Pesek, Adam

Subject: FW:

-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Thursday, July 08, 2010 9:32 AM
To: Pesek, Adam
Subject: RE:

Adam,
Attached is a list of ARG processes and our best estimate for the process configuration factor. The sulfur recovery throughput is quite high but this is b/c it is showing the amount of refinery fuel gas that is desulfurized daily. I think it's inconsequential anyways b/c there's no weighing factor associated w/ it. Let me know if you have any questions w/ the list.

I spent the last few weeks building my house. I originally expected to be back in the office on Tuesday but today is my first day back.

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Pesek, Adam

From: Trulear.Brian@epamail.epa.gov
Sent: Wednesday, June 23, 2010 12:50 PM
To: Pesek, Adam
Cc: MacKnight.Evelyn@epamail.epa.gov; Weber.Peter@epamail.epa.gov; Cruz.Francisco@epamail.epa.gov; Balog, David
Subject: American Refining Group Draft Permit (PA0002674)

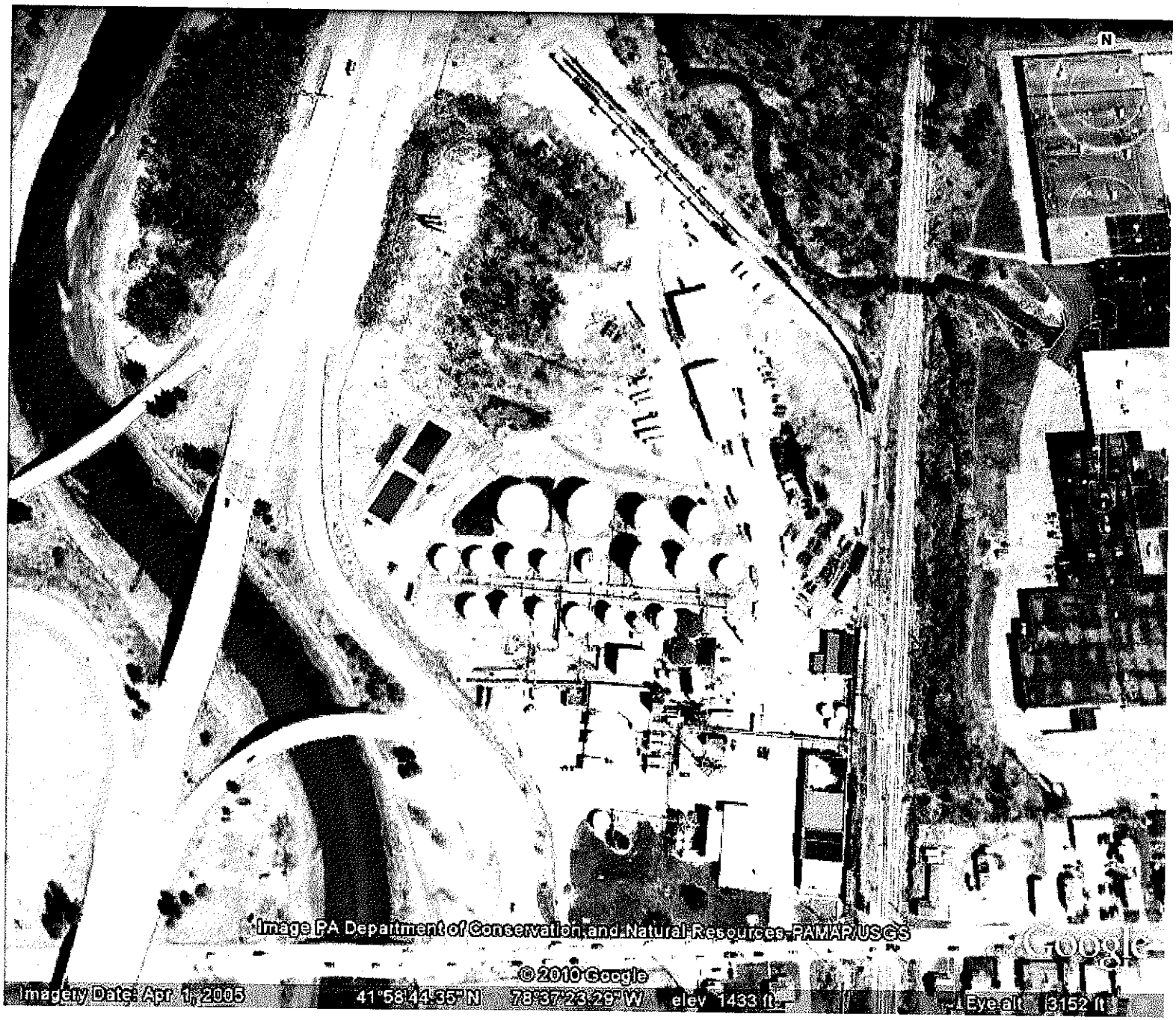
Adam,

We received the draft permit renewal for American Refining Group on June 1, 2010. In the interest of focusing available resources, EPA has exercised its discretion in the review of this State-submitted draft permit and has chosen to perform a limited review. I reviewed the checklist and looked at any changes from the previous permit as well as the methodology to establish the technology based limits. As a result of this limited review, I have the following comment.

On Page 4 of the checklist, the answer to question II.D.4.e. suggests that there are parameters being discharged from this facility that have a reasonable potential to violate standards but were not given numeric effluent limits. According to 40 CFR 122.44(d)(1), the permit must contain effluent limits for pollutants that show reasonable potential. Please explain your response to this question.

Prior to finalizing this permit, please address the above comments and provide me with any changes to the draft permit. In addition, please forward to me any changes to the Fact Sheet / Pollution Report / WQPR, if necessary. If you prefer, electronic versions of these documents can be sent instead of hard copies. Electronic versions of all final permit documents and Fact Sheets / Pollution Reports / WQPRs are preferred as well. Any questions, give me a call.

Thanks,
Brian P. Trulear
NPDES Permits Branch (3WP41)
Office of Permits & Enforcement
Water Protection Division
EPA Region III
Phone: 215-814-5723
Fax: 215-814-2302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Eye alt 3152 ft

Pesek, Adam

From: Jason Goodling [jgoodling@amref.com]
Sent: Thursday, June 10, 2010 2:43 PM
To: Pesek, Adam
Subject: RE: Comment No. 1 - Contaminated Groundwater

Hi Adam,
The issue with the waste water and groundwater remediation program is a little confusing. I'll give you the steps from past to present...
1) When the WITCO corporation owned the refinery (prior ~1997), contaminated groundwater from recovery wells was hard-piped to what is now ARG's WWTP.
2) In ~1997 the refinery was privately purchased but WITCO still had environmental cleanup operations. As such, the groundwater recovery wells installed by WITCO (and still owned by WITCO) were still pumped to what then became ARG's WWTP. ARG charged WITCO for the use of its WWTP to treat this groundwater.
3) At some point in this process, WITCO was obtained by Chemtura (the name that you hear today).
4) After ARG came into existence in 1997 there were miscellaneous small spills that necessitated the installation of ARG recovery wells. This is where the division between ARG recovery wells and our previous owner's wells began.
5) In ~2004 Chemtura installed its own WWTP and began directing its recovered contaminated ground water to the new plant. At this point all Chemtura well water was sent to their WWTP and all ARG water was directed to its own WWTP.

Previous NPDES applications included a diagram of the Chemtura recovery wells hard piped to the ARG WWTP. When we saw that the diagram was still included in the latest NPDES application, we requested that it be removed since that water was no longer sent to ARG's WWTP. We should have specifically requested that the diagram was taken out of the application rather than "groundwater" in general because ARG still sends small amounts of remediation well water (from ARG wells) to the MEK Unit separator (via a vacuum recovery truck) which is located upstream of the WWTP. This is the reason that we'd like to keep "groundwater" as a contributing flow to 002. ARG's recovery well groundwater would have been represented in last June's NPDES permit application analytical data.

Earlier this spring, we discussed the effects that directing Chemtura well water into the wwtp would have on the NPDES permit (due to Chemtura's bankruptcy and the uncertainty of their remaining cleanup obligation issues). This project has not been done to date and we have no set plans to do this anytime in the future.

We can talk this over one the phone if it makes it easier to understand. Let me know if you have any questions. Thanks,
Jason

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-----Original Message-----
From: Pesek, Adam [mailto:apesek@state.pa.us]
Sent: Thursday, June 10, 2010 11:43 AM
To: Jason Goodling
Subject: Comment No. 1 - Contaminated Groundwater

Good Morning Jason,

As you mentioned in comment one or your letter, you requested that you wanted "contaminated groundwater from recovery operations" inserted back in as a source of wastewater. We corresponded about what needed to be

done in order to tie this wastewater into 002 in late March/early April with a compiled list in my email on April 1st. I didn't know you were going ahead with the addition of the recovery well water, but please provide the discharge information I mentioned in the April 1st email ASAP. Thanks.

