Evaluation of Analytical Reporting Errors Generated as Described in SW-846 Method 8261A

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Abstract: SW-846 Method 8261A incorporates the vacuum distillation of analytes from samples, and their recoveries are characterized by internal standards. The internal standards measure recoveries with confidence intervals as functions of physical properties. The frequency these confidence intervals include true values was very close to theoretical predictions. The ruggedness of the Method's generation of confidence intervals was tested by analyzing water samples that were altered using salt, glycerin, oil, and detergent as well as increasing sample volume size. Quality control requirements were established for identifying when results might not be normally distributed. There were 11,260 analyte results, of which 90.8% of the data passed quality controls. Their distribution about true value was near theoretical values (71.3, 95.0, and 99.2% for one, two and three sigma deviations).

Introduction

The level of uncertainty in environmental analyses is of concern for those who use analytical data to make environmental decisions [1]. The National Environmental Laboratory Accreditation Conference (NELAC) has recommended that member laboratories estimate their measurement confidence interval for all analyses [2]. SW-846 Method 8261A has a unique attribute in that it provides a calculation of confidence intervals for each result [3].

Internal standards are normally used to compensate analyte responses for varying recoveries that could be related to matrix or injection losses (*e.g.*, SW-846 Method 8260C) [4 and 5]. The internal standard that is selected to characterize the recovery of an analyte is typically selected by the proximity of their gas chromatographic retention times. The use of internal standards in the vacuum distillation procedure, Method 8261A, is not in the usual sense in that internal standards in Method 8261A are selected by their ability to characterize the effects of boiling point and relative volatility on analyte recovery. Compensating for the effects of these properties on each analyte an accurate determination of concentration is provided [6].

Method 8261A determines recovery based on boiling point and on relative volatility, described as

$$R_T = R_\alpha \times R_\beta \qquad (1).$$

The term R_T is the total predicted recovery and R_α and R_β are the recovery based on relative volatility and boiling point, respectively [7].

The incorporation of multiple internal standards to measure these effects on recovery by boiling point and relative volatility also allow the generation of confidence intervals [7]. The total variance for both relative volatility effects and boiling point relative to equation 1 is

$$r_T^{\ 2} = r_\alpha^{\ 2} + r_\beta^{\ 2} \qquad (2).$$

The term r_T^2 is the total variance and r_α^2 and r_β^2 are the variances associated with relative volatility and boiling point, respectively [7]. The total internal standard correction error for an analyte and the analyte calibration error were propagated for the confidence interval reported and investigated for use as the analytical error.

An assumption of this work is that if the Method 8261A confidence interval reflects the analytical error then the confidence interval around a result includes a true concentration at a frequency described by the empirical rule of normally distributed data. That is, a Method 8261A generated concentration and one standard deviation should include a true value (spiked concentration) 68% of the time (and 95% of the time with two standard deviations and 99.7% with three standard deviations).

The ability of confidence interval to describe the analytical error was tested by analyzing water with ingredients added to induce matrix effects. The ingredient concentrations were increased to an amount that was expected to cause errors in the analyses with an additional intent to identify limits for using confidence intervals to describe analytical error. Replicate analyses provided the data for calculating the frequency that confidence intervals described the amount of analyte added to the samples. Because each analyte data set was small, a less restrictive Chebyshev’s inequality was used in place of the empirical rule to describe the minimum acceptable frequency of accurately describing known concentrations [8].

Experimental

GC/MS: The vacuum distiller is interfaced to a GC/MS so that the vacuum distillate is transferred directly to the GC/MS for analysis after a distillation. In this study, the GC/MS was a Thermo DSQ mass spectrometer and Trace GC. The GC capillary column was a 30 m x 0.25 mm i.d., 1.5 µm film VOCOL column (Supelco, Bellefonte, PA). The GC operating conditions were 2.5 min at -20 °C, 40 °C/min ramp to 60 °C, 5 °C/min ramp to 120 °C and held at 120 °C for 1 min, 20 °C/min ramp to 220 °C and held for 12 min resulting in a GC run time of 34 min. The injection was split 60:1 with a constant flow rate of 1.4 ml/min. The mass spectrometer scanned between 35 and 300 amu at 1 scan/sec.

