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Purpose

This technical memorandum is a follow-up to three NWQL Rapi-Notes (see NWQL Rapi-Notes 03-001, 03-003, and 03-018)* regarding the identification of low-level chronic laboratory blank contamination in the wastewater analysis method, Schedule 1433. The memorandum documents changes that have been made in sample preparation for Schedule 1433 that reduce or eliminate laboratory contamination and interferences for all but a few compounds.

*Rapi-Notes are available to USGS employees. Printed copies are available on request.

Background

Laboratory Schedule 1433 (SH1433, formerly custom lab code 8043) was developed to identify a broad spectrum of organic compounds likely to be found in urban wastewater discharge that have a wide range of chemical and physical properties. The method was implemented in July 2001 as an official USGS method (Zaugg and others, 2002). Sample collection and processing procedures (Wilde and others, 2003) must be followed to avoid inadvertent introduction of contamination to the sample because several method compounds are present in commonly used products, such as soaps, fragrances, insect repellants, and beverages. Water samples are filtered in the field through 0.7-µm

nominal pore diameter, glass-fiber filters (Sandstrom, 1985), and the samples are shipped overnight, chilled and maintained at 4ºC to the NWQL. The filtered-water samples are extracted using polymeric N-vinylpyrrolidone divinylbenzene resin solid-phase extraction (SPE) cartridges. The extracts are analyzed for 64 selected analytes and 3 surrogate compounds by capillary-column gas chromatography with electron ionization mass spectrometry under full-scan conditions. A list of current method compounds, as well as sampling requirements can be accessed by USGS customers at the NWQL web site (http://wwwnwql.cr.usgs.gov/USGS/USGS_gen.html) by selecting "LIMS Catalog" and requesting Schedule 1433. Schedule 1433 currently (November 2005) uses interim reporting levels (IRLs), which are temporary reporting levels that were determined during original method validation (Zaugg and others, 2002).

During calendar year 2003, 17-beta-estradiol [parameter code (P) 62053A], equilenin (P62074A), estrone (P62484A), and ethynyl estradiol (P62052A) and interferences were frequently detected in laboratory blank samples, sometimes at concentrations comparable to those reported in environmental samples, although always below their IRLs. The NWQL then released three Rapi-Notes* (03-001, 03-003, 03-018) from January 22 – May 20, 2003, requesting that estimated concentrations of the four hormones not be reported or published for water samples that were analyzed by Schedule 1433. Subsequently, the four hormones were officially removed from Schedule 1433 as of July 2004. However, it was determined that the method reporting levels for the hormones were valid (Rapi-Note* 03-003) so that the reported non-detections or "less than values" could be published.

Further review of Schedule 1433 laboratory set blank data also indicated contamination and (or) interferences for other method compounds. About half of the method compounds had contamination and (or) interferences that were reported in greater than 10 percent of the laboratory set blanks (the frequency of detection in laboratory blanks used by the NWQL to indicate chronic contamination), usually at concentrations well below the IRL. Even with mass spectral methods capable of reporting data less than the reporting level (Childress and others, 1999), it is difficult to interpret sample results without a consistent distinction between concentrations reported in the laboratory blanks and the environmental samples.

Scope

In calendar year 2004, the NWQL evaluated Schedule 1433 sample preparation to identify and reduce low-level laboratory contamination that has been present from method inception July 2001 until method improvements were made on August 5, 2004. Laboratory blank and field blank results were compared, leading to the identification of four compounds, which if low-level concentrations were reported in samples, the concentrations might be biased high because of potential laboratory contamination. As a result, data users need to carefully interpret low-level sample results using appropriate laboratory and field blank samples.

Schedule 1433 is used to determine a variety of compounds, making it difficult to effectively remove background interferences in the sample matrices without also removing method analytes. The SPE resin used for sample preparation also contributes considerably to background interferences. These potential sources of interferences, and the widespread occurrence of several Schedule 1433 compounds that are common in personal-care products, make it difficult to avoid unintentional contamination during sample collection and processing. To reduce laboratory contamination, it was first necessary to characterize its sources as thoroughly as possible. Interferences and contamination near background levels have been reported in laboratory blanks for Schedule 1433 to help characterize the sources of this low-level contamination, even though these interferences often do

not pass the mass spectral quality criteria necessary for reporting compounds in environmental samples. Accounting for the maximum amount of contamination and interference in the laboratory set blank sample in this manner has made it easier for the analyst to report only compounds in samples that meet all qualitative criteria and are at greater concentrations than occur in the laboratory reagent water set blank(s). A typical example of Schedule 1433 contamination (which can be qualified and identified as a method compound) together with interferences from other compounds in reagent water blank samples is shown in figure 1 for caffeine. Any caffeine contamination that meets qualification criteria occurs above background (interference signals) at a concentration greater than about 0.02 µg/L. Figure 1 illustrates the episodic nature of caffeine contamination which is also typical of contamination for other analytes in Schedule 1433.

If the original (uncensored) laboratory reagent-water blank data for Schedule 1433 are accessed at the NWQL Sample Status page (http://nwql.cr.usgs.gov/usgs/sampstatus/index.cfm) both compound detections and interferences (many at low concentrations that do not meet qualitative criteria) have been reported. This practice is not consistent with other NWQL methods that only report contamination that has met qualitative criteria, and thus can cause confusion interpreting sample data with respect to the laboratory set blank because the detection frequency of compounds in laboratory blanks can appear to be greater than in environmental samples or field blanks. After January 1, 2006 only laboratory blank results that meet all qualitative GC/MS criteria (retention time, mass spectrometric ion abundance ratios, and mass spectra) will be reported for Schedule 1433.

