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

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This document is a supplement to the article “Evaluation of Analytical Reporting Errors Generated as Described in SW-846 Method 8261A”. Information that was too specific for the article is included here.

Results and Discussion

The frequencies that confidence intervals included the true value were tested by analyte against Chebyshev’s rule. Analytes that did not meet these criteria in a matrix were considered outliers and are listed in Supplement Table 1. The outlier status of some analytes was due to a very small confidence interval or a large difference in the continuing calibration check. These data were used to generate the minimum on standard deviation confidence interval of 6% and continuing calibration check difference of 40%.

A discussion of observations by matrix follows.

Salt water samples

Only the results for four analytes (dichlorofluoromethane, tetrachloroethene, carbon tetrachloride, and cis-1,4-dichlorobutene) were outliers. It was found that dichlorodifluoromethane would not be an outlier if its results (12 of 30) were not included when its continuing calibration standard indicated differences of more than 40% from initial calibration.

The other three compounds were seen to have very conservative confidence intervals and if a minimum confidence interval of 6% was applied, then they were no longer outliers. This suggests that, while periodically the confidence interval in a result may be determined to be quite small, 6% was the minimum experimental error.

The ranges of internal standard relative responses and surrogate recoveries observed in these analyses were taken as acceptable as there was no observed link in their variations to outliers.

Water volume changes

After applying the 6% minimum relative deviation for results and a 40% continuing calibration criterion determined for the salt water matrix, five analytes were outliers (the volatile gases dichlorodifluoromethane, chloromethane, vinyl chloride, and bromomethane, and the semivolatile acetophenone).

The outlier results (results where measured concentrations were more than three confidence intervals distance from the spiked value) that contributed to the five analytes being outliers could not be linked to observed variations in the internal standard relative responses. Also the surrogate recovery data did not appear to be associated with the outlier results for the volatile gases. This indicates that the gases may not be correlated to either the surrogates or the internal standards used in this study and that an additional gas surrogate should be incorporated for monitoring the gas analyte results.

However it was found that by increasing the minimum recovery limit of two surrogates with properties similar to acetophenone (*i.e.*, acetophenone-*d*₅ and nitrobenzene-*d*₅) to 52 and 69% respectively resulted in qualifying those acetophenone results that caused the compound to be an outlier. The remaining acetophenone results met the criteria. Therefore lower recovery limits for acetophenone-*d*₅ and nitrobenzene-*d*₅ were implemented at 52 and 69% respectively. The ranges of internal standard relative responses were taken as acceptable as no outliers were linked to them.

Glycerin

After raising the minimum confidence interval to 6% of a result and implementing the 40% maximum continuing calibration difference, only vinyl chloride remained an outlier. Vinyl chloride outlier results were not linked to any of the internal standard or surrogate variations. Vinyl chloride would not have been an outlier if the minimum confidence interval were 7%. However without other indications that 7% should be a minimum confidence interval, this outlier was included with results that met QC.

The ranges of internal standard relative responses were all taken as acceptable as there was no indication that linked any of them to the outlier.

Detergent

It was observed that a dehydrohalogenation of the analytes 1,1,2,2-tetrachloroethane and pentachloroethane to yield trichloroethene and tetrachloroethene respectively, occurred in the presence of the detergent used to modify the water matrix. Therefore, these four analytes were removed from the analyte list for the analyses of the water/detergent matrix.

After applying the 6% minimum confidence interval for results and a maximum continuing calibration criterion of 40%, there were only four outliers, methyl acetate, acetophenone, 1-methylnaphthalene and 2-methylnaphthalene.

Nitromethane-¹³C and ethyl acetate-¹³C, were surrogates for the non-purgeable class of analytes of which methyl acetate was associated. The recovery ranges of nitromethane-¹³C and ethyl acetate-¹³C observed for analyses of detergent samples were 59-111% and 63-125 % respectively. Raising the lower limit of the surrogate nitromethane-¹³C to 69% and ethyl acetate-¹³C to 76% qualified the results that caused methyl acetate to be an outlier.

The surrogates acetophenone-*d*₅ and nitrobenzene-*d*₅ were observed to be acceptable surrogates for the analyte acetophenone during the analyses of various volumes of water. The range of the surrogate recoveries in the water/detergent matrix were 116-235% and 97-176% for acetophenone-*d*₅ and nitrobenzene-*d*₅ respectively. By making the upper recovery limit of 174% for acetophenone-*d*₅ and 132% for nitrobenzene-*d*₅, the outlier data was qualified and the remaining acetophenone results met criteria.