Vacuum Distiller: A Cincinnati Analytical Instruments Model VDC1012 vacuum distiller (Rochester, NY) performed the distillations in the study. Samples were vacuum distilled for 7.5 min with a 2.5 min transfer to the GC/MS through a transfer line held at 200 °C.

Quantitation: Calibration was performed as described in Method 8261A. The internal standards used in this study are presented in Table 1. Methyl cyclohexane-d_{14}, ethylbenzene-d_{10}, and 2-chloroethanol-d_4 are new internal standards that were added for this study. The software used to perform calibration was obtained from the Environmental Protection Agency's web pages [9].

The surrogates used to monitor method performance are presented in Table 2. These analytes were monitored as representative of three class of compounds: volatile class was for compounds with boiling point less than 159 ºC, non-purgeable class as the volatile class but with relative volatility greater than 100 ºC, and the semi-volatile class representing compounds that boil at or above 159 ºC.

The analytes in this study are presented in Table 3. Their calibration range is in units of mass and was nominally 5 to 500 ng per analyte. A review of calibration ranges was conducted to ensure the range was linear for each analyte. The lower points of some analytes were not used in generating their calibration curves when interferences at the lower point were observed. The lowest standard mass in each analyte calibration curve was used as the limit of quantitation (LOQ). Any analyte response that fell below the LOQ was considered as potentially less accurate and segregated from results that fell within the calibration range.

Samples: Varying amounts of a modifier added to water was intended to induce severe matrix effects that would impact accuracy of results. Matrix modifiers consisted of salt, glycerin, peanut oil, and varying water volume. Each of these modifiers was evaluated at three amounts. In addition, three different levels of analyte concentration were analyzed at each modified amount. The amounts of the spikes were 0.5 and 0.2 of the upper limit of the calibration range and at the limit of quantitation (0.02 of upper limit). A batch of analyses representing each spike level and each modifier level was performed in one day and the batch was repeated five times.

Salt: This modifier was added to water to mimic water with varying amounts of dissolved solids. 0.1, 0.3, and 1 g of salt was added to 5 mL water to induce matrix effects.

Water volume: The volume of water in the vacuum distilled sample was increased from the standard 5-mL volume to evaluate what effects were observed with larger samples. The sample volumes of water were 5, 25, and 50 mL.

Glycerin: This modifier was added to test effects from having dissolved organic material in water. The amounts of glycerin added to the samples were 0.1, 0.3 and 1.0 g.

Detergent: This modifier was added to test the effects from having a surfactant as well as foaming during distillation. The amounts of liquid detergent (Skilcraft® All-Purpose Cleaner) were 0.05, 0.1 and 0.2 mL.

Oil: An oil modifier was added to water to test effects from having a free organic phase in water. While the amounts added would be observed as a second phase in a water sample this modifier would expect to impart extreme matrix effects. Peanut oil was used as the oil as it was clear of the analytes used in the study. The amounts of peanut oil added to 5 mL water samples were 0.1, 0.3, and 1.0 g.

Results and Discussion

Quality control parameters did not have limits at the beginning of this study. When outliers were found and related to a quality control value, that value was considered outside the acceptable range. Values that had no associated outliers nearest to the outlier value became a control limit. In this manner limits evolved for all of the quality control parameters on the basis of observed impact on the ability of confidence intervals to describe analytical error.

