <i>beta</i> -coprostanol	fecal sterol	20
bisphenol A	polymers	10
phthalic anhydride	plastics	12
tributyl phosphate	plasticizer	14
triphenyl phosphate	plasticizer	13
2-butoxy-ethanol phosphate	plasticizer	15
bis-(2-ethylhexyl) phthalate	plasticizer	16
bis-(2-ethylhexyl) adipate	plasticizer	11
codeine	analgesic	6

The wide range of compounds detected (table 1), demonstrates the usefulness of this method for identifying anthropogenic contaminants over a wide range of sample types. The method also was used on wastewater and river waters samples collected from the Great Lakes region in March, 1998. The river water samples were collected at the surface, near the bank, whereas the wastewater effluents were

collected at the outfall. All samples appeared relatively clear of sediment, and none of the samples were filtered prior to extraction.

The analytical results for these samples are summarized in table 2 and figure 2. All 8 sewage treatment plant (STP) samples on the right side of the table show elevated octyl- and nonylphenol-ethoxylate levels over the river water samples.

Table 2. Results for analysis of river and wastewater samples collected March, 1998, as part of NRP-USEPA study. [concentrations in micrograms per liter unless otherwise indicated; nd, not detected at about 0.01 microgram per liter]

COMPOUND	Sampling Locations											
	IR	DR	MR	ST	NS	CA	SE	ME	BL	JI	DE	
total organic carbon (mg/L)	7.0	6.9	10	7.6	6.3	7.6	8.5	12	9.6	17	12	
4-methylphenol	nd	nd	nd	nd	nd	0.2	0.0	nd	nd	nd	0.8	
4- <i>t</i> -butylphenol	nd	nd	nd	0.1	0.2	nd	0.3	0.3	0.1	0.3	1.0	
4- <i>t</i> -pentylphenol	nd	nd	nd	0.3	nd	nd	nd	0.3	nd	0.3	0.9	
2,6-di- <i>t</i> -butylphenol	nd	nd	nd	nd	nd	nd	nd	0.2	0.1	nd	0.1	
2,6-di- <i>t</i> -butylbenzoquinone	nd	0.2	nd	0.5	0.6	0.6	0.9	0.8	0.8	0.7	1.4	
butylated hydroxyanisole	nd	0.3	nd	0.6	0.6	0.6	1.2	1.3	0.9	0.2	0.2	
butylated hydroxytoluene	nd	nd	nd	0.0	0.0	0.1	0.1	nd	0.3	0.0	0.1	
4- <i>n</i> -octylphenol	nd	nd	nd	nd	nd	nd	nd	0.2	nd	nd	nd	
4-octylphenol	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.4	
4-nonylphenol (total)	nd	1.1	nd	1.7	1.6	1.4	1.5	2.1	0.9	2.5	19	
4-nonylphenol monoethoxylate (total)	nd	1.5	nd	4.0	13	5.8	6.0	11	1.5	9.0	55	
4-nonylphenol diethoxylate (total)	nd	0.5	nd	5.0	7.0	3.7	2.9	19	0.8	28	110	
4-nonylphenol triethoxylate (total)	nd	nd	nd	nd	nd	nd	nd	2.0	nd	3.0	17	
4-nonylphenol tetraethoxylate (total)	nd	nd	nd	nd	nd	nd	nd	1.2	nd	nd	5.0	
4-octylphenol monoethoxylate	nd	nd	nd	0.5	1.0	0.5	0.6	6.0	0.3	0.8	3.2	
4-octylphenol diethoxylate	nd	nd	nd	1.5	1.5	0.8	0.7	4.0	nd	6.0	25	
4-octylphenol triethoxylate	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	22	
caffeine	0.2	0.2	0.1	0.1	0.1	0.3	0.1	2.4	0.2	0.7	4.0	
bisphenol A	nd	0.2	nd	0.4	nd	0.6	nd	nd	nd	0.9	2.7	
coprostanol	nd	nd	nd	0.5	0.6	0.3	0.2	1.3	0.1	0.8	14	
cholesterol	0.6	0.6	0.6	1.2	1.1	1.0	0.7	2.2	0.6	1.7	8.0	
Surrogate Standards*	%	%	%	%	%	%	%	%	%	%	%	
d ₂₁ -butylated hydroxytoluene	55	47	57	38	70	91	36	43	70	21	65	
d ₆ bisphenol A	70	94	111	108	110	114	104	122	114	94	120	
4- <i>n</i> -nonylphenol	71	91	104	82	120	125	95	134	131	96	123	
17- α -estradiol	84	82	92	99	75	105	80	109	111	83	126	
¹³ C ₆ 4- <i>n</i> -nonylphenol	91	80	149	90	122	124	108	130	137	107	131	
¹³ C ₆ 4- <i>n</i> -nonylphenol monoethoxylate	80	129	126	137	152	137	155	206	142	210	257	
¹³ C ₆ 4- <i>n</i> -nonylphenol diethoxylate	35	43	51	51	48	41	74	113	46	109	17	
¹³ C ₆ 4- <i>n</i> -nonylphenol triethoxylate	35	43	51	51	48	41	74	113	46	109	17	