Looking nice out,

Adam
Adam J. Pesek | Environmental Engineering Specialist
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Pesek, Adam

From: Moore, Bonita
Sent: Wednesday, June 09, 2010 12:46 PM
To: Barron, Thomas; Pesek, Adam
Cc: Wetherell, John; Shulman, Arleen
Subject: RE: Oil & Grease Sampling/Analysis

Hi Adam,

There are a couple of issues that need to be addressed here:

- EPA Method 1664 (now 1664a) is an approved method for Oil and Grease analysis.
- Method 1664a does have a provision to allow for composite samples. Please note that section 8.3 of the method states,

"The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low preludes the collection of composite samples for the determination of oil and grease. **Therefore, samples must be collected as grab samples.** If a composite measurement is **required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged. Alternatively, samples can be collected in the field and composite in the laboratory. "**

In order for the lab to composite the sample, the required sample size would be divided into separate smaller sample sizes. Each smaller sample would then be extracted and collected into one collection vessel for the final oil and grease determination. The procedure would require extended extraction time, the use of more solvent for the extraction and an overall increase in the cost of the analysis.

After reading through Method 1664a, I do not think it is in the best interest of Department to allow for lab composite sampling. From the statement you made below the Department has a new policy and requires I-max for Oil and Grease determination. I think we should be consistent and honor our policy.

- Please note that the Department would have to **require** composite samples in the permit.
- The proposed alternate composite sample procedure as stated above would allow for biased low Oil and Grease determinations.
- The alternate composite sample procedure would require more reagent and be costly.

Please let me know if I can be of any further help.

Thanks

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-----Original Message-----
From: Barron, Thomas
Sent: Wednesday, June 09, 2010 10:51 AM
To: Pesek, Adam
Cc: Wetherell, John; Moore, Bonita; Shulman, Arleen
Subject: RE: Oil & Grease Sampling/Analysis

Hi Adam,

Your question is larger than just whether the Department approves the "lab compositing" variation described for USEPA Method 1664, so I have included others on this reply to get their input as well. I believe this is more than a simple methods approval or question of analytical capabilities; should they be allowed to average or composite samples or results to avoid the higher test results?

The Secretary expressed some rather strong objections to how companies resort to data and sample manipulation in order to achieve compliance with permit or other requirements. While this came up during discussions of proposed rulemaking for sulfur limits in commercial fuel oil, his response seemed to be more general - permitting / reporting requirements. Arleen, are you able to shed additional insight into the discussion you were having with the Secretary on this issue during yesterday's EQB Briefing? Did I read his response properly?

Bonita can help answer the methods approval question since she worked on methods development while at the BOL, and had specific dealings with the oil & grease analytical methods being developed by the Department.

Thanks!

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-----Original Message-----
From: Pesek, Adam
Sent: Tuesday, June 08, 2010 3:25 PM
To: Barron, Thomas
Cc: Wetherell, John
Subject: FW: Oil & Grease Sampling/Analysis

Tom,

Does the Department approve of the below described method (USEPA Method 1664) for the analysis of Oil & Grease? They intend to bypass the need to report I-max on the DMRs for Oil & Grease that they would be required to do according to the new policy on reporting of I-max using current collection methods.

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-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Monday, June 07, 2010 10:35 AM
To: Pesek, Adam
Subject: Oil & Grease Sampling/Analysis

Adam,

We have recently been discussing the Department's proposed change in all NPDES permits to require the inclusion of instantaneous maximum limits and the reporting of any i-max limit exceedance in a grab sample. Currently, ARG is not required to report instantaneous oil and grease grab results and mathematically averages each

3 daily grabs into a daily composite number for loading calculation purposes. The Department's current practice requires that i-max limits must be applied for any grab samples and the Department has correctly noted that O&G samples cannot be composited in the field.

While it is true that O&G samples cannot be composited during collection, there is a procedure in USEPA Method 1664 for the compositing of O&G samples prior to analysis. Section 8.3 of Method 1664 discusses the allowable practice of collecting multiple grab samples which are then separately extracted at the lab with hexane and composited together prior to analysis. It appears that ARG could use this variation of Method 1664 for Outfall 002 by collecting three sample containers daily and having those samples lab composited prior to chemical analysis. This would be in place of the current methodology whereby the 3 samples are separately analyzed and the results averaged for reporting. The only change that would need to be made to the permit would be a description of the allowable laboratory compositing of the O&G samples. This could be accomplished by changing the "Required Sample Type" description for O&G on page 2 of the permit to specify "3 sample lab composite" and include a footnote explaining that the three samples collected for a given day must be separately extracted prior to being lab composited for analysis.

Please let me know your thoughts on this.

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<< Method 1664.pdf (1 MB) >>

http://www.epa.gov/waterscience/methods/method/oil/1664.html
Last updated on Thursday, December 17, 2009

Clean Water Act Analytical Methods

You are here: EPA Home Water Water Science Analytical Methods Approved Methods Oil and Grease Method 1664, Revision A

Analytical Methods

EPA-821-R-98-002; February 1999

Method 1664, Revision A: N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry

Print Version (PDF) (213 K, 28 pp.)

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Introduction

As a party to the Montreal Protocol on Substances that Deplete the Ozone Layer and as required by law under the Clean Air Act Amendments of 1990 (CAAA), the United States is committed to controlling and eventually phasing out the use of chlorofluorocarbons (CFCs). In support of these efforts, Method 1664 was developed by the United States Environmental Protection Agency Office of Science and Technology to replace previously used gravimetric procedures that employed Freon-113, a Class I CFC, as the extraction solvent for the determination of oil and grease and non-polar material.

Method 1664 is a performance-based method applicable to aqueous matrices that requires the use of n-hexane as the extraction solvent and gravimetry as the determinative technique. Alternative extraction and concentration techniques are allowed, provided that all performance specifications are met. In addition, QC procedures designed to monitor precision and accuracy have been incorporated into Method 1664.

Contact us if you have questions concerning this method.

1.0 Scope and Application

1.1—This method is for determination of n-hexane extractable material (HEM; oil and grease) and n-hexane extractable material that is not adsorbed by silica gel (SGT-HEM; non-polar material) in surface and saline waters and industrial and domestic aqueous wastes. Extractable materials that may be determined are relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials. The method is based on prior Environmental Protection Agency (EPA) methods for determination of "oil and grease" and "total petroleum hydrocarbons" (References 16.1 and 16.2).
1.2—This method is for use in the Environmental Protection Agency's (EPA's) survey and monitoring programs under the Clean Water Act; the Resource Conservation and Recovery Act; the Comprehensive Environmental Response, Compensation, and Liability Act; and other EPA regulatory programs. "Oil and grease" is a conventional pollutant under the Clean Water Act and codified at 40 CFR 401.16. The term "n- hexane extractable material" reflects that this method can used to determine materials other than oils and greases. Similarly, the term "silica gel treated n-hexane extractable material" reflects that this method can be used to determine material that is not adsorbed by silica gel (non- polar material).
1.3—This method is not applicable to measurement of materials that volatilize at temperatures below approximately 85 C. Petroleum fuels from gasoline through #2 fuel oil may be partially lost in the solvent removal operation.
1.4—Some crude oils and heavy fuel oils contain a significant percentage of materials that are not soluble in n-hexane. Accordingly, recoveries of these materials may be low.
1.5—This method is capable of measuring HEM and SGT-HEM in the range of 5 to 1000 mg/L, and may be extended to higher levels by analysis of a smaller sample volume collected separately.
1.6—For HEM and SGT-HEM in this method, the method detection limit (MDL) is 1.4 mg/L and the minimum level of quantitation (ML) is 5.0 mg/L (Reference 16.3).
1.7—The laboratory is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in Sections 9.1.2 and 9.2.3.
1.8—Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.
1.9—Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

2.0 Summary of Method

2.1—A 1-L sample is acidified to pH <2 and serially extracted three times with n-hexane in a separatory funnel. The extract is dried over sodium sulfate.
2.2—The solvent is distilled from the extract and the HEM is desiccated and weighed. If

the HEM is to be used for determination of SGT-HEM, the HEM is redissolved in n-hexane.
2.3—For SGT-HEM determination, an amount of silica gel proportionate to the amount of HEM is added to the solution containing the redissolved HEM to remove polar materials. The solution is filtered to remove the silica gel, the solvent is distilled, and the SGT-HEM is desiccated and weighed.
2.4—Quality is assured through calibration and testing of the extraction, distillation, and gravimetric systems.

3.0 Definitions

3.1—HEM and SGT-HEM are method-defined analytes; i.e., the definitions of both HEM and SGT-HEM are dependent on the procedure used. The nature of the oils and/or greases, and the presence of extractable non-oily matter in the sample will influence the material measured and interpretation of results.
3.2—Definitions for terms used in this method are given in the glossary at the end of the method.

