ASSESSMENT OF SULFOLANE SPLIT-SAMPLE DATA

ASSOCIATED WITH THE FLINT HILLS RESOURCES FUEL REFINERY

IN FAIRBANKS, ALASKA

December 9, 2009

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Executive Summary

Environmental Standards, Inc. (Environmental Standards) performed a data quality assessment of laboratory data for samples that were split (as distinct samples) and submitted to two separate laboratories for the analysis of sulfolane. The two accredited commercial laboratories that received the split samples associated with the Flint Hills Resources Fuel Refinery in Fairbanks, Alaska, were SGS Environmental Services, Inc. (SGS) of Anchorage, Alaska, and Pace Analytical Services, Inc. (Pace) of Minneapolis, Minnesota.

Recently, disparity has been noted for the split-sample data reported by the two contract laboratories. In particular, for some split samples, SGS reported that sulfolane was not present above a particular concentration (referred to as a "Reporting Limit") while Pace reported detecting sulfolane within a factor of two-times the SGS reporting limit. For example, consider the following split sample:

Sample	SGS	Pace
Well-2	< 10 ppb	24 ppb

Because of this apparent disparity, Environmental Standards was retained to investigate and to determine possible reasons for the differences in the reported split-sample results between the two laboratories.

After critically evaluating the methodology, calibrations, quality control, and raw analytical data from both laboratories, Environmental Standards reached two conclusions.

- SGS is capable of detecting and reporting sulfolane below its stated Reporting Limit.
- Some of the instrument calibration data used by Pace yield an inaccurate bias for low-level results (*e.g.,* 5 - 50 ppb). For sulfolane results above 80 ppb, Pace's calibration bias diminishes substantially and good agreement can be expected between the SGS reported and Pace reported split-sample results.

With regard to the first conclusion, the raw data provided by SGS enables Environmental Standards to observe confident sulfolane detections below the SGS Reporting Limit.

With regard to second conclusion, the raw data provided by Pace enabled Environmental Standards to requantitate sulfolane results using a correct calibration model.

These two conclusions explain the apparent disparity between SGS and Pace and provide an avenue for Pace to correct and reissue its sulfolane analytical results. If the project requires sulfolane sensitivity below 10 ppb, SGS can be requested to reissue its data to report levels less than its Reporting Limit. If both laboratories reissue their data based on the conclusions, there will likely be good agreement between the sulfolane data for past and future groundwater split samples.

Detailed Discussion

Environmental Standards, Inc. (Environmental Standards) was retained to assess the quality of sulfolane analytical data in various groundwater split samples. The split-sample data were generated by SGS Environmental Services, Inc. (SGS) of Anchorage, Alaska, and by Pace Analytical Services, Inc. (Pace) of Minneapolis, Minnesota, in association with the Flint Hills Resources Fuel Refinery in Fairbanks, Alaska. The purpose of this assessment was to investigate and, if possible, explain the reasons for differences in the reported sample results between the two laboratories.

Environmental Standards' assessment included a critical assessment of each laboratory data set with a specific focus to identify and explain the differences in the reported results. The overall assessment was divided into three parts. First, a basic review of each laboratory's reported data packages and supporting method performance data was conducted. Second, both laboratories analytical techniques were reviewed and compared through a formal comparison of the standard operating procedures (SOPs). Finally, a "root cause" evaluation for any data or reporting anomalies that suggested a reason for the disparate results was performed.

Initially, both laboratories were requested to provide their preparation and analytical SOPs and complete Level IV (inclusive of raw data) analytical data packages, specifically for the split samples in question. Subsequently, additional information, including the method detection limit (MDL) studies, the initial method validation precision and accuracy information, and analyst initial demonstration of competency (IDC), was requested from each laboratory.

Data Package Observations

The Level IV laboratory data deliverables provided were sufficient to support a thorough evaluation of the sulfolane analyses. Fourteen samples (as well as associated quality control [QC] samples) included in sample delivery groups (SDGs) 1095969 (collected on 10/9/09), 1095975 (collected on 10/12/09), and 1096920 (collected on 11/5/09) were provided by SGS. Fifteen samples (as well as associated QC samples) included in SDGs 10117032 (collected on 11/13/09), 10117146 (collected on 11/14/09), and 10117323 (collected on 11/17/09) were provided by Pace. Unfortunately, the sample sets provided by each laboratory were exclusive and data for a common sample from both laboratories was not provided at the time of this assessment; however, this limitation did not hinder the identification of the cause of the split-sample disparity.

