Alaska Department of Environmental Conservation
Division of Spill Prevention and Response
Contaminated Sites Program

Technical Memorandum – 21-001 **Effective Date** December 22, 2021

Biogenic Interference and Silica Gel Cleanup

Summary

This document replaces Technical Memorandum 06-001 *Biogenic Interference and Silica Gel Cleanup*, May 18, 2006. This memo describes the process for documenting biological interference in samples collected during site cleanup activities. It also describes the laboratory method for conducting silica gel cleanup as part of the AK 102/103 (Diesel Range Organics/Residual Range Organics) laboratory method.[1]

Purpose

The purpose of this technical memorandum is to address the issue of biogenic material and biogenic interference in soil and water samples. It states the requirements for determining and documenting the presence of biogenic material at sites regulated under 18 Alaska Administrative Code (AAC) 75 and 18 AAC 78. It also describes the proper method for laboratories to conduct the sample analysis.

Background

In 1999, the Alaska Department of Environmental Conservation (DEC) published state-specific laboratory methods for the analysis of petroleum hydrocarbons in soil and water matrices:

- AK 102 for Diesel Range Organics (DRO)
- AK 103 for Residual Range Organics (RRO)[2]

These methods are in Appendix D of the *Underground Storage Tank (UST) Procedures Manual*, March 22, 2017, and adopted by reference in regulation, both in 18 AAC 75, Oil and Other Hazardous Substances Pollution Control and in 18 AAC 78, Underground Storage Tanks. DEC has promulgated cleanup levels for DRO and RRO in soil and groundwater under the site cleanup rules.

The AK 102/103 methods are not selective and, thus do not differentiate petrogenic analytes from non-petrogenic analytes. As a result, they are susceptible to interferences from other components of similar behavior. In many Alaska soil samples, these interferences are negligible; however, in some soils (e.g., tundra peat), significant amounts of biogenic materials are present. These biogenic materials can be carried through the sample extraction process and then quantified and reported as DRO and/or RRO in accordance with the AK 102/103 methods. Biogenic interference concentrations may occur at levels well above regulatory cleanup levels.

Surface water often has biogenic material floating on the top of the water surface. This material gives off a sheen like a petroleum sheen on the water's surface. Groundwater samples can also contain biogenic materials, but usually not to the extent that they occur in soil and surface water samples. More often, groundwater contains degradates of petroleum. As petroleum in soil degrades,

[1] This document does not apply to the Washington Extractable Petroleum Hydrocarbon (EPH) or Volatile Petroleum Hydrocarbon (VPH) methods.

[2] DEC also published the AK 101 method for Gasoline Range Organics. The AK 101 method is not impacted by biogenic interference and is not discussed in this tech memo.

it becomes more oxygenated and more polar. When these petrogenic chemicals become more polar, they become more soluble in water.

A sample cleanup step using silica gel to remove the biogenic materials and polar hydrocarbons is a common technique used in several different petroleum extraction methods. However, the published AK 102/103 methods do not contain any discussion of biogenic interference or silica gel cleanup. In the silica gel cleanup, a sample extract is adsorbed onto a packed silica gel column, and then eluted with a solvent such as methylene chloride. The biogenic materials and any petrogenic polar hydrocarbons are retained on the silica gel, while the non-polar hydrocarbons elute through the column and are collected at the end of the column.

Action

In order to accurately characterize a site, DEC allows the use of a silica gel cleanup on soil, groundwater, and surface water samples. It is important to note that most biogenic interference is seen in soil samples. Rarely do groundwater samples have enough biogenic material to exceed the 18 AAC 75.345, Table C cleanup levels. Demonstration of significant concentrations of biogenic material in groundwater are very difficult. Surface water sheen can be petrogenic or biogenic, which is easily differentiated using the "stick test"[3].

The need, or possible need, to identify biogenic interference should be addressed in the site characterization work plan. While the presence of biogenic interference can occasionally be unexpected, it is likely that a review of the site history and soil types present at the site will indicate that it may be necessary. If unexpected biogenic interference is encountered and not addressed in the site characterization work plan, contact the assigned DEC project manager as soon as possible.

When biogenic interference is suspected, the site characterization work plan should include:

- Photographing the site and soil types;
- Identifying soil types and determining their depths;
- Collecting samples from the contaminated areas at the site; and
- Collecting two to three background samples from similar depths and soil strata, but outside the area of contamination. For surface waters, collect samples from nearby, uncontaminated surface waters.