There were 45 results for each analyte in water type (modified with one of the options). 15 samples spiked at one-half the upper calibration limit, 15 samples spiked at one-fifth the upper calibration limit, and 15 samples spiked at the LOQ. Because spikes at the LOQ would be expected to be confounded by background interference, the initial interpretation of results was of spikes above the LOQ. This resulted in sets of 30 results for each analyte in each water type. These sets were used to compare confidence intervals with analytical error and determine limits of quality control (QC) parameters. After establishing quality control limits then the evaluation of method confidence intervals as analytical error was performed.

It was an assumption of the study that if an analyte was an outlier there would be an observable cause that would also impact one of the QC parameters. Data were reviewed by matrix so that any severe effects would be readily apparent. Each analyte set failing Chebyshev's rule was examined for analyses where the true value fell outside the three standard deviation confidence interval. The next step was to determine if an *outlier* result was due to a matrix effect on a class (volatile, non-purgeable, or semivolatile compounds), a matrix effect on subset of a class, or a variation unique to the determination of an analyte concentration.

Outlier results were first compared to the continuing calibration check (in distilled water) that is run prior to sample analyses. Outlier analytes relating to this parameter were rare and were only obvious when the continuing calibration varied more than 40% from the calibration curve.

Unexpectedly, one of the more frequent factors for causing outliers was when the one standard deviation confidence interval was small, even though the result was near true value (e.g., 90 ± 3%). This occurrence would be expected when the calibration or internal standard determined recoveries understated the calibration error for an analyte. Therefore a minimum of 6% for one-standard deviation, 12% for two-standard deviations and 18% for three-standard deviations were used.

Matrix effects were expected to impact responses of the internal standards and/or produce inaccurate recovery data for surrogate compounds. Therefore, one QC parameter used in this study was that the response (area counts) of an internal standard distilled from a sample compared to its response distilled from the day's continuing calibration standard. A subset of the Method 8261 internal standards was monitored for consistency as performed in Superfund's Contract Laboratory Program (CLP) methods [10]. The CLP limits on variation in the internal standards (as %) are presented in Table 4. For this study two additional Method 8261 internal standards from the non-purgeable class of analytes were also monitored.

The matrices being analyzed were expected to cause large variations in the monitoring internal standards responses relative to those in calibration. When an internal standard relative response (high or low) corresponds with the occurrences of multiple outlier analytes, it was assumed to affect its class of compounds. The acceptable internal standard ranges found in this study are reported in Table 4. There is a surprising consistency of this study's determined ranges and those used for Superfund's CLP.

The surrogate compounds and their recommended recovery ranges are from Method 8261A and they are listed in Table 5. To simplify the review process and to clarify control limits, the surrogate recoveries were monitored without their associated uncertainties. As with the monitoring of internal standards, it was expected that the study would find a range of recoveries for each surrogate that would reflect that the analyte results would be normally distributed about their true values. The acceptable surrogate recoveries found are reported in Table 5. Again there is a consistency in this study's ranges and that reported for the method.

Acetone and diethyl ether were removed from the initial suite of analytes for this study due to the contribution of interferences throughout the calibration range. A few analytes had interference (or background contamination) at the lowest standard amount (0.02 of upper limit) and that level was not used in the calibration curve for those analytes. This low level interference was found to affect methylene chloride, 2-butanone, acetonitrile, dichlorodifluoromethane, and methyl acetate. Carbon disulfide was not an analyte at the start of the study and so was absent in the studies investigating salt and water volume effects.

It was also observed that the recoveries for analytes (e.g., gases), not bracketed by internal standards in both boiling point and relative volatility, were not reliably characterized. And if these analytes did not have a representative surrogate, outliers would occur that could not be detected by the study QC parameters.

It was found that acetophenone-d_5 and nitrobenzene-d_5 were surrogates only relating to nitrobenzene and acetophenone. Therefore, in this study, these surrogates were only used to monitor these two analytes as a class.

The evaluation of confidence intervals as measurement of analytical error was conducted for analytical results passed their respective quality controls. If the monitoring internal standards or surrogates for a class fell outside the acceptable range, all analytes in the class were not included in the evaluation. Any analyte that had a continuing calibration difference at or above 40% was similarly excluded. A minimum confidence interval of 6% was used for all analytes.

