

# STATE OF ALASKA

## DEPARTMENT OF ENVIRONMENTAL CONSERVATION DIVISION OF SPILL PREVENTION AND RESPONSE CONTAMINATED SITES PROGRAM

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January 21, 2010

Flint Hills Resources Alaska LLC  
Attn: Elizabeth Page  
1100 H&H Lane  
North Pole, Alaska 99705

Re: Laboratory Standard Operating Procedures for Analysis of Sulfolane in Water for the Flint Hills Resources North Pole Refinery, North Pole Alaska

Dear Ms. Page:

As you are aware, members of the Technical Project Team (TPT) for the North Pole Refinery Contaminated Sites Investigation and Remediation, have discussed issues related to the various laboratory methods used to analyze for sulfolane. This letter is intended to clarify the requirements for laboratory analysis of sulfolane in groundwater in order to generate accurate and consistent data for decisions that need to be made under the site cleanup rules 18 AAC 75.325 - 18 AAC 75.390. To date, the Alaska Department of Environmental Conservation (DEC) has allowed laboratories to analyze for sulfolane using a modified version of the EPA Method 8270 and their own standard operating procedures. Upon review of the 2010 garden study results, some discrepancies were noted between the two primary commercial laboratories analyzing the samples from the North Pole Refinery investigation. While the TPT feels that all the data collected to date is useable for project management purposes, further refinement of the analytical method is needed to provide the highest level of consistency and quality assurance moving forward.

The TPT has reviewed the data quality indicators and available standard operating procedures for the analysis of sulfolane in water and identified the scope, key elements and data quality criteria that should be met for consistent, defensible results. These elements are attached as Tables 1 and 2. DEC requests that by March 1, 2011, these key elements and quality control requirements be met by all laboratories analyzing water samples for sulfolane in order for the results to be accepted by DEC for regulatory compliance.

To provide the highest level of regulatory review while also making an effort to expedite this process for the North Pole Refinery Project, DEC has decided to have the review of the SOPs and performance demonstration data be completed through the TPT Chemistry Subgroup, which includes the lead chemists from the State EHL, the Public Health Laboratory and DEC Division of Spill Prevention and Response. To facilitate this process, DEC requests FHR distribute this letter with attachments to all laboratories you wish to use on this project and consolidate all of their SOPs and

performance demonstration data for one submittal to the TPT. Once the subgroup approves the SOPs, DEC will issue an approval to FHR for use of those laboratories for analysis of water for sulfolane.

Please note that criteria for soil will be forthcoming and we will request a similar process for that media. If you have any questions regarding this letter, contact Ann Farris at (907) 451-2104 or via electronic mail at [ann.farris@alaska.gov](mailto:ann.farris@alaska.gov). Thank you for your assistance and attention to this matter.

Sincerely,

A handwritten signature in cursive script that reads "Ann Farris".

Ann Farris  
DEC Contaminated Sites Project Manager

Table 1. Laboratory Key Elements for Sulfolane Analysis in Water

<b>Key Element</b>	<b>Method Criteria</b>
<b>Reference Method</b>	SOP shall include references for method basis.
<b>Internal Standard (sulfolane-d8)</b>	Quantitation of sulfolane based on isotope dilution method using sulfolane-d8. Sulfolane-d8 added pre-extraction. Final extract concentration near the mid-point calibration concentration.  Use m/z 128 for quantifying and m/z 46, 62, and 64 as qualifier ions. See ion ratio criteria below.
<b>Recovery Criteria for Internal Standard</b>	Absolute recovery (quantitation based on recovery standard) 50 – 120%.
<b>Recovery Standard</b>	Naphthalene-d8 added post-extraction.
<b>Recovery Criteria for Recovery Standard</b>	Area count -50 to +100% relative to the continuing calibration verification.
<b>Additional Surrogates – Pre-extraction</b>	A minimum of one surrogate (in addition to the internal standard sulfolane-d8) should be added pre-extraction. Suggested surrogate nitrobenzene-d5. Recovery criteria to be internally derived.
<b>Extraction Sample Amounts</b>	Extraction volume sufficient to meet detection criteria, generally, 100 mL to 1 L should be sufficient. Extraction volume and the final extract volume must be specified in SOP.
<b>Extraction Method</b>	At discretion of labs sufficient to meet data quality objectives.
<b>GC/MSD Method</b>	Full Scan Mode, recommended mass range m/z 40 to 250 or higher. Scan rate greater than 10 scans across peak (at 10% peak height). Daily tune MS consistent with laboratory quality assurance project plan (QAPP).
<b>GC/MSD Calibration</b>	Low calibration point needs to be able to quantitate 5 parts per billion (ppb) at a minimum in water. At least two calibration points need to be set below the action level of 25 ppb. The concentration of the internal standard, sulfolane-d8 should be the same in all calibration standards and sample extract. Off-site samples have been observed at concentrations up to approximately 300 ppb.
<b>Quantification/Qualifier Ions for Sulfolane</b>	Quantification ion on m/z 120; Qualifier ions (QI) at m/z 41, 55 and 56. All four ions should be used and QI ratios defined.
<b>Ion Ratios (sulfolane and sulfolane-d8)</b>	Relative intensities of the qualifier ions need to be within 30% of the daily reference standard for two of three QI. If these ratio criteria in at least two QI, attempt to resolve the matrix interference. If matrix interference cannot be resolved, QI failure must be reported to FHR and DEC Project Managers within 1 week of failure. Ion ratios must be displayed in the raw data.