All samples must be collected and preserved in accordance with the AK 102/103 methods. Samples must be submitted to an analytical laboratory approved under the Contaminated Sites Laboratory Approval Program (http://dec.alaska.gov/spar/csp/lab-approval). Please note that the Laboratory Approval Program does not issue special approvals for the silica gel cleanup technique.

After the laboratory has completed analysis of the samples, they should issue a data package. In addition to the information required by the Technical Memorandum *Minimum Quality Assurance Requirements for Sample Handling, Reports, and Laboratory Data*, October 2019, the data package must include:

- Pre- and post-silica chromatograms and DRO/RRO concentrations for each:
    - Quality Control (QC) sample;
    - Field sample with suspected biogenic interference; and
    - Background sample.

[3] Use a stick to break up the sheen. Petroleum sheen will typically coalesce, while bacteria sheen will remain broken apart.

- Pattern interpretation in the case narrative. For each chromatogram, the laboratory should state whether or not the pattern is consistent with biogenic interference, petroleum, neither, or both.

The site characterization report should identify whether or not biogenic interference is present at the site and support that by discussing the analytical data including sample chromatogram interpretation, site photos, soil descriptions, site characteristics, etc. If applicable, the report could show that biogenic material is present in the samples collected from the soil outside the contaminated area, as well as how the biogenic pattern changes after treatment with silica gel.

The interpretation of the pre- and post-silica chromatograms is both qualitative and quantitative. The qualitative interpretation requires comparing pre- and post-silica chromatograms of samples to chromatograms of diesel and oil standards to determine if the chromatographic pattern in the sample is consistent with petroleum, biogenic material, or a mixture of the two. If the qualitative analysis of the chromatogram shows only petrogenic compounds present, then the appropriate concentrations of DRO and/or RRO in the sample to use in data reporting are the higher of the pre- or post-silica concentrations. If the chromatogram shows only biogenic material present, then the appropriate concentration of DRO and/or RRO to report is non-detect, even if a concentration is reported. If the chromatogram shows a mixture of biogenic and petrogenic materials, the post-silica concentration reported is the DRO and/or RRO concentration present, even if minor amounts of biogenic material remain in the post-silica gel chromatography pattern.

Because biogenic material can vary widely across a site, silica gel cannot be used to establish a site-wide "background concentration" or "average concentration."

If silica gel cleanup is used on groundwater samples, the site characterization report must be able to show that the material removed from the extract was biogenic material and not petrogenic polar hydrocarbons. Petrogenic polar compounds formed by the degradation of petroleum are still petrogenic hydrocarbons and must be included in the calculations of DRO and RRO concentrations at the site.

If the weight of evidence supports the presence of biogenic interference in the AK 102/103 sample results, DEC may agree to utilize the silica gel cleanup results for site decision-making purposes.

AK 102/103 Silica Gel Cleanup Laboratory Method

1. Objective

This laboratory method serves as a companion to the AK 102/103 methods contained in the Appendix D of the *Underground Storage Tank (UST) Procedures Manual*, March 22, 2017.

Alaskan samples containing organic plant material may contribute to DRO and/or RRO analytical results when using the AK 102/103 methods. Interpretation of the sample chromatogram for qualitative match of the chromatograph pattern to known sources of fuel products and/or biogenic interference must be performed by an experienced analyst. Once biogenic interference has been determined to be present, the following procedure may be used as an analytical tool to evaluate the contribution of the biogenic interference to the original sample results.

2. Method Summary

2.1 A sample extract that has been prepared utilizing the standard AK 102/103 methodology, is flushed through a silica gel column using methylene chloride.

2.2 This silica gel cleanup MUST also be performed on all QC samples in the analytical batch associated with the field sample. At a minimum, this must include the Method Blank (MB), Laboratory Control Sample(s) (LCS) and LCS Duplicate(s) (LCSD). All QC results must be reported with the results of the field samples, before and after cleanup.

2.3 Samples before and after cleanup must be run on the same type of gas chromatography column with the same stationary phase material and running the same temperature program.