The methylnaphthalene outliers could not be qualified by a low or high recovery of the semivolatile surrogates without unnecessarily qualifying all of the semivolatile analyte results. Therefore it would be necessary to add a methylnaphthalene surrogate specific to the methylnaphthalenes for the purpose of qualifying their results. For the purpose of evaluating the rest of the analytes in the semivolatile class, the methylnaphthalene results were not used.

Oil

The oil matrix was by far the most severe in inhibiting recovery of analytes, and there was an obvious two-phase makeup of the samples. The starting point for the evaluation was to apply the limits of internal standard and surrogate recoveries gathered for the previous matrices and apply to the oil matrix data.

There was so little QC limits met for the 1g oil in water matrix that the data from the analyses of this mixture were not used. The monitoring internal standard relative response in all of the remaining oil-water samples fell below the minimum found for the other matrices. Of the remaining analytes (volatile and non-purgeable classes) there were no outliers.

Analytes

The combined results by analyte are presented in Supplement Table 2. The frequency that the confidence intervals includes the true value meet Chebyshev's rule for each analyte when the QC limits in the study were met. Many analytes behaved well even when QC limits were not met. The determined results compared to true values are also reported by analyte in Table2.

Supplemental Table 1. Outlier Analytes and Quality Control Limits Needed to Qualify Outlier Results

Outlier Analytes	Added Ingredients									
	salt		water		glycerin		detergent		oil	
	min c.i. ^a	Max CC ^b	min c.i.	Max CC	min c.i.	Max CC	min c.i.	Max CC	min c.i.	Max CC
dichlorodifluoromethane	20	40	27	41					18	60
chloromethane			22	15					25	44
vinyl chloride			19	<10 ^c	7	<10			10	19
bromomethane			11	<10						
trichlorofluoromethane					5	<10	6	<10		
propionitrile			11	40						
methyl acetate							17	<10		
carbon disulfide							6	<10		
1,1,1-trichloroethane			5	<10						
carbon tetrachloride	6	<10	6	<10						
bromodichloromethane									9	<10
4-methyl-2-pentanone									15	16
2-hexanone									16	<10
dibromochloromethane									9	<10
tetrachloroethene	2	19								
1,1,1,2-tetrachloroethane									9	<10
<i>cis</i> -1,4-dichloro-2-butene	6	13								<10
1,1,2,2-tetrachloroethane									15	<10
1,3,5-trimethylbenzene									7	<10
2-chlorotoluene									8	<10
<i>tert</i> -butylbenzene									9	<10
pentachloroethane									13	<10
nitrobenzene									55	10
acetophenone			16	34			21	<10		
2-methylnaphthalene							19	14	23	24
1-methylnaphthalene									24	<10

^a Minimum confidence interval value that will eliminate an outlier analyte.

^b The difference that a continuing calibration varies from the initial calibration that results in a qualification of an analyte result and eliminate the analyte from outlier status.

^c If the maximum difference between a continuing calibrations the initial calibration fell below 10% a qualification of outlier results by this parameter was not desirable.

