

**ALASKA DEPARTMENT OF ENVIRONMENTAL CONSERVATION
DIVISION OF SPILL PREVENTION AND RESPONSE
CONTAMINATED SITES REMEDIATION PROGRAM**

Technical Memorandum - 06-001

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Biogenic Interference and Silica Gel Cleanup

PURPOSE:

The Alaska Department of Environmental Conservation (DEC) has developed state specific laboratory methods for the analysis of petroleum hydrocarbons in soil and water matrices, AK101 for Gasoline Range Organics (GRO), AK102 for Diesel Range Organics (DRO) and AK103 for Residual Range Organics (RRO). The methods are located in Appendix D of the Underground Storage Tank (UST) Procedures Manual, November 7, 2002. Additionally, they are adopted by reference in regulation, both in 18 AAC 75 Oil and Other Hazardous Substances Pollution Control, {18 AAC 75.355 (d)}, and in 18 AAC 78 Underground Storage Tanks, (18 AAC 78.007). This technical memorandum addresses the issue of “naturally occurring organic material” (NOM) and/or “biogenic interference” specifically in relation to methods AK102 and AK103. It also provides the laboratory and reporting requirements for utilizing a silica gel cleanup procedure as a method for evaluating the presence of biogenics and thier contribution to the AK102/AK103 sample results.

BACKGROUND:

It is well established that the currently promulgated AK102 and AK103 methods for petroleum range organic analysis are complicated by biogenic interference. NOM or biogenics are present in many soils and especially prevalent in certain Alaskan soils, e.g. tundra peat. As a result, biogenic interference is the term that is used to describe the NOM that is quantified and reported as DRO and/or RRO in accordance with the AK102 and AK103 methods. Biogenic interference concentrations may occur at levels well above regulatory cleanup levels.

Likewise, silica gel cleanup is a well established analytical procedure utilized to separate analytes from interfering compounds of different polarity. The majority of “fresh” or non-biodegraded petroleum hydrocarbons are considered non-polar compounds. Depending on the soil makeup, the majority of the biogenic compounds may be polar or semi-polar in nature. The silica gel cleanup procedure will preferentially remove polar and semi-polar compound.

In order to ensure consistent data when evaluating the presence and degree of biogenic interference at a contaminated site, the department provides the following laboratory procedure and data reporting requirements.

I. Laboratory Procedure for Silica Gel Cleanup

1. Objective

Alaskan samples containing organic plant material are especially susceptible to background biogenic interference and may result in false positive results for DRO or RRO defined petroleum hydrocarbon ranges. Interpretation of the sample chromatogram **MUST** be done by an experienced analyst for qualitative match of the chromatograph pattern to known sources of fuel product and/or biogenic interference. Once biogenic interference has been determined, this procedure may be used as an analytical tool to evaluate the contribution of biogenic interference to the original sample results.

2. Method Summary

- 2.1 A sample extract that has been prepared **and analyzed** utilizing the standard AK102/AK103 methodology, is flushed through a silica gel column using methylene chloride.

Note: The extract must not be acidified. An acid cleanup step is not allowed.

- 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. See QC section of this appendix for required control limits.

3. Apparatus and Materials

- 3.1 Drying oven: an oven capable of maintaining 150°C is used for drying of sodium sulfate and activation/storage of silica gel.
- 3.2 Glassware
- 3.2.1 Turbo Vap tubes
- 3.2.2 10mL 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 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 appendix.
- IMPORTANT:** silica gel must be activated by placing in a 150°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.
- 3.3.4 Glass wool - Pesticide grade or better.

4. Procedure

4.1 Preparing the column

- 4.1.1 Cut the top off a 10mL 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 3mL 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 1 volume of methylene chloride.

Note: Overloading of the silica gel column capacity may occur with extracts containing elevated concentrations of biogenics. 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 Fill the column to the ~1.5 ml mark with methylene chloride. Allow methylene chloride to drain down to the sand and discard.
- 4.2.2 Pipette an aliquot of sample from the vial into the column.
- 4.2.3 Immediately fill the column with methylene chloride up to the –1.5 ml mark.
- 4.2.4 When the methylene chloride reaches the 0 ml mark, begin collection of the sample into a 15 ml centrifuge tube.
- 4.2.5 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.
- 4.2.6 Using an appropriate concentration device, concentrate extract to the required volume.

5. Quality Control

- 5.1 Calibration requirements and limits are the same as specified in AK102 and AK103.
- 5.2 QC Results that are outside of the following 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.

Table 2
**Acceptance Criteria for QC Samples
 After Silica Gel Cleanup**

	Control Limits	
	% Recovery	Relative % Difference
DRO Recovery:		
Lab Control Samples & Duplicates	70-125	20
Surrogate Recovery:		
Quality Control Sample	70-125	
Field Sample	50-150	

II. Data Reporting Requirements

The department requires the following data to be submitted for the evaluation of biogenic interference in AK102 DRO and AK103 RRO sample results.

1. Comparison samples.
 - a. In general, three to five comparison samples must be collected from similar depth and soil strata. The exact number of comparison samples will be determined by the project data quality objectives. The samples will be analyzed for Total Organic Carbon (TOC) and AK102/AK103, before and after silica gel cleanup. The sample results will be utilized for chromatographic interpretation only, to establish the presence of biogenic interference at the site, the general biogenic chromatographic fingerprint and the effectiveness of the silica gel cleanup procedure. The results will not be used to establish a “background concentration” or “average concentration.”
2. Analytical Data
 - a. The samples must be extracted only once, per methods AK102/AK103
 - b. Standard AK102/AK103 sample analysis must be performed and reported
 - c. Silica gel column cleanup procedure must performed on the same extract
*Note – A silica gel “slurry” or “swirl” is not acceptable
 - d. The silica gel cleanup procedure must be performed and reported for all associated quality control (QC) samples
 - i. Minimum required – Method Blank, LCS and LCS Duplicate
 - e. QC and Surrogate results must be within method specified limits for both analyses (before and after silica gel cleanup).
 - f. All sample results and chromatograms and a narrative report must be submitted to the department for evaluation.
3. Evaluation
 - a. Results of samples analyzed using the silica gel cleanup procedure will not be accepted as representative of a site without completion of the comparison process described above.
 - b. The presence of biogenic interference must be clearly demonstrated in the background samples. The site samples should contain chromatographically similar biogenic fingerprints. The department will not accept silica gel cleanup results for samples that do not exhibit biogenics and/or only chromatographically exhibit petroleum hydrocarbon contamination.
 - c. If the weight of evidence supports the presence of biogenic interference in the AK102 and AK103 sample results, the department may agree to utilize the silica gel cleanup results for site decision purposes.