The gases behavior in water was not well characterized by the internal standards or surrogates. An internal standard or surrogate with similar characteristics such as vinyl chloride-d_2 is recommended. Similarly, methylnaphthalene behavior is not well characterized in the water/detergent matrix and additional high-boiling internal standard grouping is needed. The detergent used also chemically reacted with some of the analytes and their results for this matrix were not used. The 1 g oil matrix was removed from this study as almost all results were being qualified and its obvious two-phase appearance.

When the QC parameters were within the acceptable ranges, the frequency confidence intervals included the known values is presented by matrix in Table 6. Combining all the results from the various matrices yielded 11,260 results of which only 1041 were qualified. The frequencies the confidence intervals include the true values were near theoretical for the one, two, and three standard deviation (71.3, 95.0, and 99.2%). In addition, every analyte in the study had frequencies that met Chebyshev's rule.

The QC limits were then applied to the analyses of the LOQ-spiked samples. An additional criterion was that a result was not used when the analyte was also found to be in blanks at ½ the concentration of the LOQ spikes. The frequency these confidence intervals included the true values did not match theoretical prediction as closely as the mid-concentration spikes. This is likely due to an inherent integration error or background contribution at the lower calibration point. It is interesting to note that by raising the minimum one standard deviation confidence intervals to 15%, the confidence intervals included the true values near empirical rule frequencies (Table 6).

More specific information is available as a supplement to this article. Contained in the supplement is a discussion of results by matrix. Average recovery and frequency that each analyte's confidence interval included the true value is also presented for when QC is met or not met. The analytes impacted by continuing calibration limits and minimum confidence intervals are also presented.

Conclusion

The confidence intervals reported with Method 8261 results are a good measure of the analytical error. Implementing quality controls to ensure confidence intervals measure analytical error are generally less strict than quality controls generally required of similar methodology. It would be expected that the Method 8261 approach for determining analytical error could be applied to other protocols as long as all of the properties contributing to experimental errors are measured.

Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded and performed the analytical research described. This manuscript has been subjected to the EPA's review and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 1. Internal Standards used for Method 8261A Quantitation

Range		Grouping	
Type	Values	Internal standards	Value[a]
Relative volatility	0.62 to 3.72	Methyl cyclohexane- d_{14}	.62
		hexafluorobenzene	.86
		ethylbenzene-d_{10}	3.6
		1,4-difluorobenzene	3.83
	3.72 to 6.20	ethylbenzene-d_{10}	3.6
		1,4-difluorobenzene	3.83
		o-xylene-d_{10}	6.14
		chlorobenzene-d_5	6.27
	6.2 to 29.2	*o*-xylene-d_{10}	6.14
		chlorobenzene-d_5	6.27
		1,2-dibromoethane-d_4	26.
		Diethyl ether-d_{10}	32.5
	29.2 to 478	1,2-dibromoethane-d_4	26.
		Diethyl ether-d_{10}	32.5
		tetrahydrofuran-d_8	355
		acetone-d_6	600
	478 to 5800	tetrahydrofuran-d_8	355
		acetone-d_6	600
		1,4-dioxane-d_8	5800
	5800 to 14400	acetone-d_6	600
		1,4-dioxane-d_8	5800
		2-chloroethanol-d_4	13800
		pyridine-d_5	15000
Boiling point	85 to 155 (°C)	pentafluorobenzene	85(°C)
		toluene-d_8	111
		bromobenzene-d_5	155
	155 to 213	bromobenzene-d_5	155
		1,2-dichlorobenzene-d_4	181
		1,2,4-trichlorobenzene-d_3	213
	213 to 241	1,2,4-trichlorobenzene-d_3	213
		napththalene-d_8	217
		1-methylnaphthalene-d_{10}	241

[a] Values are from references 3 and 7.