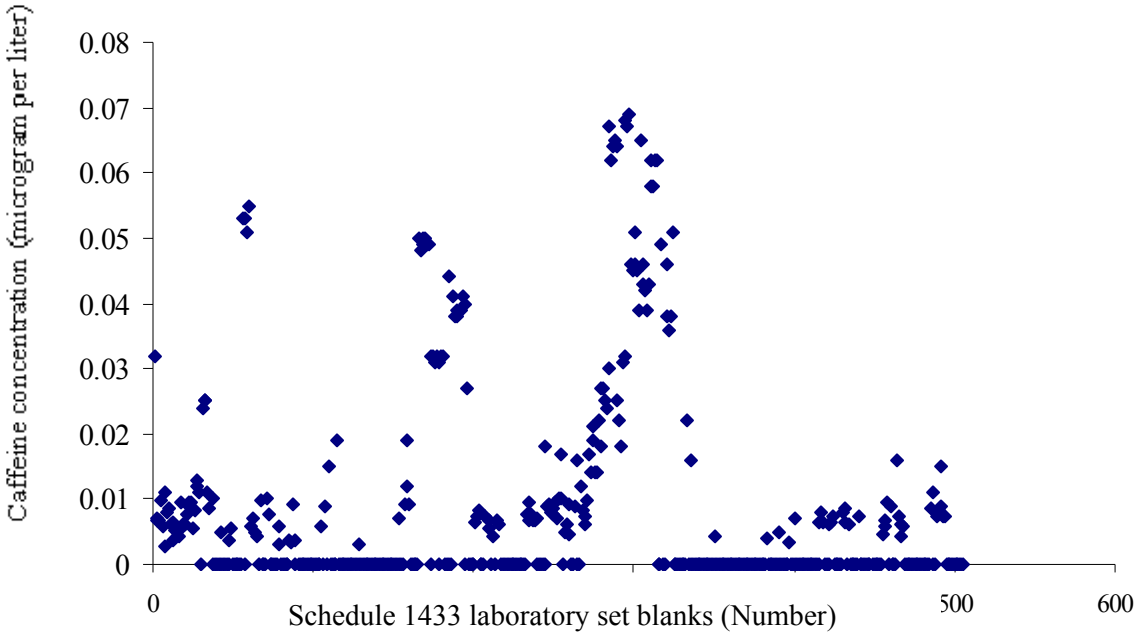

Figure 1. Concentration of caffeine (and interferences) present in 505 Schedule 1433 laboratory reagent-water blanks analyzed since method inception (June 2001) to May 2005.

Results

The process of identifying sources of laboratory contamination for this schedule required a comprehensive evaluation of laboratory air, SPE cartridges, glassware, and solutions that come in contact with the sample. This investigation established that three aspects of sample preparation primarily were responsible for contamination: (1) excessive exposure of the SPE cartridge to ambient laboratory air; (2) improper storage of SPE cartridges following cleaning; and (3) the use of polypropylene reservoirs to hold solvent for eluting the method analytes from the SPE cartridge.

Exposure of the cartridges to laboratory air during cleaning and air-drying varied from a few minutes, up to several hours. The SPE cartridges are no longer air-dried after cleaning.

Storage of the cartridges varied from a day to several days. The SPE cartridges are no longer stored after cleaning, but are cleaned immediately prior to sample preparation. Both of these improvements were implemented at the NWQL on August 5, 2004, and all samples received on or after Julian date 218 were prepared using this new protocol.

In addition, during experiments when the solvent used to elute the SPE cartridge was held in the polypropylene reservoir (for about five times as long as is normally required for sample preparation), the elution solvent became contaminated with low levels (0.2 – 0.8 µg/µL) of surfactants (alkylphenols and alkylphenol ethoxylates) that leached from the plastic. However, these low concentrations produced with excessive leaching times did not produce mass spectra that could meet qualitative criteria required to report the alkylphenolic compounds in samples. The polypropylene reservoirs have been replaced with glass reservoirs that can be thoroughly cleaned, baked, and reused. The NWQL began using glass reservoirs in January 2005, and all samples received after Julian date 16 have been processed with this modification, which has helped to reduce contamination for the five alkylphenol compounds footnoted in Table 1. These sample preparation modifications have been documented in revisions to the method standard operating procedure (SOP), and all analysts have been trained based on this updated procedure.

Table 1. Schedule 1433 laboratory set blank contamination before and after implementation of several method improvements on August 5, 2004, as confirmed by reduction in percent detection frequency and 95th percentile concentration.