Supplement Table 2. Summary of Results by Analyte

Compound	Total Results	Results ^b	Results for when QC Limits met					Results for when QC Limits not met			
			Recovery (%)		Confidence Intervals ^a (%)			Recovery (%)		Results Affected	
			Average	Dev ^c	1	2	3	Average	Dev		
dichlorodifluoromethane	110	74	73.3	20.7	47.3	82.4	94.6	39.3	15.4	36	
chloromethane	110	92	84.5	15.4	62.0	98.9	100.0	52.2	14.7	18	
vinylchloride	110	105	91.9	12.1	41.9	67.6	91.4	60.1	11.2	5	
bromomethane	110	105	87.2	10.5	49.5	77.1	93.3	79.8	10.5	5	
chloroethane	140	95	88.6	21.7	71.6	90.5	98.9	90.2	18.5	45	
trichlorofluoromethane	140	135	94.3	7.9	52.6	84.4	97.8	93.7	8.2	5	
1,1,2-trichloro-1,2,2-trifluoroethane	140	135	103.3	7.3	76.3	95.6	100.0	94.1	7.7	5	
1,1-dichloroethene	140	129	101.3	11.1	62.8	95.3	100.0	100.0	9.7	11	
iodomethane	140	135	99.9	11.4	63.0	88.9	99.3	100.5	8.9	5	
allylchloride	140	129	103.2	10.8	83.7	98.4	100.0	113.3	14.5	11	
acetonitrile	140	114	94.8	22.7	67.5	86.8	96.5	87.1	17.3	26	
methyl acetate	140	131	80.0	11.6	67.9	91.6	97.7	76.6	2.9	9	
carbon disulfide	80	75	92.7	8.0	44.0	70.7	97.3	104.8	32.6	5	
methylene chloride	140	135	93.9	8.8	69.6	97.8	99.3	86.6	7.0	5	
MTBE	140	135	100.3	6.0	89.6	100.0	100.0	98.0	10.0	5	
acrylonitrile	140	131	103.1	14.1	87.0	99.2	100.0	104.7	11.2	9	
<i>trans</i> -1,2-dichloroethene	140	135	101.4	6.2	83.0	100.0	100.0	105.3	9.8	5	
1,1-dichloroethane	140	135	103.3	6.0	69.6	97.0	100.0	96.9	5.5	5	
2,2-dichloropropane	140	135	98.6	5.8	86.7	97.8	100.0	104.8	7.3	5	
propionitrile	140	125	105.7	22.5	57.6	84.0	93.6	111.3	28.7	15	
2-butanone	140	105	80.7	11.5	47.6	97.1	99.0	76.3	6.8	35	
<i>cis</i> -1,2-dichloroethene	140	135	105.4	6.3	60.7	88.9	98.5	106.4	8.8	5	
methacrylonitrile	140	131	98.6	9.8	77.1	98.5	100.0	97.2	5.1	9	
chloroform	140	135	99.3	7.8	68.1	96.3	100.0	95.1	6.1	5	
bromochloromethane	140	129	106.3	7.9	58.1	93.0	100.0	107.0	7.6	11	
cyclohexane	140	135	105.1	6.2	60.0	94.1	100.0	108.2	10.0	5	

1,1,1-trichloroethane	140	135	105.1	6.8	62.2	91.9	97.8	109.5	10.9	5
1,1-dichloropropene	140	135	105.9	7.2	65.9	97.8	100.0	103.7	10.0	5
carbon_tetrachloride	140	135	106.4	8.1	53.3	85.2	97.0	114.7	9.4	5
1,2-dichloroethane	140	135	100.6	6.1	88.9	100.0	100.0	112.6	11.1	5
benzene	140	135	98.3	6.8	71.9	97.8	100.0	98.2	8.9	5
trichloroethene	110	105	104.0	5.8	67.6	98.1	100.0	104.7	4.2	5
methyl_cyclohexane	140	135	110.1	7.6	44.4	77.0	95.6	105.6	6.3	5
1,2-dichloropropane	140	135	102.8	6.5	77.0	100.0	100.0	96.0	5.2	5
methylmethacrylate	140	135	101.0	9.2	76.3	98.5	99.3	106.1	3.9	5
dibromomethane	140	135	105.3	9.0	75.6	99.3	100.0	112.6	12.6	5
bromodichloromethane	140	135	105.8	8.5	65.9	96.3	99.3	98.5	12.9	5
1,4-dioxane	140	131	98.6	5.5	94.7	100.0	100.0	97.2	3.8	9
4-methyl-2-pentanone	140	131	102.6	14.1	66.4	94.7	100.0	109.2	9.8	9
<i>trans</i> -1,3-dichloropropene	140	135	102.2	5.0	85.9	99.3	100.0	108.0	7.3	5
toluene	140	135	95.9	7.7	86.7	100.0	100.0	101.6	7.9	5
<i>cis</i> -1,3-dichloropropene	140	135	104.5	5.7	78.5	98.5	100.0	115.2	13.4	5
2-hexanone	140	131	111.6	12.7	59.5	95.4	100.0	118.3	6.7	9
1,1,2-trichloroethane	140	135	106.1	6.7	87.4	98.5	100.0	120.3	15.2	5
1,3-dichloropropane	140	135	106.3	5.4	79.3	100.0	100.0	110.9	8.7	5
tetrachloroethene	110	105	108.5	7.5	56.2	94.3	100.0	105.6	5.3	5
dibromochloromethane	140	135	106.3	8.9	78.5	100.0	100.0	104.5	10.6	5
1,2-dibromoethane	140	135	110.6	6.9	69.6	98.5	100.0	119.9	7.3	5
chlorobenzene	140	135	100.9	5.7	78.5	98.5	100.0	99.7	6.1	5
1,1,1,2-tetrachloroethane	140	135	102.3	6.8	76.3	96.3	100.0	97.5	8.7	5
ethylbenzene	140	135	102.1	5.7	72.6	97.0	100.0	99.7	5.2	5
<i>m,p</i> -xylenes	140	135	101.0	6.8	72.6	96.3	100.0	100.2	6.8	5
<i>o</i> -xylene	140	135	99.9	5.9	78.5	96.3	99.3	94.8	7.7	5
styrene	140	135	100.2	6.3	83.7	99.3	100.0	92.9	4.9	5