<b>Key Element</b>	<b>Method Criteria</b>
<b>Method Detection Limit (MDL)</b>	MDL not to exceed 5 ppb in water. LOQ (limit of quantitation) not to exceed 10 ppb in water. Report J-values between MDL and LOQ.
<b>Tailing criteria and integration</b>	Sulfolane and sulfolane-d8 peak tailing not to exceed a factor of two calculated on the unmodified software integrated peak (consistent with tailing factor equation from SW-846 Method 8270D). Manual integration only performed if necessary. Submit before and after extracted ion current profile (EICP) documentation with the report.
<b>Data flagging</b>	Data flagged based on laboratory standard practices. All flags used should be defined.
<b>Sample Collection, Handling, and Preservation</b>	Pre-cleaned appropriate sized amber bottle. Placed on ice and kept above freezing but below 6°C. Samples must be extracted within 7 days and the extract must be analyzed within 40 days of extraction.
<b>Demonstration Criteria</b>	For initial demonstration of performance, analyze a minimum of five extracted LCS QC samples at 25 ppb, each showing recoveries of $\pm 20\%$ and $RSD \leq 30\%$ .

Table 2. Quality Control Requirements

<b>Description</b>	<b>Frequency</b>	<b>Criteria</b>	<b>Corrective Action</b>
<b>Initial Calibration</b>	As needed	$r^2 \geq 0.99$ or $r \geq 0.995$	Repeat initial calibration.
<b>Initial Calibration Verification (ICV)</b>	Immediately following Initial Calibration	Second source, %Drift $\leq 20\%$	Investigate, reanalyze, recalibrate.
<b>Continuous Calibration Verification (CCV)</b>	After MS tuning and before sample analysis, every 20 injections thereafter, and at end of analytical sequence, or within a 12 hour tuning period, whichever is shorter. CCV concentration at action level, equivalent to 25 ppb in a sample.	%Drift $\leq 20\%$	Reanalyze CCV. If second re-analysis fails then perform initial calibration. Samples that were not bracketed by acceptable CCV must be reanalyzed.
<b>Method Blank (MB)</b>	Every preparation batch/event, or 20 samples, whichever is less	< MDL	Re-analyze MB. If MB > MDL or LOQ but ND in samples then no action needed. If MB > MDL then re-extract and re-analyze batch. Flag data with "B" qualifier, if insufficient sample for extraction.
<b>Laboratory Control Sample (LCS)</b>	Every preparation batch/event, or 20 samples, whichever is less. LCS concentration at action level, equivalent to 25 ppb in a sample. Spiking standard is prepared in water or a water-miscible solvent.	70 – 120%	Re-analyze LCS. If %R > acceptance criteria but ND in samples no action needed. Otherwise re-extract and re-analyze batch.
<b>Surrogate (additional, i.e., nitrobenzene-d5)</b>	Each sample and QC	In-house developed limits TBD, not to exceed 50 – 150%	Re-analyze and evaluate. If second analysis fails criteria, re-exact and reanalyze.
<b>Matrix Spike/Matrix Spike Duplicate (MS/MSD) and Sample Duplicate (DUP)</b>	An MS/MSD pair every preparation batch with 10 or more samples, up to 20. If preparation batch is less than 10 samples,	RPD for DUP and MS/MSD $\leq 25\%$ ; MS/MSD Recovery 60 – 140%	Qualify data and narrative any obvious matrix effects.

<b>Description</b>	<b>Frequency</b>	<b>Criteria</b>	<b>Corrective Action</b>
	analyze sample duplicate. Spiking standard is prepared in water or a water-miscible solvent.		
<b>Internal Standard (sulfolane-d8) Recovery</b>	Each sample and QC. Spiking standard is prepared in water or a water-miscible solvent.	50-120%	Re-extract and flag if second re-extraction/re-analysis fails criteria.
<b>Recovery Standard (naphthalene-d8)</b>	Each sample and QC	Area Count -50 – +100% relative to the continuing calibration verification	Re-analyze and flag if second analysis fails criteria.