[IRL, interim reporting level; N, number of blank samples; LB, laboratory blank; %, percent; µg/L, microgram per liter; Unk, unknown; NA, not applicable; --, not calculated because the detection frequency in laboratory blanks is less than 5 percent; AP, air particulate matter; R, compound removed from the method; Res, reservoir; Int, interference]

Compound	Parameter/ method code[1]	IRL (µg/L)	LB detection frequency (%) Before change (N=341)	LB detection frequency (%) After change (N=165)	LB 95th percentile (µg/L) Before change (N=341)	LB 95th percentile (µg/L) After change (N=165)	Contam-ination source
17-*beta*-Estradiol[5]	62053A	5.0	9	R	0.102	R	Unk
Equilenin[5]	62074A	5.0	10	R	.035	R	Unk
Estrone[5]	62484A	5.0	54	R	.450	R	Unk
Ethynyl estradiol[5]	62052A	5.0	20	R	.290	R	Unk

Table 1. Schedule 1433 laboratory set blank contamination before and after method improvements August 5, 2004 as confirmed by reduction in percent detection frequency and 95th percentile concentration—Continued.

Compound	Parameter/ method code[1]	IRL (µg/L)	LB detection frequency (%) Before change (N=341)	LB detection frequency (%) After change (N=165)	LB 95th percentile (µg/L) Before change (N=341)	LB 95th percentile (µg/L) After change (N=165)	Contam-ination source
1,4-Dichlorobenzene[2]	34572A	.5	83	8	.050	0.002	Air
1-Methylnaphthalene[4]	62054A	.5	77	48	.023	.005	Air
2,6-Dimethylnaphthalene[2]	62055A	.5	36	2	.025	--	Air
2-Methylnaphthalene[4]	62056A	.5	82	62	.033	.007	Air
3-*beta*-Coprostanol	62057A	2.0	42	22	.670	.150	AP
3-Methyl-1H-indole (Skatol)[6]	62058A	1.0	4	1	--	--	NA
3-*tert*-Butyl-4-hydroxyanisole (BHA)[6]	62059A	5.0	3	2	--	--	NA
4-Cumylphenol[6]	62060A	1.0	5	4	.001	--	Res
4-*n*-Octylphenol[6]	62061A	1.0	2	1	--	--	Res
4-*tert*-Octylphenol[3]	62062A	1.0	57	34	.083	.016	Res
5-Methyl-1H-benzotriazole	62063A	2.0	4	1	--	--	NA
Acetophenone[4]	62064A	.5	86	90	.140	.150	Unk
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	62065A	.5	34	4	.038	--	Air
Anthracene[2,6]	34221A	.5	4	1	--	--	NA
Anthraquinone[2]	62066A	.5	3	1	--	--	NA
Benzo[*a*]pyrene[2]	34248A	.5	9	2	.012	--	AP
Benzophenone	62067A	.5	12	4	.006	--	Air
beta-Sitosterol	62068A	2.0	29	14	.920	.170	AP
beta-Stigmastanol	62086A	2.0	36	15	1.100	.170	AP
Bisphenol A[6]	62069A	1.0	28	13	.110	.084	Unk, plastic
Bromacil[2, 6]	04029E	.5	0	0	--	--	NA
Bromoform[2,6]	34288A	.5	0	0	--	--	NA
Caffeine[2,4]	50305B	.5	52	20	.053	.008	Air, contact
Camphor	62070A	.5	14	3	.006	--	Air
Carbaryl[2]	82680F	.5	0	0	--	--	NA
Carbazole	62071A	.5	9	1	.003	--	NA
Chlorpyrifos [2, 6]	38933F	0.5	0	0	--	--	NA
Cholesterol	62072A	2.0	46	8	0.910	0.220	AP
Cotinine	62005A	1.0	1	1	--	--	NA
Diazinon[2, 6]	39572F	.5	0	0	--	--	NA
Dichlorvos [2,	38775B	1.0	0	0	--	--	NA
d-Limonene[6]	62073A	.5	42	10	.054	.011	Air
Fluoranthene[2]	34377A	.5	18	6	.018	.001	Air
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	62075A	.5	11	2	.003	--	Air
Indole[6]	62076A	.5	2	1	--	--	NA

Table 1. Schedule 1433 laboratory set blank contamination before and after method improvements August 5, 2004 as confirmed by reduction in percent detection frequency and 95th percentile concentration—Continued.

Compound	Parameter/ method code[1]	IRL (µg/L)	LB detection frequency (%) Before change (N=341)	LB detection frequency (%) After change (N=165)	LB 95th percent (µg/L) Before change (N=341)	LB 95th percent (µg/L) After change (N=165)	Contam-ination source
Isoborneol	62077A	.5	1	0	--	--	NA
Isophorone[2]	34409A	.5	43	2	.160	--	Int
Isopropylbenzene (cumene)	62078A	.5	70	16	.020	.002	Air
Isoquinoline [2]	62079A	.5	4	1	--	--	NA
Menthol	62080A	.5	8	1	.001	--	Air
Metalaxyl [2]	50359B	.5	4	1	--	--	NA
Methyl salicylate[6]	62081A	.5	24	5	.011	.001	Air
Metolachlor[2]	39415F	.5	0	0	--	--	NA
N,N-diethyl-meta-toluamide (DEET)	62082A	.5	1	1	--	--	NA
Naphthalene [2, 4]	34443A	.5	92	75	.040	.012	Air
Nonylphenol, diethoxy- (total, NPEO2)[3,4]	62083A	5.0	68	47	2.400	1.000	Res
Octylphenol, diethoxy- (OPEO2)[3,4]	61705A	1.0	35	9	.120	.009	Res
Octylphenol, monoethoxy- (OPEO1)[3,4]	61706A	1.0	55	29	.650	.077	Res
para-Cresol[2,6]	62084A	1.0	8	7	.011	.009	NA
para-Nonylphenol (total)[3,4,6]	62085A	5.0	89	77	1.800	.300	Res
Pentachlorophenol[2]	34459A	2.0	1	0	--	--	NA
Phenanthrene[2]	34462A	.5	66	32	.017	.002	Air
Phenol[2,4,6]	34466A	.5	74	84	.210	.330	Unk
Prometon[2]	04037F	.5	2	1	--	--	NA
Pyrene[2]	34470A	.5	22	5	.023	.001	Air
Tetrachloroethylene[2,4]	34476A	.5	61	17	.056	.013	Air
Tri(2-butoxyethyl) phosphate	62093A	0.5	8	2	.070	--	NA
Tri(2-chloroethyl) phosphate	62087A	.5	4	1	--	--	NA
Tributyl phosphate	62089A	.5	9	1	0.039	--	NA
Triclosan[6]	62090A	1.0	7	1	--	--	NA
Triethyl citrate (ethyl citrate)	62091A	.5	15	1	.018	--	NA
Triphenyl phosphate	62092A	.5	9	2	.001	--	NA
Tris(dichloroisopropyl) phosphate	62088A	.5	4	1	--	--	NA