STP - Sewage treatment plant

IR, Illinois River, Ottawa, Ill.

MR, Minnesota River, Minneapolis, Minn.

NS, North Side STP, Skokie, Ill.

SE, Seneca STP, Eagan, Minn.

BL, Blue Lake STP, Shakopee, Minn.

DE, Detroit STP, Detroit, Mich

DR, Des Plains River, Joliet, Ill.

ST, Stickney STP, Cicero, Ill.

CA, Calumet STP, Chicago, Ill.

ME, Metropolitan STP, Ramsey, Minn.

JI, Jones Island STP, Milwaukee, Wisc.

*High percent recovery values for ¹³C labeled surrogate compounds are due to compounds being spiked at low concentration levels (1 microgram per liter).

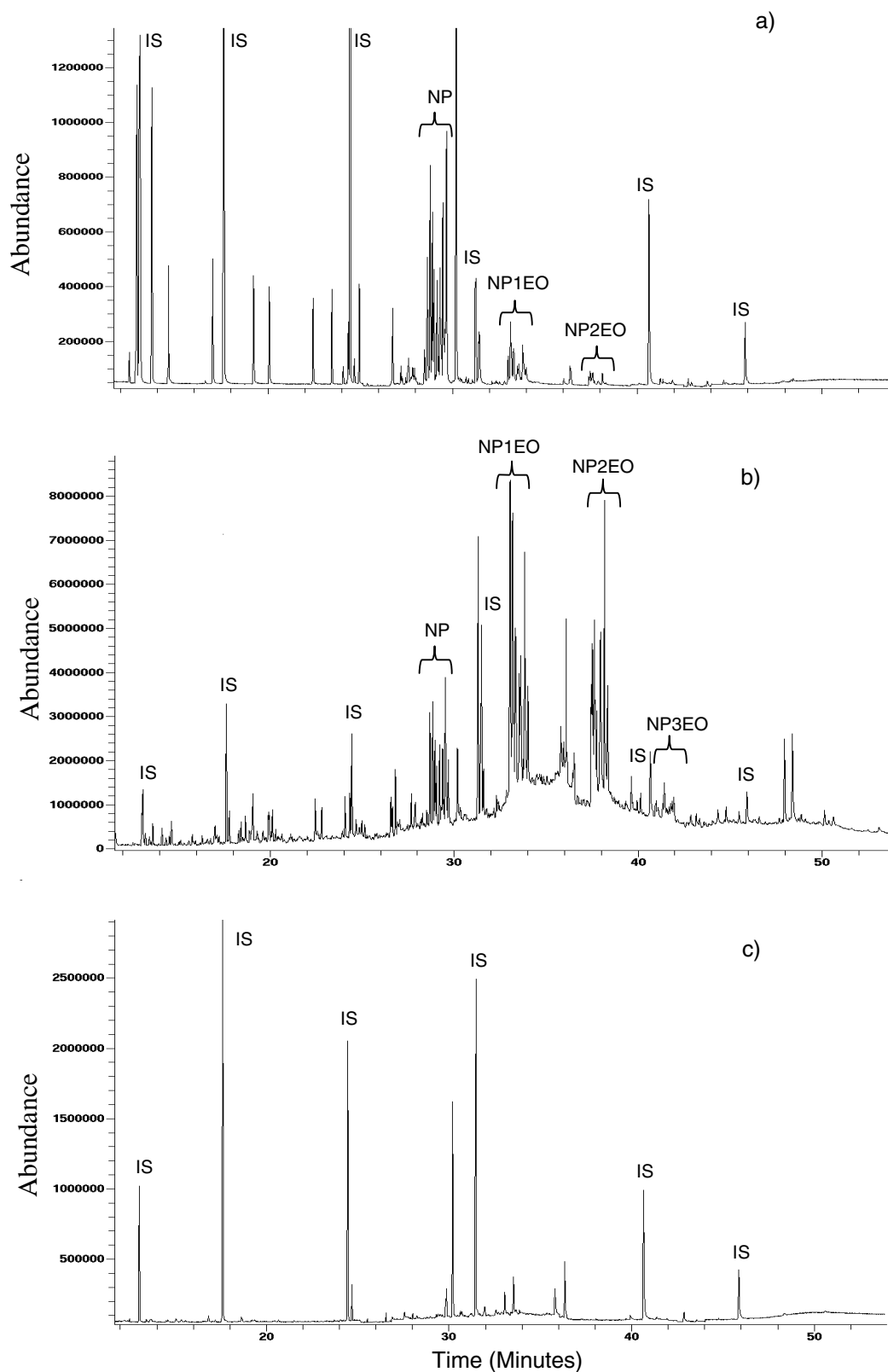


Figure 2. Total ion chromatograms from SIM GC/MS of (a) one microgram per liter standard mix, (b) Detroit wastewater, March 1998, and (c) Minnesota River, March 1998. [IS, internal standard; NP, 4-nonylphenol; NP1-3EO, 4-nonylphenol-mono, di, or triethoxylate]

The STP samples also have higher concentrations of antioxidants (BHA, BHT), as well as the oxidized form, 2,6-di-*t*-butylbenzoquinone. Several surrogate compounds were used in this study to monitor method efficiency and reproducibility. The surrogate standards consist of representative deuterated, carbon 13 labeled, or straight chained (*n*) compounds. Total organic carbon (TOC) values are also given for reference.

The use of SIM mass spectrometry decreases the number of compound peaks seen, and increase the instrument sensitivity by monitoring only ions specific to the compounds of interest. The CLLE GC/MS chromatograms (fig. 2) collected in the SIM mode show the isomeric nature of the NP and NPEO homologs. Under the GC/MS conditions used in this method, approximately 13 separate isomeric peaks are resolved for NP and each NPEO homolog. Resolution and response of NPEO homologs decrease with an increase of EO units with NP4EO being about the maximum quantifiable homolog. The chromatogram from the Minnesota River (fig. 2c) shows a sample with relatively few wastewater compounds present.

DISCUSSION

The method provides an efficient means of detecting several anthropogenic compounds that otherwise might not be possible by USGS or USEPA approved methods. More than one half of the target compounds have been detected in recent samples submitted to the NWQL by projects specifically designed to monitor municipal wastewater. Many of the compounds are endocrine-system disrupters (NP and NPEO's), whereas others, such as caffeine and fecal sterols, are excellent indicators of wastewater. Even though the method is not particularly sensitive for the fecal sterols, it has proven to be an effective way to identify their presence at somewhat higher concentration levels than might be obtained by a more specific method.

REFERENCES

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