Method Detection Limit Studies and Precision and Accuracy Data

Both laboratories provided an acceptable method detection limit (MDL) study and used a reporting limit of 10-ppb for the sulfolane analyses. Surrogate recoveries for all analyses were within acceptance limits and the laboratory blank analyses were free of contamination. Laboratory control sample (LCS) analyses were acceptable in all cases and all internal standard responses met criteria. Pace performed matrix spike/matrix spike duplicate (MS/MSD) analyses on one project sample in each SDG and the recoveries and precision were within acceptance limits. SGS did not perform MS/MSD analyses. The sulfolane calibrations performed by the laboratories met method acceptance criteria; however, the calibration model employed by Pace appears to be biased for results reported at the low end of the calibration range. A detailed evaluation of the calibrations is provided below.

Comparison of Standard Operating Procedures

The SOPs for the two laboratories were found to be very different, but there were no fundamental problems observed with the preparatory and analytical methods selected. A comprehensive summary of the comparison is provided on the Attachment. Note that additional SOPs were included in the comparison after the initial scope-of-work was defined.

Root Cause Evaluation

Part 1 - Sulfolane Detections Below the Quantitation Limit

Evaluation of the SGS raw data revealed that when SGS reported "non-detected" values for Sulfolane as "ND < 10 ppb" (where 10 ppb was the reporting limit), there were, in fact, positive results for Sulfolane in most cases *below* the reporting limit *but* above the SGS MDL. Examples of this scenario are summarized on Table 1; the actual value from the instrument quantitation report is presented in parenthesis. The value in these cases was below the reporting limit and was reported as non-detected. Additionally, these values are at or near the MDL, and therefore, may be expected to vary widely in accuracy and are primarily of value as a qualitative determination of presence at low concentration levels.

Table 1
Summary of Select Reported Versus Observed Sulfolane Values

Site	SGS Sulfolane (Reported/ Observed) Value	PACE Sulfolane Reported Value	Quantitation Limit	Units
Well-1	ND (1.12)*	ND	10	ppb
Well-2	ND (5.61)	23.8**	10	ppb
Effluent	ND (2.7)*	20.3**	10	ppb

* These values were detected below the MDL of 3.1 ppb. Although technically not-detected, the instrument raw data and mass spectra do indicate that the compound may, in fact, be present and that the actual MDL may be lower.

** Note that the data for the two Pace values reported herein for comparison were not available for review; however, values at comparable levels were reviewed and are discussed below.

Part 2 - Instrument Calibrations

Both laboratories used linear regression calibration curves that are technically consistent with the reference method (SW-846 Method 8270C) that each laboratory utilized. The basic acceptance criterion for the evaluation of a linear regression is a correlation coefficient (r^2) > 0.99; the correlation coefficient reported by each laboratory is within this criterion. Linear regression curves, however, do have limitations. One such example is that the "weighting" (or importance) of individual standard points within a linear regression is proportional to the concentration of the standards; therefore, a 20-ppm sulfolane standard is 80-times more important in contributing to a favorable correlation coefficient than a 0.25-ppm sulfolane standard. There are ways to correct for this, by "weighting" the curve, but this procedure is not normally employed by most laboratories unless required for a particular reason of compliance. As a result, an unweighted curve may have significant error at the lower concentration range. In the most recent versions of SW-846 (*e.g.*, Methods 8000C), the US EPA has added additional criteria to account for this periodically occurring problem. In more recent methods, laboratories

are required to evaluate each calibration point within a regression curve and to ensure that each calibration point is within 20% of its nominal value when calculated against the curve.

Using this assessment criterion to evaluate both laboratory curves revealed issues relevant to this data comparison. In the SGS calibration curve, each calibration point was quantitated to be within 20% of its nominal value. For the Pace calibration curve, the middle calibration points (*viz*., Level 3 through 6) are well within this criterion, but the level 2 calibration point is more than 20% higher than its nominal value and the level 1 calibration point is more than *200%* of its nominal value. This is indicative of a very poor fit for the curve at the low concentration range and indicates that all values below 100-ppb are biased high estimates.

It is possible for Pace to recalculate the data using an alternative curve technique, but it is not practical for Environmental Standards to review these data without access to the electronic raw data. In order to calculate estimated values for the Pace analytical results within the affected range of the curve, several low-level samples were recalculated using alternative quantitation techniques. For comparison, the calculation was performed using the nearest calibration standard (the 40-ppb standard) and an average response factor for the curve. These results are presented on Table 2.