4.0 Interferences

4.1—Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents and purification of solvents may be required.
4.2—All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory blanks as described in Section 9.4.
4.3—Glassware is cleaned by washing in hot water containing detergent, rinsing with tap and distilled water, and rinsing with solvent or baking. Boiling flasks that will contain the extracted residue are dried in an oven at 105 115 C and stored in a desiccator.
4.4—Sodium sulfate and silica gel fines have the potential to inflate results for HEM and SGT-HEM by passing through the filter paper. If the filter paper specified in this method is inadequate for removal of these fines, use of a 0.45-micron filter is recommended.
4.5—Interferences extracted from samples will vary considerably from source to source, depending upon the diversity of the site being sampled. For those instances in which samples are thought to consist of complex matrices containing substances (such as particulates or detergents) that may interfere with the extraction procedure, a smaller sample may need to be collected for analysis.

5.0 Safety

5.1—The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level. It is suggested that the laboratory perform personal hygiene monitoring of each analyst that uses this method. This monitoring should be performed using Occupational Safety and Health Administration (OSHA) or National Institute of Occupational Safety and Health (NIOSH) approved personal hygiene monitoring methods. Results of this monitoring should be made available to the analyst.
5.2—n-Hexane has been shown to have increased neurotoxic effects over other hexanes and some other solvents. OSHA has proposed a time-weighted average (TWA) of 50 parts-per-million (ppm); NIOSH concurs that an 8-hour TWA/permissible exposure limit (PEL) of 50 ppm is appropriate for n- hexane; and the American Conference of Governmental Industrial Hygienists (ACGIH) has published a threshold limit value (TLV) of 50 ppm for n- hexane. Inhalation of n-hexane should be minimized by performing all operations with n-hexane in an explosion-proof hood or well-ventilated area.

5.3—n-Hexane has a flash point of -23 C (-9 F), has explosive limits in air in the range of 1 - 7 percent, and poses a serious fire risk when heated or exposed to flame. n-Hexane can react vigorously with oxidizing materials. The laboratory should include procedures in its operations that address the safe handling of n-hexane.
5.4—Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.
5.5—This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.4 16.6.

6.0 Equipment and Supplies

NOTE: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1—Sampling equipment.
6.1.1—Sample collection bottles Glass, approximately 1-L, with PTFE-lined screw cap.

NOTE: In those instances necessitating collection of a sample known or suspected to contain >500 mg/L of HEM (Section 8.1.2), a smaller sample container may be used.

6.1.2—Cleaning.
6.1.2.1—Bottles Detergent water wash, tap water rinse, cap with aluminum foil, and bake at 200 250°C for 1 h minimum prior to use. Solvent rinse may be used in place of baking.
6.1.2.2—Liners for screw caps Detergent water wash, tap water and solvent rinse, and bake at 110 200°C for 1 h minimum prior to use.
6.1.3—Bottles and liners must be lot-certified to be free of artifacts by running laboratory blanks according to this method (per Section 9.4). If blanks from bottles and/or liners without cleaning or with fewer cleaning steps than required above show no detectable materials, the bottle and liner cleaning steps that do not eliminate these artifacts may be omitted.
6.2—Equipment for glassware cleaning.
6.2.1—Laboratory sink with overhead fume hood.
6.2.2—Oven--Capable of maintaining a temperature within ± 2C in the range of 70-250C.
6.3—Equipment for calibration.
6.3.1—Analytical Balance--Capable of weighing 0.1 mg.
6.3.2—Volumetric flask--Glass, 100-mL.
6.3.3—Vials--Assorted sizes, with PTFE-lined screw caps.
6.3.4—Volumetric pipette--Glass, 5-mL.
6.4—Equipment for sample extraction.
6.4.1—Balance (optional)--Top loading, capable of weighing 500-2000g within ± 1%
6.4.2—Glass stirring rod.
6.4.3—Separatory funnel--Glass, 2000-mL, with PTFE stopcock.
6.4.4—Funnel--Large, glass, for pouring sample into separatory funnel.
6.4.5—Centrifuge (optional)--Explosion proof, capable of spinning at least four 100-mL glass centrifuge tubes at 2400 rpm minimum.
6.4.6—Centrifuge tubes (optional)--100-mL glass.
6.5—Equipment for removal of water, sodium sulfate, and silica gel fines.
6.5.1—Funnel--Analytical, glass.

6.5.2—Filter paper--Whatman No. 40 (or equivalent), to fit funnel.

6.6—Equipment for solvent distillation.

6.6.1—Water bath or Steam bath--Explosion-proof, capable of maintaining a temperature of at least 85C.

6.6.2—Flask--Boiling, 125-mL (Corning No. 4100 or equivalent).

6.6.3—Distilling head--Claisen (VWR Scientific No. 26339-005, or equivalent), includes Claisen-type connecting tube and condenser.

6.6.4—Distilling adaptor (attached to the distilling head and to the distillate collection flask for recovery of solvent).

6.6.5—Distillate collection flask (attached to the distilling adaptor for collection of the distilled solvent).

6.6.6—Ice bath or recirculating chiller (to aid in the condensation and collection of the distilled solvent).

6.6.7—Vacuum--Vacuum pump or other source of vacuum.

6.6.8—Tongs, for handling the boiling flask (Baxter Scientific Products No. T5007-2, or equivalent).

6.6.9—Desiccator--Cabinet- or jar-type, capable of keeping the boiling flask (Section 6.6.2) dry during cooling.

6.6.10—Hood-Explosion-proof, capable of accommodating the equipment used for solvent distillation (Section 6.6.1-6.6.5).

6.7—Equipment for removal of adsorbable materials.

6.7.1—Magnetic stirrer.

6.7.2—PTFE-coated magnetic stirring bars.

6.7.3—Graduated cylinder--500-mL, capable of measuring ± 5 mL.

6.7.4—Pipettes--Assorted sizes, calibrated to within ± 0.5 percent.

7.0 Reagents and Standards

7.1—Reagent water--Water in which HEM is not detected at or above the minimum level (ML) of this method. Bottled distilled water or water prepared by passage of tap water through activated carbon have been shown to be acceptable sources of reagent water.

7.2—Hydrochloric acid or sulfuric acid--ACS. Mix equal volumes of concentrated HCl and reagent water or 1 part H_2SO_4 and 3 parts reagent water to produce an approximately 6N solution.

7.3—n-Hexane--85% minimum purity, 99.0% min. saturated C_6 isomers, residue less than 1 mg/L.

7.4—Acetone--ACS, residue less than 1 mg/L.

7.5—Sodium sulfate--ACS, granular anhydrous. Dry at 200-250 C for 24 h minimum and store in a tightly sealed container until use.

NOTE: Powdered sodium sulfate should not be used because traces of water may cause it to solidify.

7.6—Boiling chips--Silicon carbide or fluoropolymer.

7.7—Silica gel--Anhydrous, 75 - 150 micrometers, Davisil Grade 923 (Supelco 21447-7A, or equivalent). Dry at 200-250C for 24 h minimum and store in a desiccator or tightly sealed container. Determine the n-hexane soluble material content of the silica gel by extracting 30 g of silica gel with n-hexane and distilling the n-hexane to dryness. The silica gel must contain less than 5 mg of n-hexane soluble material per 30 g (< 0.17 mg/g).

7.8—Hexadecane--98% minimum purity.

7.9—Stearic acid--98% minimum purity.

7.10—Hexadecane/stearic acid (1:1) spiking solution--Prepare in acetone at a concentration of 2 mg/mL each.

7.10.1—Place 200 ± 2 mg stearic acid and 200 ± 2 mg hexadecane in a 100-mL volumetric flask and fill to the mark with acetone.

NOTE: The solution may require warming for complete dissolution of stearic acid.

7.10.2—After the hexadecane and stearic acid have dissolved, transfer the solution to a 100-150 mL vial with fluoropolymer-lined cap. Mark the solution level on the vial and store in the dark at room temperature.
7.10.3—Immediately prior to use, verify the level on the vial and bring to volume with acetone, if required. Warm to redissolve all visible precipitate.

NOTE: If there is doubt of the concentration, remove 10.0 ± 0.1 mL with a volumetric pipet, place in a tared weighing pan, and evaporate to dryness in a fume hood. The weight must be 40 ± 1 mg. If not, prepare a fresh solution (Section 7.10.1).

7.11—Precision and recovery (PAR) standard--Using a pipet, spike 10.0 ± 0.1 mL of the hexadecane/stearic acid spiking solution (Section 7.10) into 950-1050 mL of reagent water to produce concentrations of approximately 20 mg/L each of hexadecane and stearic acid. The PAR standard is used for the determination of initial (Section 9.2.2) and ongoing (Section 9.6) precision and recovery.
7.12—The spiking solutions should be checked frequently for signs of degradation or evaporation using the test noted in Section 7.10.3, and must be replaced after six months, or sooner if degradation has occurred.