3. Apparatus and Methods

3.1 Drying oven: an oven capable of maintaining 150^{o}C is used for activation/storage of silica gel.

3.2 Glassware

3.2.1 Turbo Vap tubes

3.2.2 10 ml graduated disposable pipettes or equivalent

3.3 Reagents

3.3.1 Methylene chloride - analytical grade or better, must be demonstrated to be below method detection limits for diesel range and residual range contaminants.

3.3.2 Ottawa sand – cleaned/baked sand used for soil method blanks.

3.3.3 Silica gel - Anhydrous, 60 - 100 mesh. Commercially available prepacked extraction cartridges may be used provided they meet all quality control performance criteria listed in this document.

IMPORTANT: Silica gel must be activated by placing in a 150^{o}C oven prior to use. Additionally, prolonged exposure to moist air may result in reduced or deficient method performance. Activated silica gel should be stored in a manner as to prevent moisture exposure. It is recommended that the silica gel be stored in the oven

continually prior to use. Commercially available prepacked extraction cartridges should be stored and used in accordance with the manufacturer's instructions.

3.3.4 Glass wool - Pesticide grade or better.

4. Procedure

4.1 Preparing the column

4.1.1 Cut the top off a 10 ml disposable volumetric Pasteur pipette using a triangular file.

4.1.2 Place a small plug of glass wool into the pipette and slide it down into the taper.

4.1.3 Add a few grams of Ottawa sand to cover the glass wool and provide a flat bed for the silica gel.

4.1.4 Add silica gel to the pipette, with occasional shaking to ensure uniform packing, up to the 3 ml mark. Alternatively, the silica gel may be added as a "slurry" with methylene chloride to minimize channeling.

4.1.5 Add another few grams of Ottawa sand to provide some protection to the silica gel bed.

4.1.6 Pre-elute the column with at least one volume of methylene chloride.

Note: Overloading of the silica gel column capacity may occur with extracts containing elevated concentrations of biogenic material. Dilution or adjustment of the sample extract volume prior to clean up may be necessary to avoid unwanted breakthrough.

4.2 Extract Preparation

4.2.1 Obtaining the extract

4.2.1.1 Split Extraction - Prepare one batch of samples. Extract a MB, LCS/LCSD, and samples using methylene chloride per the AK 102/103 method. Condense the extracts down to a small volume (i.e. 2 ml). Divide each of the extracts into 1ml portions. One set of 1 ml portions is transferred to GC vials as the "pre-silica" QC and samples. The second set of 1ml portions is put through the silica gel cleanup, condensed, and transferred to GC vials as the "post-silica" QC and samples.

4.2.1.2 Post-analysis cleanup - Prepare one batch of samples. Take them through the whole extraction process and analyze them on the instrument. Then, once the extracts have been analyzed on the instrument, run them through silica gel. Then re-analyze them for post-silica results.

4.2.2 Fill the column to the ~1.5 ml mark with methylene chloride. Allow methylene chloride to drain down to the sand and discard.

4.2.3 Pipette an aliquot of sample from the vial into the column.

4.2.4 Immediately fill the column with methylene chloride up to the ~1.5 ml mark.

4.2.5 When the methylene chloride reaches the 0 ml mark, begin collection of the sample into a 15 ml centrifuge tube.

4.2.6 When the methylene chloride reaches the sand, refill the column to the ~1.5 ml mark and continue collecting the sample. Repeat this step twice and allow methylene chloride to drain finish dripping from column.

4.2.7 Concentrate extract to the required volume using an appropriate concentration device.

4.3 Gas Chromatography

4.3.1 Gas chromatography should be performed in accordance with the AK 102/103 methods.

4.3.2 In order to accurately compare chromatograms from samples before and after cleanup, it is highly recommended to analyze all extracts on the same instrument and gas chromatography column. At a minimum, the samples must be analyzed on the same type of gas chromatography column with the same stationary phase material and running the same temperature program.

5. Quality Control

5.1 Calibration requirements and limits are the same as specified in AK 102/103.

5.2 QC sample recovery requirements and limits are the same as specified in AK 102/103. Results that are outside of the AK 102/103 control limits must be flagged.

5.3 The analysis of a matrix spike and matrix spike duplicate is highly recommended when this procedure is used.

References

DEC (2017) *Underground Storage Tank Procedures Manual.*

DEC (2019) Technical Memorandum *Minimum Quality Assurance Requirements for Sample Handling, Reports, and Laboratory Data*