[1]Parameter codes define sample constituent variables linked to compound analytical results stored in the National Water Information System data base. Method letter code is for Schedule 1433.

[2]Compound also can be analyzed by at least one other method at the NWQL.

[3]Alkylphenolic compound contamination improved after polypropylene reservoirs were replaced with glass reservoirs January 2005; and the number of blanks is 35 for these compounds.

[4]Compound might remain a chronic contaminant in laboratory blanks.

[5]Hormone compounds were removed from this method in July 2003.

For all but a few of the method compounds, the laboratory blank contamination and interferences have been reduced to levels that are less than the concentration required for qualitative GC/MS identification (meaning that these low-level background interferences could not be mistaken for method compounds in samples, although they potentially might contribute to the reported concentrations, as discussed later). The majority of the frequently reported detections in Table 1 are low-level interferences (not method compounds) from the sample preparation process. About 70 percent of the laboratory blank detection frequency for caffeine (Table 1) does not meet the GC/MS qualification criteria used for reporting results in environmental samples (see the discussion about figure 1). At least this same percentage of unqualified background interference contributes to the detection frequency of the other method compounds listed in Table 1.

Two compounds [phenol (P34466A) and acetophenone (P62064A)] have been determined to be chronic blank contaminants (defined as detected in greater than 10 percent of the laboratory reagent water blanks) with sample results considered as if contamination is always present, even if the compound is not detected in the corresponding laboratory set blank. Schedule 1433 is currently (January 2006) being evaluated by the long-term method detection level (LT-MDL) procedure (Childress, 1999), which will result in annual review and update of LRLs as necessary to be consistent with LT-MDL data and associated laboratory blank data. If chronic blank compounds such as phenol, acetophenone, and some of the alkylphenolic compounds continue to exhibit persistent contamination their laboratory reporting levels (LRLs) might be raised to compensate for potential contamination.

Reduction in blank contamination of the sterol compounds (Table 1) from minimization of air contact with the SPE cartridge might not be expected based on their low vapor pressures; however, these compounds have been detected in laboratory air samples at the Denver Federal Center on occasion. Replacing the polypropylene elution reservoirs with glass reservoirs has reduced the alkylphenol contamination considerably and well below LRLs and the concentration needed for GC/MS qualitative identification criteria.

Field blank samples are exposed to all the potential sources of contamination in sample collection, transport, preparation and analysis, and are useful for evaluating the possibility of Schedule 1433 contamination because their results are reported using the same GC/MS qualification criteria as for environmental samples. Field blank results for Schedule 1433 are tabulated in Table 2 for before and after method improvements were implemented at the NWQL on August 5, 2004. Although the frequency of detections in field blanks might be expected to be higher than in laboratory blanks, only 5 compounds (Table 2, footnote 1) have been reported in greater than 10 percent of field blank samples (the frequency of detection in laboratory blanks used by the NWQL to indicate chronic contamination). In addition, if laboratory contamination has had a noticeable impact on field results, the frequency of detection and (or) the amount of contamination in field blanks might be expected to decrease concurrently with the decrease in contamination of laboratory blanks (Table 1) when method improvements were made at the NWQL starting August 5, 2004. Out of the 7 compounds (Table 2, footnote 2) that might have contributed to field blank contamination, acetophenone concentration and frequency of detection demonstrated the most noticeable reduction after method improvements. There is indication that laboratory contamination might have contributed to reported concentrations of cholesterol, NPEO2, tetrachloroethylene, and isopropyl benzene (cumene), but the concentrations of these compounds are always reported as estimated by Schedule 1433 and are qualified with an “E” remark code. There also appears to be a possibility that triphenyl phosphate concentrations might have been impacted by laboratory contamination, but no sample results have

been reported to date (November 1, 2005) for this compound below the 95th percentile (Table 1, 0.001 µg/L) of laboratory contamination. Many of the method compounds appear to have increased field blank contamination [frequency of occurrence and (or) amount of contamination] after laboratory improvements (Table2, footnote 3). This is most likely a result of an increase in the capability to confidently identify method compounds in samples when there has been a substantial reduction in laboratory contamination or interference.