8.0 Sample Collection, Preservation, and Storage

8.1—Collect approximately one liter of representative sample in a glass bottle following conventional sampling practices (Reference 16.7), except that the bottle must not be pre-rinsed with sample before collection. To allow for potential QC failures, it is recommended that additional sample aliquots be collected.
8.1.1—If analysis is to be delayed for more than four hours, adjust the sample pH to less than 2 with HCl or H_2SO_4 solution (Section 7.2) at the time of collection, and refrigerate at 0-4C (40 CFR 136, Table II). To establish the volume of HCl or H_2SO_4 required, collect a separate aliquot, adjust the pH of this aliquot to less than 2 with acid, and add the volume of acid determined to each sample bottle prior to collection. Do not dip pH paper, a pH electrode, a stirring rod, or other materials into a sample that will be used for HEM or SGT-HEM determination because substances in the sample may adhere to these items.
8.1.2—If a sample is known or suspected to contain greater than 500 mg/L of extractable material, collect a proportionately smaller volume of sample (the volume required will depend upon the estimated amount of extractable material) in a glass bottle. Add a proportionately smaller amount of HCl or H_2SO_4 solution to the smaller sample if preservation is necessary.
8.2—Collect an additional one or two aliquots (1 L, additional smaller volume, or both) of a sample for each set of twenty samples or less for the matrix spike and, if used, the matrix spike duplicate.

NOTE: For those circumstances requiring the collection of multiple aliquots of one sample, each aliquot is to be collected in either of the following ways: 1) collect simultaneously in parallel, if possible, or 2) collect as grab samples in rapid succession.

8.3—The high probability that extractable matter may adhere to sampling equipment and result in measurements that are biased low precludes the collection of composite samples for determination of oil and grease. Therefore, samples must be collected as grab samples. If a composite measurement is required, individual grab samples collected at prescribed time intervals must be analyzed separately and the concentrations averaged. Alternatively, samples can be collected in the field and composited in the laboratory. For example, collect four individual 250-mL samples over the course of a day. In the laboratory, pour each 250-mL sample into the separatory funnel, rinse each of the four bottles (and caps) sequentially with 30 mL of n-hexane, and use the 30 mL of n-hexane for the extraction (Section 11.3).
8.4—All samples must be refrigerated at 0-4C from the time of collection until extraction (40 CFR 136, Table II).

8.5—All samples must be analyzed within 28 days of the date and time of collection (40 CFR 136, Table II).

9.0 Quality Control

9.1—Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 16.8). The minimum requirements of this program consist of an initial demonstration of laboratory capability, ongoing analyses of standards and blanks as a test of continued performance, and analysis of a matrix spike (MS) to assess recovery. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1—The laboratory shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2—In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve separations or lower the costs of measurements, provided that all performance specifications are met. These options include alternate extraction and concentration devices and procedures such as solid-phase extraction, continuous liquid-liquid extraction, and Kuderna-Danish concentration. Alternate determinative techniques, such as infrared spectroscopy or immunoassay, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for HEM and/or SGT-HEM in the sample of interest. Specificity is defined as producing results equivalent to the results produced by this method for analytical standards (Section 9.2.2) and, where applicable, environmental samples (Section 9.2.3), and that meet all of the QC criteria stated in this method.

9.1.2.1—Each time a modification is made to this method, the laboratory is required to repeat the IPR test in Section 9.2.2 to demonstrate that the modification produces results equivalent to or superior to results produced by this method. If the detection limit of the method will be affected by the modification, the laboratory must demonstrate that the MDL (40 CFR Part 136, Appendix B) is less than or equal to the MDL in this method or one-third the regulatory compliance limit, whichever is higher. If the modified method is to be used for compliance monitoring, the discharger/generator must also demonstrate that the modified method recovers an amount of HEM and/or SGT-HEM equivalent to the amount recovered by this method on each specific discharge/waste stream. The tests required for this equivalency demonstration are given in Section 9.2.3.

9.1.2.2—The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1—The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2—A listing of pollutant(s) measured (HEM and/or SGT-HEM).

9.1.2.2.3—A narrative stating reason(s) for the modification.

9.1.2.2.4—Results from all quality control (QC) tests comparing the modified method to this method, including:

- Calibration (Section 10).
- Calibration verification (Section 9.5).
- Initial precision and recovery (Section 9.2.2).
- Analysis of blanks (Section 9.4).
- Accuracy assessment (Section 9.3).
- Ongoing precision and recovery (Section 9.6).
- Method detection limit (Section 9.2.1).

9.1.2.2.5—Data that will allow an independent reviewer to validate each determination by tracing the instrument output (weight or other signal) to the final result. These data are to include:

- Sample numbers and other identifiers.

- Extraction dates.
- Analysis dates and times.
- Analysis sequence/run chronology.
- Sample weight or volume (Section 11.1.4).
- Extract volume for SGT-HEM (Section 11.5.2).
- Make and model of analytical balance and weights traceable to NIST.
- Copies of logbooks, printer tapes, and other recordings of raw data.
- Data system outputs, and other data to link the raw data to the results reported.

9.1.3—Analysis of a matrix spike (MS) is required to demonstrate recovery and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Section 9.3.

9.1.4—Analyses of laboratory blanks are required to demonstrate freedom from contamination. The procedure and criteria for analysis of a blank are described in Section 9.4.

9.1.5—The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery (OPR) sample that the analysis system is in control. These procedures are described in Sections 9.5 and 9.6, respectively.

9.1.6—The laboratory should maintain records to define the quality of data that is generated. Development of accuracy statements is described in Sections 9.3.7 and 9.6.3.

9.1.7—Accompanying QC for the determination of HEM and/or SGT-HEM is required per analytical batch. For the definition of an analytical batch, see the glossary at the end of this method.

9.2—Initial demonstration of laboratory capability.

9.2.1—Method Detection Limit (MDL)--To establish the ability to detect HEM and SGT-HEM, the laboratory shall determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL in Section 1.6 or less than 1/3 the regulatory compliance limit must be achieved prior to the practice of this method.

9.2.2—Initial precision and recovery (IPR)--To establish the ability to generate acceptable precision and accuracy, the laboratory shall perform the following operations:

9.2.2.1—Determine the concentration of HEM and/or SGT-HEM in four samples of the PAR standard (Section 7.11) according to the procedure beginning in Section 11.

9.2.2.2—Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for HEM and for SGT-HEM (if determined). When determining SGT-HEM, the true concentration (T) must be divided by 2 to reflect the concentration of hexadecane that remains after removal of stearic acid. Use the following equation for calculation of the standard deviation of the percent recovery:

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n - 1}}$$

where:
n = Number of samples
x = % Recovery in each sample

9.2.2.3—Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

9.2.3—Equivalency demonstration for application of a method modification to

compliance monitoring--To establish the ability of a modification of this method to recover an amount of HEM and/or SGT-HEM equivalent to the amount recovered by this method from a specific discharge/waste stream, proceed as follows:

9.2.3.1—Collect, extract, concentrate, and weigh the HEM or SGT-HEM in two sets of four aliquots of unspiked wastewater. One set of four wastewater aliquots is analyzed according to the protocol in Section 11 of this method and the other set of four aliquots is analyzed using the modified method.

9.2.3.2—Calculate the average concentration of HEM and SGT-HEM for the set of results from this method and for the set of results from the modified method. The average concentration using the modified method must be 78 to 114 percent of the average concentration produced by this method for HEM and 64 to 132 percent of the average concentration produced by this method for SGT-HEM. If not, the modified method may not be used.

NOTE: If the average concentration of the four results produced using this method and the average concentration of the four results produced using the modified method are below the minimum level (Section 1.6), and if the equivalency test of the modified method is passed for spikes of reference standards into reagent water (Section 9.2.2), the modified method is deemed to be equivalent to this method for determining HEM and or SGT-HEM on that specific discharge/waste stream.

9.3—Matrix spikes--The laboratory must spike a minimum of 5 percent of all samples from a given sampling site or, if for compliance monitoring, from a given discharge/waste stream (matrix spike). The sample aliquot shall be spiked with the hexadecane/stearic acid spiking solution (Section 7.10). A duplicate matrix spike (MSD) is recommended but not required.

9.3.1—The concentration of the spike in the sample shall be determined as follows:

9.3.1.1—If, as in compliance monitoring, the concentration of HEM or SGT-HEM in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit, at 1 to 5 times the background concentration of the sample (determined in Section 9.3.2), or at the concentration of the OPR (Section 9.4), whichever concentration is highest.

9.3.1.2—If the concentration of HEM or SGT-HEM in a sample is not being checked against a limit, the spike shall be at the concentration of the precision and recovery standard (Section 7.11) or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2—Analyze one sample aliquot out of each set of 20 samples from each site or discharge/waste stream according to the procedure beginning in Section 11 to determine the background concentration (B) of HEM or SGT-HEM.