Table 2
A Comparison of Pace and SGS Sulfolane Results in Select Samples
After Requantitation of Pace Results

Sample Point	SGS Reported Result	Pace Reported Result	Pace Result (Recalculated from 40-ppb Standard)	Pace Result (Recalculated using Average Response Factor
2600 Roseanne Ct.	ND (<10 ppb)	23.1 ppb	6.4 ppb	6.6
1489-111409-159	ND (<10 ppb)	20.4 ppb	3.2 ppb	3.2
1489-111409-155	31.6 ppb	45.5 ppb	25.1	25.6

These estimated recalculated values for the Pace low-level results are much more comparable to the corresponding SGS data and indicate a systematic high bias in the results below the 100-ppb standard using the regression curve. It is important to note that as the concentration of sulfolane increases in samples above approximately 80 ppb, the calibration bias diminishes substantially and good agreement would be expected between SGS and Pace results (all other factors being equal)

Conclusion

Critical assessment of data provided by SGS and Pace revealed two critical factors that caused the disparate results reported for sulfolane by the two laboratories. First, SGS did not report results detected below the quantitation limit but above the MDL. Secondly, Pace did not employ a “best fit” curve, which should limit error throughout the calibration range to ≤ 20%. Corrections to the data relative to these two factors for a limited number of samples strongly suggest that the data are highly comparable when these two factors are corrected.

ATTACHMENT

SOP Comparison for the Analysis of Sulfolane (Pace Minneapolis vs. SGS Alaska)

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
SOP					
Format	Analyte Specific SOP	Analyte Specific Report	Analyte Specific SOP	Generic SOP that is being used for Sulfolane	The performance characteristics of Sulfolane are sufficiently unique that a customized approach would normally be favored.
Clarity	Appropriately Clear	Narrative focuses on selected details of interest	Appropriately Clear	Unclear whether sample is prepared by SW-846 Method 8270 preparation or by PAH SIM preparation. Analytical SOP indicates full-scan GC/MS analysis.	No Comment
SAMPLE HANDLING					
Sample Container	40-mL amber volatile vial	Matrix = plant tissue; sample preparation and handling not comparable	40-mL volatile vial, tint not specified	1-liter sample in amber glass bottleware	No Comment

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
Sample Preservation	Sample is stored at 4 ± 2°C	NA	Store samples at > 0°C but < 6°C from collection to analysis	Sample is stored at 4 ± 2°C if handled as a Method 8270 sample; sample is neutralized and stored at 4 ± 2°C if handled as a PAH SIM sample	The behavior of sulfolane at lower temperatures is not certain and is an issue of concern. It is expected that sulfolane remains in solution due to its high solubility in water; however, the melting point (aka, freezing point) is 27.5°C; therefore, it may have performance related issues in cold solutions. For example, the laboratories do not indicate whether they refrigerate or freeze the extracts and standards. At a minimum, ensuring that samples and standards are at room temperature at the time of preparation and analysis is a concern.
Holding time	7 days to extraction and 40 days to analysis	NA	7 days to extraction and 40 days to analysis	7 days to extraction and 40 days to analysis	No Comment

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
SAMPLE PREPARATION					
Apparatus and Technology	Liquid-Liquid Vortex in 100-mL screw top vial	NA	Liquid-Liquid Shake-out (LLS) in 40-mL volatile vial	Non-Standard Liquid-Liquid Extractor (LLE) for a non- standard period of time (< 4 hours).	Normally, LLE is the superior technique, but due to the abbreviated extraction by SGS, the LLS may be the equivalent extraction method. The laboratory method performance data indicates that both approaches perform reasonably well.
Sample Volume and Bottle Rinse	10-mL aliquot taken from 40-mL vial	1 mL	25-mL aliquot taken from 40-mL vial	Assumed to be 1000 mL, from 1000-mL bottle based on SOP.	Due to the high solubility of sulfolane, not rinsing the bottle should not be a problem; however, as noted previously, the temperature may be an issue. It is not known at what temperature the sulfolane will begin to fall out of solution.
Extraction Solvent	Toluene	Toluene	Methylene Chloride	Methylene Chloride	As noted above the method performance data generally indicate that both the toluene extraction and the methylene chloride extraction perform adequately.