Schedule 1433 contamination is complex and unpredictable [episodic (periodic), and can vary by over an order of magnitude in concentration (see Figure 1 for caffeine)], and wastewater sample matrices are generally complex as well. Therefore, if concentrations in environmental samples have been reported below the lowest calibration standard routinely used in this method (0.08 µg/L) and the 95th percentile concentration of laboratory blanks (Table 1), results need to be interpreted cautiously. This precaution is particularly important for the Schedule 1433 sample results that were generated before method improvements were implemented August 5, 2004 and for the 4 compounds always reported with estimated concentrations [cholesterol, NPEO2, tetrachloroethylene, and isopropyl benzene (cumene)] that were discussed previously. After method improvements were made, only about 0.5 % of all the reported sample data have been reported below the more recent 95th percentile blank concentrations (Table 1).

Two recent source water-quality assessment (SWQA) reviews of the National Water-Quality Assessment (NAWQA) program data also indicate that acetophenone and phenol sample data should be interpreted cautiously because of frequent detections in both field and laboratory blank samples at concentrations that are important relative to reported sample concentrations (Jim Kingsbury, U.S. Geological Survey, written communications, 2004 and 2005). Kingsbury cautioned that if results for phenol and acetophenone are reported, that they should be qualified with information about data quality from both the laboratory and field blanks. Kingsbury also suggested that all results for phenol should be flagged in NWIS with the "V" remark code to indicate that the analyte was detected in both the environmental sample and the associated field blank.

DEET (N,N-diethyl-*meta*-toluamide; an insect repellent) was frequently detected in field blanks [about 35 percent of surface- and ground-water field blanks (Jim Kingsbury, U.S. Geological Survey, written communications, 2004 and 2005)], but has been detected in only about 1 percent of laboratory reagent-water blank samples (Table 1).
Kingsbury concluded that localized detections of DEET and benzophenone in field blanks indicated that contamination from these compounds is related largely to the field environment, and reported concentrations generally do not need to be flagged with the "V" remark code unless these compounds were also detected in the associated field blank (see clarification in Kingsbury and others, 2004 and 2005).

In 2004, an experiment was conducted at the NWQL to demonstrate the potential for unintentional DEET contamination when DEET is worn by field personnel collecting and filtering samples (Mark Sandstrom, U.S. Geological Survey, written communication, May 25, 2004). Well-water samples collected and filtered by field crews that wore DEET were always contaminated with concentrations of DEET between 0.2 – 0.3 µg/L, whereas samples processed by crews that did not use insect repellent containing DEET were not contaminated.

Table 2. Schedule 1433 field blank results (percent detection frequency and 95th percentile concentration) for samples processed before and after implementation of laboratory method improvements on August 5, 2004.

[N, number of blank samples; FB, field blank; %, percent; µg/L, microgram per liter; --, not calculated because the detection frequency in field blanks is less than 5 percent]

Compound	FB detection frequency (%)		FB 95th percentile (µg/L)	
	Before change (N=258)	After change (N=222)	Before change (N=258)	After change (N=222)
1,4-Dichlorobenzene	7.4	8.1	0.05	0.03
1-Methylnaphthalene[3]	1.9	4.5	--	--
2,6-Dimethylnaphthalene	1.2	.9	--	--
2-Methylnaphthalene[3]	2.7	5.9	--	.01
3-*beta*-Coprostanol	1.2	3.2	--	--
3-Methyl-1H-indole (Skatol)	.8	0.0	--	--
3-*tert*-Butyl-4-hydroxyanisole (BHA)	.4	0.0	--	--
4-Cumylphenol	.4	.5	--	--
4-*n*-Octylphenol	0.0	0.0	--	--
4-*tert*-Octylphenol	3.5	2.3	--	--
5-Methyl-1H-benzotriazole	0.0	.5	--	--
Acetophenone[1,2]	31.0	5.0	.25	.03
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	4.7	7.2	--	.01
Anthracene	0.0	0.0	--	--
Anthraquinone	.4	0.0	--	--
Benzo[*a*]pyrene	1.2	0.0	--	--
Benzophenone[1,3]	14.3	29.7	.09	.08
beta-Sitosterol	3.5	4.0	--	--
beta-Stigmastanol	4.1	4.2	--	--
Bisphenol A	3.1	5.4	--	.12
Bromacil	0.0	0.0	--	--
Bromoform	2.3	.5	--	--
Caffeine	8.1	8.7	.02	.02
Camphor[3]	.8	4.0	--	--
Carbaryl	0.0	0.0	--	--
Carbazole	.8	.5	--	--
Chlorpyrifos	0.0	0.0	--	--
Cholesterol[2]	7.4	5.4	.86	.41
Cotinine	1.2	0.0	--	--
Diazinon	0.0	0.0	--	--
Dichlorvos	0.0	0.0	--	--
d-Limonene	2.7	3.2	--	--
Fluoranthene	3.1	3.2	--	--

Table 2. Schedule 1433 field blank results (percent detection frequency and 95th percentile concentration) for samples processed before and after implementation of laboratory method improvements on August 5, 2004—Continued.