9.3.2.1—If necessary, prepare a standard solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

NOTE: Samples containing high concentrations (

100 mg /L) of HEM will require a large volume of spiking solution (Section 7.10) for the MS (and MSD). If the concentration of HEM is expected to exceed 1000 mg/L, smaller sample volumes should be collected for the background measurement and MS (and MSD) so that the amount of HEM plus the amount spiked does not exceed 1000 mg/L.

9.3.2.2—Spike the additional sample aliquot(s) with the spiking solution and analyze the aliquot(s) to determine the concentration after spiking (A).

9.3.3—Calculate the percent recovery (P) of HEM or SGT-HEM in each aliquot using the following equation:

Equation 2

$$P = \frac{100\ (A - B)}{T}$$

where:

A = Measured concentration of analyte after spiking

B = Measured background concentration of HEM or SGT-HEM

T = True concentration of the spike

When determining SGT-HEM, the true concentration (T) must be divided by 2 to reflect the concentration of hexadecane that remains after removal of stearic acid.

9.3.4—Compare the percent recovery of the HEM or SGT-HEM with the corresponding QC acceptance criteria in Table 1.

9.3.4.1—If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria in Table 1, an interference is present. In this case, the result may not be reported or used for purposes regulatory compliance purposes and the laboratory must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge/waste stream should be resampled. If the interference is attributable to a matrix problem, the laboratory must modify the method, repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS (and MSD, if performed). Most matrix interference problems are attributable to the formation of emulsions in the extraction. Section 11.3.5 provides suggestions for overcoming emulsion problems.

9.3.4.2—If the results of both the spike and the ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample batch reanalyzed. All samples must be associated with a valid MS (and MSD, if performed).

9.3.5—If an MSD was analyzed, compute the relative percent difference (RPD) between the MS and MSD (not between the two recoveries) using the following equation:

Equation 3

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

D_1 = Concentration of HEM or SGT-HEM in the sample

D_2 = Concentration of HEM or SGT-HEM in the second (duplicate) sample

9.3.6—The relative percent difference for duplicates shall meet the acceptance criteria in Table 1. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed.

9.3.7—As part of the QC program for the laboratory, it is suggested that method precision and accuracy for samples be assessed and records maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if P_a = 90% and s_p = 10% for five analyses of HEM or SGT-HEM, the accuracy interval is expressed as 70-110%. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.4—Laboratory blanks--Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1—Extract and concentrate a laboratory reagent water blank initially (i.e. with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.4.2—If material is detected in the blank at a concentration greater than the minimum level (Section 1.6), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.5—Calibration verification--Verify calibration of the balance per Section 10 before and after each analytical batch. If calibration is not verified after measurement of the analytical batch, recalibrate the balance and reweigh the batch.

9.6—Ongoing precision and recovery--To demonstrate that the analysis system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the laboratory shall perform the following operations:

9.6.1—Extract and concentrate a precision and recovery standard (Section 7.11) with each analytical batch according to the procedure beginning in Section 11.

9.6.2—Compare the recovery with the limits for ongoing precision and recovery in Table 1. If the recovery is in the range specified, the extraction, distillation, and weighing processes are in control and analysis of blanks and samples may proceed. If, however, the recovery is not in the specified range, the analytical process is not in control. In this event, correct the problem, re-extract the analytical batch, and repeat the ongoing precision and recovery test.

9.6.3—The laboratory should add results that pass the specification in Section 9.6.2 to IPR and previous OPR data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for each analyte by calculating the average percent recovery (R) and the standard deviation of the percent recovery (s_r). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if R = 95% and s_r = 5%, the accuracy is 85% to 105%.

9.7—Quality control sample (QCS)--It is suggested that the laboratory obtain a QCS from a source different from the source for the hexadecane and stearic acid used routinely in this method (Sections 7.8 and 7.9), and that the QCS be used for verification of the concentrations of HEM and SGT-HEM using the procedure given in the note in Section 7.10.3. The QCS should be analyzed monthly by laboratories performing routine analyses and less frequently by laboratories performing these analyses intermittently.

9.8—The specifications contained in this method can be met if the apparatus used is scrupulously cleaned and dedicated for the determination of HEM and SGT-HEM. The standards used for initial precision and recovery (IPR, Section 9.2.2), matrix spike (MS, Section 9.3), and ongoing precision and recovery (OPR, Section 9.6) should be identical, so that the most precise results will be obtained.

9.9—Depending upon specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10.0 Calibration and Standardization

10.1—Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights.

10.2—Calibration shall be within ± 10% (i.e. ±0.2 mg) at 2 mg and ± 0.5% (i.e. ±5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

11.0 Procedure This method is entirely empirical. Precise and accurate results can be obtained only by strict adherence to all details.

NOTE: The procedure below is based on the preparation, extraction, and analysis of a 1-L sample. If a smaller volume is collected for analysis, the laboratory should dilute the sample to 1 L with reagent water so that results across the IPR, blank, OPR, MS, and, if performed, the MSD, are consistent. It is also important that all glassware surfaces be rinsed with n-hexane to effect a quantitative transfer of the constituents in the sample and of the

hexadecane/stearic acid in the IPR, OPR, MS, and, if performed, the MSD.

11.1—Preparation of the analytical batch.
11.1.1—Bring the analytical batch of samples, including the sample aliquots for the MS (and MSD), to room temperature.
11.1.1—Place approximately 1000 mL (950-1050 mL) of reagent water (Section 7.1) in a clean sample bottle to serve as the laboratory blank.
11.1.3—Prepare the OPR (Section 9.6) using the PAR standard (Section 7.11).
11.1.4—Either mark the sample bottle at the water meniscus or weigh the bottle for later determination of sample volume. Weighing will be more accurate. Mark or weigh the MS (and MSD).

11.2—pH verification.
11.2.1—Verify that the pH of the sample is less than 2 using the following procedure:
11.2.1.1—Dip a glass stirring rod into the well mixed sample.
11.2.1.2—Withdraw the stirring rod and allow a drop of the sample to fall on or touch the pH paper.

NOTE: Do not dip the pH paper into the bottle or touch it to the sample on the lid.

11.2.1.3—Rinse the stirring rod with a small portion of n-hexane that will be used for extraction (to ensure that no extractable material is lost on the stirring rod). Collect the rinsate in the separatory funnel to be used for sample extraction.
11.2.2—If the sample is at neutral pH, add 5-6 mL of HCl or H_2SO_4 solution (Section 7.2) to the 1-L sample. If the sample is at high pH, use a proportionately larger amount of HCl or H_2SO_4 solution. If a smaller sample volume was collected, use a proportionately smaller amount of HCl or H_2SO_4 solution.
11.2.3—Replace the cap and shake the bottle to mix thoroughly. Check the pH of the sample using the procedure in Section 11.2.1. If necessary, add more acid to the sample and retest.
11.2.4—Add the appropriate amount of HCl or H_2SO_4 solution to the blank, OPR, MS (and MSD) to adjust the pH of these solutions to <2.

NOTE: The procedure detailed below is for separatory funnel liquid-liquid extraction. Solid-phase extraction (SPE) may be used at the discretion of the discharger/generator and its laboratory. However, if SPE is used, it is the responsibility of the discharger/generator and laboratory to assure that results produced are equivalent to results produced by the procedure below.

11.3—Extraction
11.3.1—Tare a clean boiling flask containing 3-5 boiling chips as follows:
11.3.1.1—Place the flask containing the chips in an oven at 105-115 C for a minimum of 2 h to dry the flask and chips.
11.3.1.2—Remove from the oven and immediately transfer to a desiccator to cool to room temperature.
11.3.1.3—When cool, remove from the desiccator with tongs and weigh immediately on a calibrated balance (Section 10).
11.3.2—Pour the sample into the separatory funnel.
11.3.3—Add 30 mL of n-hexane to the sample bottle and seal the bottle with the original bottle cap. Shake the bottle to rinse all interior surfaces of the bottle, including the lid of the bottle cap. Pour the solvent into the separatory funnel.
11.3.4—Extract the sample by shaking the separatory funnel vigorously for 2 minutes with periodic venting into a hood to release excess pressure.
11.3.5—Allow the organic phase to separate from the aqueous phase for a minimum of 10 minutes. If an emulsion forms between the phases and the emulsion is greater than one-third the volume of the solvent layer, the laboratory must employ emulsion-breaking techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of solvent phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase extraction (SPE), continuous liquid-liquid extraction, or other extraction techniques may be used to prevent emulsion

formation, provided that the requirements in Section 9.1.2 are met.
11.3.6—Drain the aqueous layer (lower layer) into the original sample container. Drain a small amount of the organic layer into the sample container to minimize the amount of water remaining in the separatory funnel.

NOTE: The amount of water remaining with the n-hexane must be minimized to prevent dissolution or clumping of the sodium sulfate in the solution drying process.