Table 2. Surrogate Compounds by Class

	Boiling Point (°C)	Relative Volatility[a]
Volatile Class (boiling point less than 159)		
Methylene chloride-d_2	40	11.10
Benzene-d_6	79	3.92
1,2-dichloropropane-d_6	95	11.00
1,1,2-trichloroethane-d_3	112	26.6
4-bromofluorobenzene	152	8.05
Non-Purgeable Class (relative volatility>100)		

Nitromethane-^{13}C	101	510
Ethylacetate-^{13}C	77	150
Pyridine-d_5	115	15000
Semi-Volatile Class (boiling point >= 159		
Decafluorobiphenyl	206	3.03
Nitrobenzene-d_5	210	87.5
Acetophenone-d_5	202	161
Naphthalene-d_8	217	18

[a] Values are from references 3 and 7.

Table 3. List of Analytes

	Relative Volatility[c]	Boiling Point[d]	Calibration Range[a]	Mid-Concentration Spike		LOQ[b]
Compound		°C	ngs	ng	ng/mL[e]	ng/mL
dichlorodifluoromethane	0.07	-30	5 - 500	50	10	1
chloromethane	1.37	-24	5 - 500	50	10	1
vinyl chloride	0.48	-13	5 - 500	50	10	1
bromomethane	1.82	4	5 - 500	50	10	1
chloroethane	1.01	12	5 - 500	50	10	1
trichlorofluoromethane	0.2	24	5 - 500	50	10	1
diethyl ether	34.9	35	10 - 1000	100	20	2
1,1,2-trichloro-1,2,2-trifluoroethane	0.4	48	5 - 500	50	10	1
acetone	600	56	10 - 1000	100	20	2
1,1-dichloroethene	0.63	37	5 - 500	50	10	1
iodomethane	2.29	42	10 - 1000	100	20	2
allylchloride	1.34	45	5 - 500	50	10	1
acetonitrile	545	82	20 - 2000	200	40	4
methyl acetate	222	57	5 - 500	50	10	1
carbon disulfide	0.31	46	5 - 500	50	10	1
methylene chloride	10.1	40	5 - 500	50	10	1
MTBE	33.7	55	5 - 500	50	10	1
acrylonitrile	161	78	10 - 1000	100	20	2
trans-1,2-dichloroethene	2.3	48	5 - 500	50	10	1
1,1-dichloroethane	4.12	57	5 - 500	50	10	1
2,2-dichloropropane	1.37	69	5 - 500	50	10	1
propionitrile	1420	97	10 - 1000	100	20	2
2-butanone	770	80	20 - 2000	200	40	4
cis-1,2-dichloroethene	5.34	60	5 - 500	50	10	1
methacrylonitrile	103	90	10 - 1000	100	20	2
chloroform	6.39	62	5 - 500	50	10	1
bromochloromethane	15.4	68	5 - 500	50	10	1
cyclohexane	0.59	81	5 - 500	50	10	1