Compound	FB detection frequency (%) Before change (N=258)	FB detection frequency (%) After change (N=222)	FB 95th percentile (µg/L) Before change (N=258)	FB 95th percentile (µg/L) After change (N=222)
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	3.5	4.1		
Indole	3.1	4.1	--	--
Isoborneol	4.1	3.2	--	--
Isophorone	1.2	0.0	--	--
Isopropylbenzene (cumene)[2]	5.0	3.2	0.12	--
Isoquinoline[3]	.4	1.4	--	--
Menthol[3]	1.9	8.1	--	0.02
Metalaxyl	0.0	0.0	--	--
Methyl salicylate	7.0	7.7	.02	.02
Metolachlor	.8	.5	--	--
N,N-diethyl-*meta*-toluamide (DEET)[1]	37.2	33.0	.21	.13
Naphthalene[1,3]	5.0	16.0	.003	.03
Nonylphenol, diethoxy- (total, NPEO2)[2]	5.0	3.2	.34	--
Octylphenol, diethoxy- (OPEO2)	2.7	2.3	--	--
Octylphenol, monoethoxy- (OPEO1)	2.3	3.2	--	--
para-Cresol	0.0	0.0	--	--
para-Nonylphenol (total)[3]	8.9	19.2	1.32	1.80
Pentachlorophenol	0.0	0.0	--	--
Phenanthrene	5.0	6.3	.002	.009
Phenol[1]	64.0	67.1	1.90	1.23
Prometon	.4	0.0	--	--
Pyrene	3.1	2.3	--	--
Tetrachloroethylene[2]	4.1	1.8	--	--
Tri(2-butoxyethyl) phosphate	3.1	3.2	--	--
Tri(2-chloroethyl) phosphate[2]	6.2	5.0	.015	.006
Tributyl phosphate[1,3]	4.7	10.4	--	0.04
Triclosan	.4	1.4	--	--
Triethyl citrate (ethyl citrate)	1.6	1.8	--	--
Triphenyl phosphate[1, 2]	11.2	9.5	.06	.03
Tris(dichloroisopropyl) phosphate	3.1	3.2	--	--

[1]Compound has been reported in greater than 10 percent of field blanks.
[2]Compound has had a substantial decrease in frequency of detections and (or) amount of contamination in field blanks after laboratory method improvements were made at the NWQL August 5, 2004.
[3]The compound frequency of detections has increased in field blanks substantially after laboratory method improvements.

Reagent water laboratory spikes were evaluated using an equivalence test [two one-sided tests (TOST)] before and after methodological changes August 5, 2004, to determine if method modifications substantially affected method recovery. Mean compound recoveries for 100 laboratory reagent water spike samples analyzed prior to method changes were compared to the mean recovery of 100 laboratory reagent water spike samples analyzed after changes were made. None of the mean compound recoveries had a difference of greater than 12 percent (when a difference threshold of 12 percent was chosen for the test), and all recoveries were well within the control limits of the method. Further examination of the compound recovery control charts from method inception, July 2001,

until May 18, 2005, revealed that no obvious changes occurred for any of the compounds at the time of the method change, and the calculated differences in mean recoveries did not comprise a long-term trend for more than 30 consecutive spike samples.

Field matrix spike recoveries for eight surface-water and ground-water samples were between 80–100 percent for most method compounds (Jim Kingsbury, NAWQA source water-quality assessment review of Schedule 1433 data, U.S. Geological Survey, written communication, 2004). Based on this very limited comparison, Kingsbury concluded that the method appears to perform similarly for environmental samples and lab reagent water spikes, and matrix effects do not appear to affect constituent recoveries appreciably. However, in accordance with the need to evaluate a greater number of matrices, the NWQL encourages the submission of field matrix spike samples for Schedule 1433 and has prepared a spiking solution that is available at One-Stop Shopping (catalog number N1430, URL, http://1stop.usgs.gov). Lab matrix spike samples can also be requested (U.S. Geological Survey, 2005).

A comparison of surrogate recoveries for caffeine-C13 and fluoranthene-*d*10, which are isotopically labeled analogs of two method compounds, also indicates that sample matrices generally do not hinder the performance for the recovery of these two compounds (Table 3). However, the recovery of the surrogate compound bisphenol A-*d*3 (Table 3) is expected to be considerably more variable in some matrices because it is subject to oxidation. Likewise, the recovery of bisphenol A in sample matrices is expected to be similar to the surrogate bisphenol A-*d*3. Decafluorobiphenyl is used as a surrogate compound because it is quite volatile and can be used to monitor for the loss of other volatile method compounds that might occur during sample preparation.

Table 3. NWQL Schedule 1433 mean surrogate recoveries and F-pseudosigma values for 1,448 environmental samples and results from 132 laboratory reagent water spikes in 2003.
[%, percent; F-PS; F-pseudosigma]

Compound	Lab Spike Mean Recovery (%)	Field Sample Mean Recovery (%)	Lab Spike F-PS (%)	Field Sample F-PS (%)
Bisphenol A-*d*3	92	74	19	35
Caffeine-C13	98	102	19	26
Decafluorobiphenyl	82	74	15	16
Fluoranthene-*d*10	110	100	24	21

Additional Considerations

Schedule 1433 is considered to be an "information-rich" method (Childress and others, 1999) with gas chromatograpic retention times, full-scan mass spectra and ion abundance ratios used for compound identifications. Consequently, the concentrations of analytes in samples less than the IRL are reported using an "E" (estimated value) remark code as long as the same qualitative requirements are met to confirm the presence of a compound whether the concentration is greater than or below the IRL. When qualitative criteria are not met in samples, the compound result is reported as < IRL. If a compound is present at a concentration less than the IRL (meets all of the GC/MS qualitative criteria) but interferences or contamination in the laboratory blank occur at an equivalent or higher concentration than in the sample, the sample result is also reported as < IRL.