11.3.7—Place a filter paper (Section 6.5.2) in a filter funnel (Section 6.5.1), add approximately 10 g of anhydrous Na_2SO_4, and rinse with a small portion of n-hexane. Discard the rinsate.

NOTE: The specific properties of a sample may necessitate the use of larger amounts of Na_2SO_4.

11.3.8—Drain the n-hexane layer (upper layer) from the separatory funnel through the Na_2SO_4 into the pre-weighed boiling flask containing the boiling chips (Section 11.3.1.3).

NOTE: It is important that water be removed in this step. Water allowed to filter through the Na_2SO_4 will dissolve some of the Na_2SO_4 and carry it into the boiling flask compromising the determination.

11.3.9—Repeat the extraction (Sections 11.3.3-11.3.6 and 11.3.8) twice more with fresh 30-mL portions of n-hexane, combining the extracts in the boiling flask.
11.3.10—Rinse the tip of the separatory funnel, the filter paper, and the funnel with 2-3 small (3-5 mL) portions of n-hexane. Collect the rinsings in the flask.

NOTE: For samples that are expected to contain a high concentration of salt (e.g., waters from oil production facilities), it may be prudent to collect the extract in a 250-mL separatory funnel and back-extract with reagent water. After back-extraction, the extract should be drained through Na_2SO_4 to remove all traces of water.

11.3.11—A milky extract indicates the presence of water. If the extract is milky, allow the solution to stand for up to one hour to allow the water to settle. Decant the solvent layer (upper layer) through sodium sulfate to remove any excess water as in Sections 11.3.7 and 11.3.8. Rinse the glassware and sodium sulfate with small portions of n-hexane to effect a quantitative transfer.
11.3.12—If only SGT-HEM is to be determined, proceed to Section 11.5.
11.4—Solvent distillation.
11.4.1—Connect the boiling flask to the distilling head apparatus and distill the solvent by immersing the lower half of the flask in a water bath or a steam bath. Adjust the water temperature as required to complete the concentration in less than 30 minutes. Collect the solvent for reuse.
11.4.2—When the temperature in the distilling head reaches approximately 70C or the flask appears almost dry, remove the distilling head. Sweep out the flask for 15 seconds with air to remove solvent vapor by inserting a glass tube connected to a vacuum source. Using tongs, immediately remove the flask from the heat source and wipe the outside surface dry to remove moisture and fingerprints.

NOTE: The laboratory should carefully monitor the flask during the final stages of distillation to assure that all of the solvent is removed and to prevent loss of the more volatile sample constituents.

11.4.3—Inspect the residue in the boiling flask for crystals. Crystal formation is an indication that sodium sulfate may have dissolved and passed into the boiling flask. This may happen if the drying capacity of the sodium sulfate is exceeded or if the sample is not adjusted to low pH. If crystals are observed, redissolve the extract in n-hexane, quantitatively transfer through a filter into another tared boiling flask, and repeat the distillation procedure (Sections 11.4.1-11.4.2).
11.4.4—Dry the boiling flask for 30 - 45 minutes in an oven maintained at 70 ± 2 C. Cool to room temperature in a desiccator and maintain in the desiccator for 30 minutes minimum. Remove with tongs and weigh immediately. Repeat the cycle of drying, cooling, desiccating, and weighing until the weight loss is less than 4 % of the previous

weight or less than 0.5 mg, whichever is less.

11.4.4.1—If the extract was from the HEM procedure, determine the HEM (W_h) by subtracting the tare weight (Section 11.3.1) from the total weight of the flask.

11.4.4.2—If the extract was from the SGT-HEM procedure (Section 11.5.5); determine the weight of SGT-HEM (W_s) by subtracting the tare weight from the total weight of the flask.

11.4.5—Determine the original sample volume (V_s) in liters by filling the sample bottle to the mark with water and measuring the volume of water in a 1- to 2-L graduated cylinder. If the sample weight was used (Section 11.1.4), weigh the empty bottle and cap and determine V_s by difference, assuming a sample density of 1.00.

11.5—SGT-HEM determination.

11.5.1—Silica gel capacity--To ensure that the capacity of the silica gel will not be exceeded, the amount of HEM must be less than 100 mg or, if above 100 mg, must be known.

11.5.1.1—If it is known that the amount of HEM is less than 100 mg, the laboratory may proceed with the determination of SGT-HEM per Sections 11.5.3-11.5.5 without determination of HEM.

11.5.1.2—If, however, the amount of HEM is not known, HEM must first be determined using the procedure in Sections 11.3-11.4.

11.5.2—Extractable materials in silica gel--Because the capacity of silica gel is not known for all substances, it is presumed that 3 g will normally adsorb 100 mg of all adsorbable materials. Therefore, for samples containing 1000 mg HEM, 30 g of silica gel will be needed. The amount of silica gel that can be used for adsorption in the SGT-HEM procedure below has been limited to 30 g because of concerns about possible extractable impurities in the silica gel. If the amount of HEM in the sample is greater than 1000 mg, split the extract per the following procedure:

11.5.2.1—Add 85-90 mL of n-hexane to the boiling flask to redissolve the HEM. If necessary, warm the solution to completely redissolve the HEM.

11.5.2.2—Quantitatively transfer the extract to a 100-mL volumetric flask. Dilute to the mark with n-hexane.

11.5.2.3—Calculate the extract volume that contains 1000 mg of extractable material according to the following equation:

Equation 4

$$V_a = \frac{1000\ V_t}{W_h}$$

where:

V_a = *Volume of aliquot to be withdrawn (mL)*

V_t = *Total volume of solvent used in Section* 11.5.2.2 *(mL)*

W_h = *Weight of extractable material HEM measurement (mg)*

11.5.2.4—Using a calibrated pipet, remove the volume to be withdrawn (V_a) and return to the boiling flask. Dilute to approximately 100 mL with n-hexane.

11.5.3—Adsorption with silica gel

11.5.3.1—Add 3.0 ± 0.3 g of anhydrous silica gel (Section 7.7) to the boiling flask for every 100 mg of HEM, or fraction thereof, to a maximum of 30 g of silica gel. For example, if the weight of HEM is 735 mg, add 3 x 8 = 24 g of silica gel.

11.5.3.2—Add a fluoropolymer-coated stirring bar to the flask and stir the solution on a magnetic stirrer for a minimum of 5 minutes.

11.5.4—Filter the solution through n-hexane moistened filter paper into a pre-dried, tared boiling flask containing several boiling chips. Rinse the silica gel and filter paper with several small amounts of n-hexane to complete the transfer.

11.5.5—Distill the solution and determine the weight of SGT-HEM per Section 11.4.

12.0 Data Analysis and Calculations

12.1—n-Hexane extractable material--Calculate the concentration of HEM ("oil and grease") in the sample per the following equation:

Equation 5

$$HEM\ (mg/L) = \frac{W_h\ (mg)}{V_s\ (L)}$$

where:

W_h = *Weight of extractable material from Section* 11.4.4.1 *(mg)*

V_s = *Sample volume from Section* 11.4.5 *(L)*

12.2—Silica gel treated n-hexane extractable material--Calculate the concentration of SGT-HEM ("non-polar material") in the sample per the equation above, substituting W_s (from Section 11.4.4.2) for W_h. If the extract was split to decrease the total amount of material to 1,000 mg, determine the corrected total weight of SGT-HEM in the un-split extract (W_c) using the following equation:

Equation 6

$$W_c\ (mg) = \frac{V_t}{V_a}\ W_d\ (mg)$$

where:

W_d = *Weight in the portion of the extract split for adsorption (Sections* 11.5.2.4 *and* 11.4.4.2*)*

V_t *and* V_a *are as defined in Equation 4*

Use the corrected total weight of SGT-HEM in the unsplit extract (W_c) to determine the total SGT-HEM in the sample by substituting W_c for W_h in Equation 5.

12.3—Reporting--Report results to three significant figures for HEM and SGT-HEM found at or above 10 mg/L, and report results to two significant figures for HEM and SGT-HEM found below 10 mg/L.

12.3.1—Samples--Report results for HEM and SGT-HEM found below the ML as < 5.0 mg/L, or as required by the permitting authority or permit.

12.3.2—Blanks--Report results for HEM and SGT-HEM found below the MDL as < 1.4 mg/L, or as required by the permitting authority or permit. Do not report results below the MDL unless required by the permitting authority or permit.

12.3.3—Results from tests performed with an analytical system that is not in control (Section 9) must not be reported or otherwise used for permitting or regulatory compliance purposes but do not relieve a discharger or permittee of timely reporting.

13.0 Method Performance

13.1—This method was validated through single laboratory studies and an inter-laboratory method validation study (Reference 16.9). Combined data from these studies show an average recovery of 93 percent for HEM and 89 percent for SGT-HEM and precision (as relative standard deviation) of 8.7 percent for HEM and 13 percent for SGT-HEM.