1,1,1-trichloroethane	1.31	74	5 - 500	50	10	1
1,1-dichloropropene	0.88	104	5 - 500	50	10	1
carbon tetrachloride	0.64	77	5 - 500	50	10	1
1,2-dichloroethane	18.7	84	5 - 500	50	10	1
benzene	3.55	80	5 - 500	50	10	1
trichloroethene	2.34	87	5 - 500	50	10	1
methyl cyclohexane	0.62	101	5 - 500	50	10	1
1,2-dichloropropane	10.9	96	5 - 500	50	10	1
methylmethacrylate	71.4	101	10 - 1000	100	20	2
dibromomethane	23.9	97	5 - 500	50	10	1
bromodichloromethane	12.3	90	5 - 500	50	10	1
1,4-dioxane	5750	101	50 - 5000	500	100	10
4-methyl-2-pentanone	120	117	20 - 2000	200	40	4
trans-1,3-dichloropropene	14.1	112	25 - 2500	250	50	5
toluene	3.88	111	5 - 500	50	10	1
cis-1,3-dichloropropene	19.6	104	25 - 2500	250	50	5
2-hexanone	131	128	10 - 1000	100	20	2
1,1,2-trichloroethane	26.2	114	5 - 500	50	10	1
1,3-dichloropropane	24.9	120	5 - 500	50	10	1
tetrachloroethene	1.43	121	5 - 500	50	10	1
dibromochloromethane	19.2	120	5 - 500	50	10	1
1,2-dibromoethane	26.7	132	5 - 500	50	10	1
chlorobenzene	6.07	132	5 - 500	50	10	1
1,1,1,2-tetrachloroethane	11.6	131	5 - 500	50	10	1
ethylbenzene	3.6	136	5 - 500	50	10	1
m,p-xylenes	3.91	138	5 - 500	50	10	1
o-xylene	5.54	144	5 - 500	50	10	1
styrene	6.87	145	5 - 500	50	10	1
isopropylbenzene	2.75	152	5 - 500	50	10	1
bromoform	23.4	150	5 - 500	50	10	1
cis-1,4-dichloro-2-butene	33.3	152	20 - 2000	200	40	4
1,1,2,2-tetrachloroethane	30.3	146	5 - 500	50	10	1
1,2,3-trichloropropane	33.6	157	5 - 500	50	10	1
propylbenzene	2.43	159	5 - 500	50	10	1
bromobenzene	7.89	156	5 - 500	50	10	1
trans-1,4-dichloro-2-butene	33.8	156	20 - 2000	200	40	4
1,3,5-trimethylbenzene	3.75	165	5 - 500	50	10	1
2-chlorotoluene	4.04	159	5 - 500	50	10	1
4-chlorotoluene	4.78	162	5 - 500	50	10	1
tert-butylbenzene	2.72	169	5 - 500	50	10	1
sec-butylbenzene	1.91	173	5 - 500	50	10	1
pentachloroethane	13.2	162	5 - 500	50	10	1
1,2,4-trimethylbenzene	4.5	169	5 - 500	50	10	1

p-isopropyltoluene	2.5	183	5 - 500	50	10	1
1,3-dichlorobenzene	5.72	173	5 - 500	50	10	1
1,4-dichlorobenzene	6.14	174	5 - 500	50	10	1
n-butylbenzene	1.88	183	5 - 500	50	10	1
1,2-dichlorobenzene	7.86	180	5 - 500	50	10	1
acetophenone	161	203	10 - 1000	100	20	2
1,2-dibromo-3-chloropropane	38.9	196	5 - 500	50	10	1
nitrobenzene	87.5	211	10 - 1000	100	20	2
1,2,4-trichlorobenzene	7.73	214	5 - 500	50	10	1
hexachlorobutadiene	2.08	215	5 - 500	50	10	1
naphthalene	16.7	218	5 - 500	50	10	1
1,2,3-trichlorobenzene	11.3	218	5 - 500	50	10	1
2-methylnaphthalene	67	245	10 - 1000	100	20	2
1-methylnaphthalene	67	245	10 - 1000	100	20	2

[a] Calibration range for Method 8261 is in units of mass and not concentration.
[b] LOQ is based on 5 mL sample with 100% recoveries. Actual LOQ will vary with recoveries and sample sizes.
[c] Relative volatility value of analytes from references 3 and 7.
[d] Boiling point of analytes in degrees Celsius.
[e] The mid-calibration point expressed as a concentration for 5-mL samples.