During this method review, it was determined that reporting changes are necessary for the compounds listed in Table 4. The instability of the GC/MS [as determined by the analysis of continuous calibration verification solutions (CCVs)] for the quantitation of the five method compounds listed in Table 4 [the four sterol compounds and tris (2-butoxyethyl) phosphate] necessitates that the concentration of these compounds is reported as estimated with the "E" remark code if the calculated CCV concentration is not within the quality assurance limit of ± 20 percent of the expected amount. Because of the high frequency of CCV failures for the above-mentioned compounds (about 30 percent), the concentration of these compounds will be permanently estimated as of February 1, 2006.

The mean recovery of 5 percent for dichlorvos in laboratory reagent water spikes, since method inception through 2003, resulted in this compound being "U-DELETED"

Table 4. Compounds that require reporting changes in Schedule 1433.

[CCV, continuous calibration verification; "E", estimated value remark code; %, percent]

Compound name	Parameter/method codes[1]	Comments	Action
3-*beta*-Coprostanol[2]	62057A	Poor CCV control	Permanently "E"
beta-Sitosterol[2]	62068A	Poor CCV control	Permanently "E"
beta-Stigmastanol[2]	62086A	Poor CCV control	Permanently "E"
Cholesterol[2]	62072A	Poor CCV control	Permanently "E"
Dichlorvos	38775B	5% mean recovery in spikes	Delete from method
Tri(2-butoxyethyl) phosphate[2]	62093A	Poor CCV control	Permanently "E"

[1]Parameter codes define sample constituent variables linked to compound analytical results stored in the National Water Information System data base.

[2]The concentration of these compounds will be permanently estimated using the "E" remark code because about 30 percent of continuous calibration verification solutions (CCVs) are not within the expected (± 20 percent) quality control limits.

(remark code, unable to determine) for all samples determined by this method beginning August 1, 2004, and consequently, dichlorvos has been removed from this method as of November 1, 2005. The 63 compounds that will be reported by schedule 1433 after February 1, 2006 are listed in Table 5. The concentration of 17 compounds always is reported as estimated for one of three reasons: unacceptably low-biased recovery (less than 60 percent) or highly variable method performance (greater than 25 percent relative standard deviation), unstable instrument response, or reference standards prepared from technical mixtures. The method reporting levels (MRLs) derived from the LT-MDL data have not changed substantially from the IRLs for most compounds, except for acetophenone which was determined to be a chronic blank contaminant.

Table 5. Compounds reported by Schedule 1433 after February 1, 2006.
[IRL, interim reporting level; MRL, method reporting level]

Compound	Parameter/ method code[1]	IRL until 2/1/2006 (µg/L)	MRL starting 2/1/2006 (µg/L)
1,4-Dichlorobenzene	34572A	0.5	0.5
1-Methylnaphthalene	62054A	.5	.5
2,6-Dimethylnaphthalene	62055A	.5	.5
2-Methylnaphthalene	62056A	.5	.5
3-Methyl-1H-indole (Skatol)[6]	62058A	1.0	1.0
4-Cumylphenol[6]	62060A	1.0	1.0
4-*n*-Octylphenol[6]	62061A	1.0	1.0
4-*tert*-Octylphenol	62062A	1.0	1.0
5-Methyl-1H-benzotriazole	62063A	2.0	2.0
Acetophenone	62064A	.5	.5
Acetyl-hexamethyl-tetrahydro-naphthalene (AHTN)	62065A	.5	.5
Anthracene[6]	34221A	.5	.5
Anthraquinone	62066A	.5	.5
Benzo[*a*]pyrene	34248A	.5	.5
Benzophenone	62067A	.5	.5
Bisphenol A[6]	62069A	1.0	1.0
Bromacil[6]	04029E	.5	.5
Caffeine	50305B	.5	.5
Camphor	62070A	.5	.5
Carbazole	62071A	.5	.5
Chlorpyrifos[6]	38933F	.5	.5
Cotinine	62005A	1.0	1.0
Diazinon[6]	39572F	.5	.5
Fluoranthene	34377A	.5	.5
Hexahydrohexamethyl-cyclopentabenzopyran (HHCB)	62075A	.5	.5
Indole[6]	62076A	.5	.5
Isoborneol	62077A	.5	.5
Isophorone	34409A	.5	.5
Isoquinoline	62079A	.5	.5
Menthol	62080A	.5	.5
Metalaxyl	50359B	.5	.5
Methyl salicylate[6]	62081A	.5	.5
Metolachlor	39415F	.5	.5

Table 5. Compounds reported by Schedule 1433 after February 1, 2006—Continued.