13.2—The method detection limit (MDL) and minimum level of quantitation (ML) are based on five studies conducted by EPA and described at proposal of Method 1664 (61 FR 1730) and as verified by data submitted in comments on the proposal of Method 1664 (Reference 16.3).

14.0 Pollution Prevention

14.1—The solvents used in this method pose little threat to the environment when recycled and managed properly.
14.2—Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.0 Waste Management

15.1—It is the laboratory's responsibility to comply with all Federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.
15.2—Samples preserved with HCl or H_2SO_4 to pH < 2 are hazardous and must be neutralized before being disposed, or must be handled as hazardous waste.
15.3—For further information on waste management, consult "The Waste Management Manual for Laboratory Personnel," and "Less is Better: Laboratory Chemical Management for Waste Reduction," both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

16.0 References

16.1—"Methods for Chemical Analysis of Water and Wastes," 3rd Edition, Environmental Protection Agency, Environmental Monitoring Systems Laboratory-Cincinnati (EMSL-Ci), Cincinnati, Ohio 45268, EPA-600/4-79-020, Method 413.1, (1983).
16.2—Ibid., Method 418.1
16.3—Guidelines Establishing Test Procedures for the Analysis of Oil and Grease and Non-polar Materials; Final Rule; Preamble, Responses to Comments, and Docket, as referenced in the Final Rule.
16.4—"Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
16.5—"OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
16.6—"Safety in Academic Chemistry Laboratories," American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.
16.7—"Standard Practices for Sampling Water," ASTM Annual Book of Standards, Part 31, D3370-76, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103-1187, 1980.
16.8—"Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL-Ci, Cincinnati, OH 45268, EPA-600/4-79-019, March 1979.
16.9—*Report of the Method 1664 Validation Studies*, April 1995. Available from the Sample Control Center (operated by DynCorp I&ET), 6101 Stevenson Avenue, Alexandria, VA 22304, (703) 461-2100.

17.0 Table 1. Acceptance Criteria for Performance Tests

Acceptance Criterion	Section	Limit (%)
Initial precision and recovery	9.2.2	
HEM Precision (s)	9.2.2.2	11
HEM Recovery (X)	9.2.2.2	83-101

SGT-HEM Precision (s)	9.2.2.2	28
SGT-HEM Recovery (X)	9.2.2.2	83-116
Matrix spike/matrix spike duplicate	9.3	
HEM Recovery	9.3.4	78-114
HEM RPD	9.3.5	18
SGT-HEM Recovery	9.3.4	64-132
SGT-HEM RPD	9.3.5	34
Ongoing precision and recovery	9.6	
HEM Recovery	9.6	78-114
SGT-HEM Recovery	9.6	64-132

18.0 Glossary of Definitions and Purposes

The definitions and purposes are specific to this method but have been conformed to common usage to the extent possible.

18.1—Units of weight and measure and their abbreviations
18.1.1—Symbols
C degrees Celsius
< less than
% percent
± plus or minus
18.1.2—Alphabetical characters
g gram
h hour
L liter
mg milligram
mg/g milligram per gram
mg/L milligram per liter
mg/mL milligram per milliliter
mL milliliter
No. number
rpm revolutions per minute
18.2—Definitions, acronyms, and abbreviations
18.2.1—Analyte: The HEM or SGT-HEM determined by this method.
18.2.2—Analytical batch: The set of samples started through the extraction process in a 12-hour shift, to a maximum of 20 field samples. Each analytical batch of 20 or fewer samples must be accompanied by a laboratory blank (Section 9.4), an ongoing precision and recovery sample (OPR, Section 9.6), and a matrix spike, (Section 9.3), resulting in a minimum of four analyses (1 sample, 1 blank, 1 OPR, and 1 MS) and a maximum of 23 analyses (20 field samples, 1 blank, 1 OPR, and 1 MS) in the batch. If greater than 20 samples are to be extracted in a 12-hour shift, the samples must be separated into analytical batches of 20 or fewer samples.
18.2.3—Discharge (matrix type): A sample medium with common characteristics across a given industrial subcategory (40 CFR parts 403-500). For example, C-stage effluents from chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category; effluent from the Continuous Casting subcategory of the Iron and Steel industrial category; publicly owned treatment work (POTW) sludge; and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory are

each a matrix type.
18.2.4—Field blank: An aliquot of reagent water that is placed in a sample container in the laboratory or in the field and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.
18.2.5—HEM: See n-Hexane extractable material.
18.2.6—n-Hexane extractable material: Material that is extracted from a sample and determined by this method (oil and grease). This material includes relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.
18.2.7—IPR: See initial precision and recovery.
18.2.8—Initial precision and recovery (IPR): Four aliquots of the diluted PAR analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method is modified.
18.2.9—Laboratory blank (method blank): An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.
18.2.10—Laboratory control sample (LCS): See Ongoing precision and recovery standard (OPR).
18.2.11—Matrix spike (MS) and matrix spike duplicate (MSD): Aliquots of an environmental sample to which known quantities of the analytes are added in the laboratory. The MS and MSD are prepared and/or analyzed exactly like a field sample. Their purpose is to quantify any additional bias and imprecision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations.
18.2.12—May: This action, activity, or procedural step is neither required nor prohibited.
18.2.13—May not: This action, activity, or procedural step is prohibited.
18.2.14—Method Detection Limit: The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.
18.2.15—Minimum Level (ML): The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.
18.2.16—Must: This action, activity, or procedural step is required.
18.2.17—Ongoing precision and recovery standard (OPR, also called a laboratory control sample): A laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and accuracy.
18.2.18—OPR: See ongoing precision and recovery standard.
18.2.19—PAR: See precision and recovery standard.
18.2.20—Precision and recovery standard: Secondary standard that is diluted and spiked to form the IPR and OPR.
18.2.21—Quality control sample (QCS): A sample containing analytes of interest at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.
18.2.22—Quantitative transfer: The process of transferring a solution from one container to another using a pipet in which as much solution as possible is transferred, followed by rinsing of the walls of the source container with a small volume of rinsing solution (e.g., n-hexane), followed by transfer of the rinsing solution, followed by a second and third rinse and transfer.
18.2.23—Reagent water: Water demonstrated to be free from HEM and SGT-HEM and

potentially interfering substances at or above the minimum level of this method.
18.2.24—Regulatory Compliance Limit: A limit on the concentration or amount of a pollutant or contaminant specified in a nationwide standard, in a permit, or otherwise established by a regulatory authority.
18.2.25—SGT-HEM: See Silica gel treated n-hexane extractable material.
18.2.26—Should: This action, activity, or procedural step is suggested but not required.
18.2.27—Silica gel treated n-hexane extractable material: Components of n-Hexane extractable material (HEM) that are not adsorbed by silica gel; i.e., non-polar material (NPM).
18.2.28—Stock solution: A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Acknowledgements

This method was prepared under the direction of William A. Telliard of the Engineering and Analysis Division within EPA's Office of Water. This document was prepared under EPA Contract No. 68-C-98-139 by DynCorp Information and Enterprise Technology.

Disclaimer

This method has been reviewed by the Engineering and Analysis Division, U.S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use.

American Refining Group, Inc. 77 N. Kendall Ave., Bradford, PA 16701

CERTIFIED MAIL #7004 2890 0004 5919 0301
Return Receipt Requested

RECEIVED
JUN 04 2010
ENVIRONMENTAL PROTECTION
NORTHWEST REGIONAL OFFICE

June 2, 2010

Mr. Adam Pesek
Water Management
PA Department of Environmental Protection
230 Chestnut Street
Meadville, PA 16335

Reference: American Refining Group
Proposed NPDES Permit PA0002674

Dear Mr. Pesek:

American Refining Group, Inc. has reviewed the PA Department of Environmental Protection's proposed draft of NPDES Permit PA0002674 for the American Refining Group Bradford refinery wastewater/stormwater outfalls that was published in the May 8, 2010 Pennsylvania Bulletin, and we offer the following comment(s):

1. A review of the draft permit reveals that language including "(c)ontaminated groundwater from groundwater recovery operations (both horizontal and vertical wells)" was removed from the description of Outfall 002 at the previous request of ARG. PADEP states that the permit can be revised if ARG needs to send groundwater from recovery operations to the WWTP. ARG now requests that the draft permit be revised to place the language regarding contaminated groundwater from groundwater recovery operations back in the permit for Outfall 002. While there is a separate treatment plant at the site currently operated by Chemtura for the treatment of contaminated groundwater from Chemtura wells, there is also contaminated groundwater being trucked by ARG from ARG wells and discharged into the MEK Unit Separator upstream of the wastewater treatment plant on Outfall 002. Thus, processed contaminated groundwater from site remedial operations is currently discharged via Outfall 002. In the event that ARG directly ties any groundwater recovery wells into the ARG wastewater treatment plant in the future, PADEP will be notified.

2. ARG wishes to explore with the Department the possibility of adding a daily or weekly Oil and Grease concentration limit to Outfalls 002 and 004 at the refinery.