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
Extraction Solvent Volume	3 x 5 mL	3 x 5 mL	3 × 10 mL	250 mL	Each of these approaches have reasonable solvent to sample ratios. However, the actual solvent to sample ratio in the extraction chamber for the SGS method is not indicated in the SOP.
Extraction Time	3 x 1 minute with 10 minute settling time	3 x 1 minute	3 × 2 minutes	≤ 4.0 hours	The SGS extraction time for a continuous liquid-liquid extractor is only a fraction of the amount of time specified in SW-846 Method 3520. The concern is whether this procedure has been adequately evaluated for poor performers such as sulfolane. Precision and accuracy data indicate that both extractions perform acceptably.
pH conditions	Sample extracted as received	NA	Sample extracted as received	HCL is used and not H_2SO_4 as specified in Method 8270: 2 ½ hours at pH < 2 and then at least 1 ½ hours at pH > 11 with excess acid and base added	Precision and accuracy data indicate that both extractions perform acceptably.
Extract Dried	No	No	Yes	Yes	It is not clear in the SOPs that the LCS is dried in the same manner as the samples (may be assumed to be the case).

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
Final Extract Volume before Concentration	15 mL	15 mL	30 mL	It is not clear how much solvent is actually recovered from the extractor, but will be ≤ 250mL	Not believed to be a significant difference
Concentrator Equipment	Vortex + N-Evap	Vortex + N-Evap	K-D ball column + N-Evap	Turbo Vap II	Not believed to be a significant difference
Concentration	N-Evap only to 1 mL	N-Evap only to 1 mL	KD to ~ 5 mL Nitrogen BD to < 1 mL	Turbo Vap only to < 1 mL	Not believed to be a significant difference
Final Volume	1 mL	1 mL	1 mL	1 mL	No Difference
Quality Control					
Instrument Tune	PFTBA and periodic BFB Tune No criteria indicated	PFTBA Only	DFTPP Run including breakdown and tailing, but not held to criteria. Used for Qualitative review only.	DFTPP Beginning of each 12 hours - standard SW-846 criterion	Not believed to be a significant difference
Surrogate	There is no mention of a surrogate, but it may be assumed that when isotope dilution is performed, the surrogate would not be necessary and when external calibration is performed, the sulfolane-d_8 could be run and reported as a surrogate.	Not discussed	2-fluorobiphenyl at 120 ppb	Normal Method 8270 acid and base surrogates at 200 ppb for acids and at 100 ppb for bases; limits not defined in SOP	Neither laboratory has included a surrogate that would be considered “representative” of the performance of sulfolane; therefore, favorable surrogate performance does not necessarily indicate the absence of performance issues.
Method Blank	1 every batch up to 20 samples < RL or 10 ppb	Not discussed	1 every batch up to 20 samples < RL or 10 ppb	1 every batch up to 20 samples < RL or 5 ppb	Not believed to be a significant difference.

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
LCS	1 every batch up to 20 samples. Evaluated to in-house limits	Not discussed	1 every batch up to 20 samples Volume equal to samples extracted with Sulfolane spike at 200 ppb.	1 every batch up to 20 samples Volume equal to samples extracted with Sulfolane spike at 100 ppb	The quality control data from the data packages indicates that both the PACE and the SGS methods perform acceptably at the levels evaluated.
MS/MSD	1 every batch up to 20 samples. Evaluated to in-house limits	Not discussed	(MS/MSD optional); limits not defined in SOP	MS/MSD only performed based on client request. RPD = 20% for waters; other limits not defined in SOP	The quality control data from the data packages indicates that both the PACE and the SGS methods perform acceptably at the levels evaluated.
Duplicate	Indicates a sample duplicate to be run every 20 samples. RPD should be ≤ 25% (check for error and flag)	Performs analytical duplicates	Only duplicate performed would be a LCSD, if performed.	Only duplicate performed would be a LCSD, if performed.	Neither PACE or SGS perform sample duplicates.
Internal Standard Concentration	Recommends Sulfolane-d_8 at 200 ppb on instrument		10-µL spike for 2.5 ppm	50 ppm	Neither laboratory uses an internal standard that would be considered "representative" of the performance of sulfolane.
Internal Standards	Indicates using either external standard or Sulfolane-d_8 as an internal standard spike before extraction (isotope dilution)		Internal Standard is naphthalene-d_8. SOP language indicates that each CCV is compared to the last CCV; however this may be improperly phrased. ± 30 sec; -50% to +100%.	Samples compared to CCV and CCV compared to ICAL. ± 30 sec for samples to CCV; -50% to +100% for sample and CCV comparisons.	Because sulfolane is markedly different from the internal standards, a favorable internal standard performance does not necessarily indicate the absence of performance issues.