Compound	Parameter/ method code[1]	IRL until 2/1/2006 (µg/L)	MRL starting 2/1/2006 (µg/L)
N,N-diethyl-*meta*-toluamide (DEET)	62082A	.5	.5
Naphthalene	34443A	.5	.5
para-Cresol[6]	62084A	1.0	1.0
Phenanthrene	34462A	.5	.5
Phenol[6]	34466A	.5	.5
Prometon	04037F	.5	.5
Pyrene	34470A	.5	.5
Tri(2-chloroethyl) phosphate	62087A	.5	.5
Tributyl phosphate	62089A	.5	.5
beta-Sitosterol[5]	62068A	2.0	2.0
beta-Stigmastanol[5]	62086A	2.0	2.0
Bromoform[2,6]	34288A	.5	.5
Carbaryl[2]	82680F	.5	.5
Cholesterol[5]	62072A	2.0	2.0
d-Limonene[2,6]	62073A	.5	.5
Isopropylbenzene (cumene)[2]	62078A	.5	.5
Nonylphenol, diethoxy- (total, NPEO2)[4]	62083A	5.0	5.0
Octylphenol, diethoxy- (OPEO2)[4]	61705A	1.0	1.0
Octylphenol, monoethoxy- (OPEO1)[4]	61706A	1.0	1.0
para-Nonylphenol (total)[4,6]	62085A	5.0	5.0
Pentachlorophenol[2]	34459A	2.0	2.0
Tetrachloroethylene[2]	34476A	.5	.5
Tri(2-butoxyethyl) phosphate[5]	62093A	.5	.5

[1]Parameter codes define sample constituent variables linked to compound analytical results stored in the National Water Information System data base. Method letter code is for Schedule 1433.

[2] Concentration is estimated because recovery is between 35 and 60 percent or variability is greater than 25 percent relative standard deviation.

[3] Concentration is estimated because of unstable instrument response.

[4] Concentration is estimated because the reference standard is prepared from a technical mixture.

[5] Concentration is estimated because continuous calibration verification solutions (CCVs) are not within the expected quality control limits.

[6]Compound might not be stable in the presence of excess chlorine.

Schedule 1433 includes 4 volatile compounds (bromoform, isopropylbenzene, *d*-Limonene, and tetrachloroethylene) that have their concentrations reported as estimated using the "E" remark code. If an accurate concentration (not estimated) of bromoform or tetrachloroethylene is needed, a separate sample should be submitted for a volatile organic compound (VOC) method. Quantitative results reported for bromoform require extra precaution (by any laboratory method) because, as documented in NWQL Rapi-Note* 04-018 (August 20, 2004), there is likely a possibility of continued bromoform formation in the sample bottle following sample collection (without the addition of a preservative) if residual chlorine, dissolved organic carbon, and bromide are present. In January 2004, a 10-day sample-holding time and sample-preservation study was conducted by Jacob Gibs (U.S. Geological Survey, written communication, 2005) and NWQL chemists to determine the potential for degradation of Schedule 1433 method compounds in unpreserved finished drinking-water samples collected from a treatment plant with 1.2 mg/L of residual chlorine and samples preserved with ascorbic acid. Sixteen compounds degraded (Table 5, footnote 6) and the bromoform concentration increased 10 percent in unpreserved samples, whereas no detectable degradation was observed in the preserved samples. In

another study, it was verified that the addition of ascorbic acid did not have a deleterious effect on the performance of Schedule 1433 method compounds (Mark Sandstrom, U.S. Geological Survey, written communication, 2004). In order to obtain reliable quantitative results for bromoform and avoid degradation of method compounds in the presence of residual chlorine, samples must be preserved [1-L amber bottles containing ascorbic acid are available at One-Stop Shopping (http://1stop.usgs.gov), stock number N1162]. The sample should not be preserved if the customer does not suspect residual chlorine. However, if a sample has not been preserved that needed to be preserved, the reported concentration of bromoform is likely to be much greater that when the sample was collected, and the NWQL recommends that the customer remove the reported bromoform concentration from NWIS. Incidentally, ascorbic acid should not be added to samples intended for the analysis of dissolved organic carbon or total organic carbon.

Conclusions

Laboratory blank contamination for Schedule 1433 has been reduced for nearly all method compounds because of improvements in cleaning and handling of solid-phase extraction cartridges prior to sample preparation and reduced exposure of solid-phase extraction cartridges to laboratory air. Also, there has been additional reduction in alkylphenol contamination after changing from polypropylene to glass reservoirs. Although there has been considerable progress reducing the overall blank contamination, a few compounds which have been routinely detected in ambient air and SPE cartridge material, might continue to exhibit blank contamination in the future (albeit at much lower levels). Improvements in the data reporting process for Schedule 1433 data, such as the addition of the “E” remark code for five compounds and current participation in the NWQL long-term method detection level procedure will result in annual evaluation and updates for laboratory reporting levels that will be consistent with both laboratory spike and blank data that will enable sample results to be more consistently reported, and distinct from potential laboratory contamination. Reporting detections that meet all of the qualitative GC/MS criteria in laboratory blanks the same way as for samples will facilitate this effort. Data users have been cautioned to carefully interpret all low-level sample results and have been given specific guidance for using both laboratory and field blank samples to assist in this effort. The reduced contamination from laboratory sample processing will enable a greater amount of low-level data to be reported for several method compounds, particularly the alkylphenols, so that field blank results will become increasingly important in this data-interpretation process. The Schedule 1433 laboratory reagent water blank contamination will continue to be closely monitored in the future.

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Effect on Data Base

The deletion of dichlorvos from Schedule 1433 and reporting the concentration of five compounds (previously unqualified) as always estimated using the "E" remark code will be implemented at the NWQL February 1, 2006. Data users need to be aware of these changes with respect to interpreting historical data.

/signed/

Chief
National Water Quality Laboratory
Branch of Analytical Services

Key words: Schedule 1433, Remark code, Blank contamination, hormones