Table 4. Experimental Responses of Internal Standards Relative to Daily Standard (by Matrix)

	SOM01[a]	salt	water	glycerin	detergent	All
Volatile Class						
1,4-difluorobenzene	50-200(60-140)[b]	105-156	52-145	96-119	88-116	52-156
chlorobenzene-d_5	50-200(60-140)	85-161	45-147	89-123	79-124	45-161
Volatile and Semivolatile Classes						
1,2-dichlorobenzene-d_4	50-200(60-140)	116-168	33-149	51-124	76-130	33-168
Non-Purgeable Class						
tetrahydrofuran-d_8	NA[c]	77-308	26-200	55-239	45-186	26-308
1,4-dioxane-d_8	NA	100-941	12-160	37-600	47-135	12-941
Semivolatile Class						
Naphthalene-d_8	50-200	110-252	23-200	45-166	61-230	23-252

[a] Range of recoveries expected for internal standards from reference 10.
[b] Values in parenthesis are for trace analyses.
[c] This internal standard not monitored in CLP protocols.

Table 5. Surrogate Range of Acceptable Recoveries Found Experimentally by Matrix

class	surrogates	Method[a]	salt	water	glycerin	detergent	Summary
Volatile	methylenechloride-d_2	75-125	92-117	68-108	84-105	83-111	68-117
	benzene-d_6	75-125	101-109	87-102	94-103	95-104	87-109
	1,2-dichloropropane-d_6	75-125	92-105	87-101	94-103	96-108	87-108
	1,1,2-trichloroethane-d_3	65-135	90-100	92-110	97-109	100-115	90-115
	4-bromofluorobenzene	75-125	96-102	89-102	93-102	99-106	89-106
Non-purgeable	nitromethane-^{13}C	65-135	85-101	72-107	86-104	(69[b])59-111	69-111
	ethyl acetate-^{13}C	65-135	82-96	87-115	95-112	(76[b])63-125	76-125
Semivolatile	decafluorobiphenyl	50-175	64-100	68-133	68-97	89-140	64-140
	nitrobenzene-d_5[c]	35-150	88-139	(70[b])69-114	53-167	97-176 (132[b])	53-176
	acetophenone-d_5[c]	35-150	90-145	(52[b])51-98	44-150	116-235(174[b])	44-181
	naphthalene-d_8	75-125	94-102	86-113	95-107	96-112	86-113

[a] Ranges posted with Method 8261A for water

[b] Surrogate windows narrowed to value in parenthesis to eliminate Chebyshev outliers

[c] These surrogates and their ranges apply to the semivolatile analytes. Narrower limits would apply if they were used for just their analogs.

Table 6. Summary of Results by Matrix

Matrix	Results Obtained[a]	Results that Meet QC Criteria Number(%)[b]	Confidence Intervals[c] (%) 1	2	3	Recovery[d] (%) Avg	dev	Removed analytes
salt water	2460	2418 (98.3)	68.7	94.0	99.3	102.5	11.0	none
water	2340	2229 (95.3)	72.3	96.3	99.3	102.7	11.3	dichlorodifluoromethane,chloromethane, vinyl chloride, and bromomethane
glycerin in water	2490	2465 (99.0)	71.5	95.3	99.2	101.0	11.8	none
detergent in water	2310	2148 (93.0)	72.7	94.3	99.1	100.4	12.7	reactants[e], and methylnaphthalenes
oil with water	1660	932 (56.1)	70.0	94.6	99.1	98.9	14.2	none
all matrices	11260	10219 (90.8)	71.3	95.0	99.2	101.3	11.8	as above by matrix

all at LOQ	5510	4455 (80.8)	50.3	80.1	91.3	104.1	24.4	as above by matrix
all at LOQ	5510	4455 (80.8)	70.1	94.1	99.1	104.1	24.4	as above with 15% minimum relative deviation

[a] The sum of all experimental determinations in the study by matrix.

[b] The sum of all analyte determinations that met criteria with comparison to total results obtained experimentally.

[c] The % frequency that a result and confidence interval include the known value at 1, 2, and 3 standard deviations.

[d] The average recovery of all analytes that meet criteria and one standard deviation.

[e] 1,1,2,2-tetrachloroethane, pentachloroethane, trichloroethene and tetrachloroethene.