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
Equipment Specifications					
Injection volume	1 µL Inject splitless for 1 minute		Not indicated	Not indicated	Not believed to be a significant issue
Instrument	6890/5973 with 7683 auto injector	5890/5970 with 7673 auto injector	6890/5973 with 7683 auto injector	5890/5971-3 with 7673 auto injector	Not believed to be a significant issue
Instrument settings	80°C for 2 min 10°C /min to 160°C 20°C /min to 280°C Hold for 5 min (~ 21 minutes)	80°C for 2 min 10°C /min to 160°C 20°C /min to 280°C Hold for 5 min (~ 21 minutes)	Quantitative and Qualitative ions are provided as in GC program with overall time of ~ 16 minutes	Instrument Program and settings not discussed. Primary and secondary ions not provided.	Not believed to be a significant issue
Column	RTX-5 30M x 0.25 mm with .25-µm film	DB-5MS 25M x 0.25 mm with .25-µm film	DB-5 30M × .25mm with .5-µm film	RTX-5 30M x 0.25 mm with 1-µm film	Not believed to be a significant issue
Masses Monitored	41 QI, 56, 120	41 QI, 56, 120	41 QI, 55, 56		Pace does evaluates two qualitative ions which is good, but they have left out the molecular ion which is **not** recommended.
Initial Calibration					
Initial Calibration Curve	0.020 ppm to 0.5 ppm	0.15 ppm to 4 ppm	6 levels - 0.25 ppm to 20 ppm	8 ppm - 5 ppm to 160 ppm with a calibration blank included in the curve	Not believed to be a significant difference
Reporting Limit based on SOP	10 ppb	Not discussed	10 ppb	5 ppb	Not believed to be a significant difference

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
Initial Calibration Criterion	Linear regression with r ≥ 0.990	Employed Linear Regression	%RSD must be ≤ 15% for each compound or a different curve fit must be utilized. The correlation coefficient must be ≥ 0.995 if a linear regression is used. The COD must be ≥ 0.990 if a quadratic curve is used with a minimum of 6 levels.	%RSD ≤ 20% for each compound or a different curve fit must be utilized. The correlation coefficient must be ≥ 0.995 if a linear regression is used. The r^2 must be ≥ 0.990 if a quadratic curve is used with a minimum of 6 levels. Curves not forced through origin	PACE standard criterion is moderately tighter
Second Source	Yes – If the acceptance criteria are not met (± 25%), the instrument must be recalibrated.	Not Discussed	Yes – If the acceptance criteria are not met (± 10%), the instrument must be recalibrated.	Yes – If the acceptance criteria are not met (± 25%), the instrument must be recalibrated.	PACE standard criterion is moderately tighter
Minimum RRF	No		No	No	Not believed to be a significant difference; however, this should be looked at in the data review to see if there are reasonable responses.

TOPIC	ADEC	HEADLEY	PACE	SGS	Comments
Continuing Calibration Verification (CCV)	0.2 ppm Before analysis, every (10) or (20) injections and at end of sequence %Difference must be ≤ 20% Note: There is an inconsistent reference for the CCV in section 9.4.1 it indicates a CCV should be performed every 10 injections and in section 11 and in table 1 it indicates every 20 injections.	Not Discussed	5 ppm Run every 12 hours; %Difference must be ≤ 20%	50 ppm Run every 12 hours; %Difference must be ≤ 20%	PACE standard concentration is at lower level than SGS, but has comparable reporting limits when the sample preparation factor differences are added.
Method Performance					
MDL & IDOC	Indicates that individual IDOCs are required for unsupervised analysis	Not Discussed	Laboratory should have MDL and IDOC available.	IDOC should be ± 30%. Laboratory should have MDL and instrument-specific data.	The method performance data reviewed as part of this evaluation indicates that both the SGS and the PACE methods perform acceptably.
Extract Handling and Dilutions					
Addition of IS and dilutions	Not Discussed	Not Discussed	Whole extract is spiked with internal standard. Dilutions must be fortified with additional internal and reanalyzed.	Whole extract is spiked with internal standard. Dilutions must be fortified with additional internal and reanalyzed.	If any reanalysis or dilution is performed, requesting and evaluating both sets of data would be appropriate.