isopropylbenzene	140	135	103.7	8.1	50.4	93.3	98.5	92.1	7.7	5
bromoform	140	135	105.2	8.7	55.6	97.8	100.0	106.6	6.9	5
<i>cis</i> -1,4-dichloro-2-butene	140	135	111.5	10.0	69.6	89.6	97.0	114.4	4.9	5
1,1,2,2-tetrachloroethane	110	105	104.3	11.4	57.1	90.5	99.0	102.0	9.0	5
1,2,3-trichloropropane	140	135	109.3	7.2	73.3	100.0	100.0	105.7	5.5	5
propylbenzene	140	119	105.1	5.3	67.2	96.6	100.0	93.1	8.0	21
bromobenzene	140	135	101.1	7.1	77.0	98.5	100.0	91.5	9.2	5
<i>trans</i> -1,4-dichloro-2-butene	140	129	110.1	8.1	81.4	100.0	100.0	115.4	8.1	11
1,3,5-trimethylbenzene	140	119	99.8	5.6	85.7	100.0	100.0	87.8	8.9	21
2-chlorotoluene	140	119	101.8	4.6	85.7	99.2	100.0	87.1	8.4	21
4-chlorotoluene	140	119	103.4	6.1	69.7	98.3	100.0	94.0	7.9	21
<i>tert</i> -butylbenzene	140	119	105.2	7.5	57.1	89.9	100.0	87.3	9.1	21
<i>sec</i> -butylbenzene	140	119	101.6	12.4	69.7	99.2	100.0	94.4	9.3	21
pentachloroethane	110	89	98.2	11.5	85.4	96.6	100.0	91.1	11.6	21
1,2,4-trimethylbenzene	140	119	94.2	9.8	94.1	100.0	100.0	87.1	9.7	21
<i>p</i> -isopropyltoluene	140	119	99.7	10.0	71.4	95.8	100.0	99.8	9.9	21
1,3-dichlorobenzene	140	119	98.5	6.0	84.9	100.0	100.0	88.2	9.0	21
1,4-dichlorobenzene	140	119	100.5	6.3	94.1	99.2	100.0	87.8	8.5	21
<i>n</i> -butylbenzene	140	119	102.4	9.8	64.7	93.3	100.0	91.7	10.2	21
1,2-dichlorobenzene	140	119	99.3	6.2	91.6	100.0	100.0	91.1	9.5	21
acetophenone	140	81	93.8	29.5	38.3	72.8	92.6	161.0	55.3	59
1,2-dibromo-3-chloropropane	140	119	111.0	9.1	71.4	98.3	100.0	125.8	12.7	21
nitrobenzene	140	78	106.2	17.7	75.6	94.9	98.7	183.6	87.4	62
1,2,4-trichlorobenzene	140	119	98.4	14.1	74.8	96.6	100.0	83.4	10.4	21
hexachlorobutadiene	140	119	91.0	12.0	53.8	88.2	97.5	87.8	10.2	21
naphthalene	140	119	103.3	8.1	94.1	100.0	100.0	110.5	14.7	21
1,2,3-trichlorobenzene	140	119	101.6	8.6	76.5	95.8	100.0	83.6	23.8	21
2-methylnaphthalene	110	88	106.7	12.7	65.9	95.5	100.0	82.5	25.4	22

1-methylnaphthalene	110	88	104.7	11.3	76.1	96.6	98.9	78.8	25.1	22
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^a The frequency that the result and confidence interval include the known value for 1, 2, and 3 standard deviations.

^b The number of analyses that were not qualified

^c One standard deviation.