3. The monitoring waiver for hex chrome, total chrome, and phenolics has been extended in the draft permit; however, the effluent limitations for each have significantly decreased as follows:

   a. Outfall 002 average monthly hex chrome decreased from 0.195 to 0.11 lbs/day.
   b. Outfall 002 daily max. hex chrome decreased from 0.429 to 0.24 lbs/day.
   c. Outfall 002 average monthly total chrome decreased from 3.08 to 1.3 lbs/day.
   d. Outfall 002 daily max. total chrome decreased from 5.3 to 3.7 lbs/day.
   e. Outfall 002 average monthly total phenolics decreased from 1.17 to 0.34 lbs/day.
   f. Outfall 002 daily max. total phenolics from 2.6 to 0.68 lbs/day.

   It is not clear to ARG why these loadings decreased so significantly; however, it appears that one reason why the allowable loadings are so low is that the Department was not initially provided with all of the different processes at the refinery for which loadings should be allocated. Please consider the allowable loading associated with each of the refinery processes that are identified in the list included with this letter as Exhibit 1. Likewise, crude distillation and crude desalting appear to have been improperly combined into a single process by the Department and given a single allocation for permitting purposes. Please contact me directly to work to review the various ARG processes, properly categorize each process and identify the correct wastewater limits that should be associated with each.

4. Outfall 002 now has a weekly fecal coliform sampling requirement that has been added for the period from May 1 through September 30. The draft permit states that"(e)ffective disinfection to control disease producing organisms from the period May 1 to September 30 shall be the production of an effluent which will contain a concentration not greater than 200/100 ml of fecal coliform colonies as a geometric mean, nor greater than 1,000/100 ml of these colonies in more than 10 percent of the samples tested." ARG is currently working to identify the source of fecal coliforms that have been identified in testing of Outfall 002. ARG has begun upstream sampling, but to date we have been unable to locate the source of the fecal coliforms. Because fecal coliforms are not believed to be associated with any of the processes in use at ARG, we are requesting a compliance schedule to allow ARG adequate time to continue trying to identify the source of the coliforms, and if it involves an improper sanitary connection, to remove it from our industrial discharge or otherwise treat it at the source to comply with the proposed permit limits.

5. The Outfall 004 description has been changed from "Foster Brook Refinery operations and stormwater" to "NCCW, boiler blowdown and stormwater." This change has significant implications due to the 5 mg/l Total Organic Carbon (TOC) limit that is imposed on "once through cooling water." A review of Outfall 004 reveals that while it contains stormwater and condensate, it does not contain any non-contact cooling water. Because Outfall 004 does not have any non-contact cooling water discharging to it, the proposed 5 mg/l TOC limit, and the daily maximum loading and instantaneous concentration TOC limits calculated from it, are inappropriate. Because this Outfall is

comprised almost entirely of stormwater and a small steady flow of steam condensate, ARG is requesting that a stormwater TOC limit of 110 mg/l be applied to Outfall ~~002.~~ 004 This limit would be consistent with the BPTs for contaminated stormwater. (40 CFR § 419.12(e)(1)).

As we have discussed recently, ARG has arranged to remove the sole significant source of industrial wastewater to Outfall 004 (the crude railcar unloading spill collection pans), and this Outfall should now qualify for effluent limits based solely upon the stormwater contribution. It is currently planned that the flow from the crude railcar unloading pans, which is currently directed to a subsurface collection sump and pumped to the separator in Outfall 004, will instead be pumped from the collection sump to an above ground storage tank. The storage tank will be routinely emptied by a vac truck and the wastewater/oil that is collected will be taken to the MEK Separator for treatment. The water from the MEK Separator then flows through the facility wastewater treatment plant and discharges at Outfall 002. In the event that the final NPDES permit is issued prior to the completion of the project to install the storage tank, ARG personnel will use a vac truck to pump the oil/wastewater directly from the subsurface collection sump to the MEK Separator until a permanent solution is in place.

6. The ARG Fact Sheet states that the total phenolics limit on Outfall 002 is ELG based, but it appears that value is actually a water quality based limit. For this reason, the fact sheet should be corrected to state that the total phenolics limit is based on the Water Quality Based Effluent Limits (WQBELs).

Please include this comment letter as part of the official administrative record relating to the above-referenced NPDES permit. If you have any questions, problems, or would like additional information or documentation regarding the above comments, please contact us at any time.

Sincerely,
American Refining Group, Inc.

Jason L. Goodling

Jason L. Goodling
Environmental Manager

Exhibit #1
Processes to be Included in the Determination of BAT Effluent Limitations for Total Chromium, Hexavalent Chromium, and Phenolic Compounds (Appendix A to Part 419)

1. Crude Processes
    a. Atmospheric Crude Distillation
    b. Crude Desalting
2. Cracking and Coking Processes
    a. Hydrotreating-Naphtha Unifiner
    b. Hydrotreating-Diesel/Lube Hydrotreater
3. Lube Processes
    a. Hydrofinishing
    b. Propane Deresining
    c. Solvent Extraction
    d. MEK-Toluene Dewaxing
    e. Deoiling-note that we discontinued deoiling operations in 2009 but still have the ability to perform the operation
4. Reforming and Alkylation Processes
    a. Catalytic Reforming
5. Other ARG processes for which no specific category is provided in 40 CFR Part 419 Appendix A
    a. Isomerization Unit
    b. LO-CAT Fuel Gas Desulfurization Unit
    c. Naphtha Fractionation Towers

5/18/10 ARG Initial Comments to PADEP NPDES Draft

[redacted] The IMAX footnote stating "The instantaneous maximum discharge limitations are for compliance use by DEP only. Do not report instantaneous maximums on the DMRS or supplemental DMRs unless specifically required on those forms to do so." has been omitted. ARG wishes to have the footnote included in the new permit. Do we need to take any steps beyond formally commenting on this? If so, what steps [redacted]

[redacted] writers will record IMAX limits on DEP-issued DMRs and in NMS and Central Office will record IMAX limits on EPA pre-print DMRs and in NMS if all of the following are met: [redacted]

[redacted] There is a grab sample requirement in the permit.

[redacted] There is no average weekly limit, maximum daily limit, or other limit between the statistical basis [redacted] average monthly and IMAX.

[redacted] Sampling frequency for the parameter is at least weekly.

[redacted] Regional offices may, at their discretion, 1) place IMAX limits for parameters with less frequent monitoring on paper DMRs and in NMS and 2) include both maximum daily and IMAX limits on paper DMRs. (Note - placing IMAX limits in the Conc. 3 field will result in the value being displayed on [redacted]

[redacted]

[redacted]

[redacted]

[redacted] 002 Loading and concentration limits have increased. Did these numbers increase because we are no longer allocating any loading to 004 (everything is now attributed to 002)? [redacted]

3.

a. 002 Average monthly BOD limit increased from 180 to 189 lbs/day.
b. 002 Daily max. BOD limit increased from 345 to 355 lbs/day.
c. 002 BOD IMAX concentration increased from 115 to 286 mg/l.
d. 002 Average monthly COD limit increased from 920 to 947 lbs/day.
e. 002 Daily max. COD limit increased from 1780 to 1832 lbs/day.
f. 002 COD IMAX concentration increased from 610 to 1435 mg/l.
g. 002 Average monthly TSS limit increased from 155 to 160 lbs/day.

h. 002 Daily max. TSS limit increased from 240 to 249 lbs/day.
i. 002 TSS IMAX concentration increased from 100 to 243 mg/l.
j. 002 Average monthly O&G limit increased from 56 to 57 lbs/day.
k. 002 Daily max. O&G limit increased from 105 to 111 lbs/day.
l. 002 Average monthly ammonia limit increased from 19 to 20 lbs/day.
m. 002 Daily max. ammonia limit increased from 42 to 44 lbs/day.
n. 002 Ammonia IMAX concentration increased from 11 to 30 mg/l.
o. 002 Average monthly sulfide limit increased from 1.04 to 1.07 lbs/day.
p. 002 Daily max. sulfide limit increased from 2.3 to 2.36 lbs/day.
q. 002 Sulfide IMAX concentration increased from 0.7 to 1.6 mg/l.

4. 002 The requirement to test for total arsenic 2x/month has been added to determine if reasonable potential exists. [redacted]
   a. Permit application testing results for effluent were 0.132 (6/4/09), 0.217 (6/11), 0.122 (6/18). The influent concentration was 0.143 on 6/25/09.
   b. What is the calculated WQB arsenic limit that our results will be compared? [redacted]
   c. Reasonable potential exists if the sample concentration is greater than ½ this limit.
5. A 5 mg/l TOC limit has been added has been added to 004 outfall. The BAT & BPT sections of the ELG's do not require COD, BOD, etc. limits for once through cooling water but do require the 5 mg/l TOC limit. Likewise, a 110 mg/l TOC limit is listed for contaminated stormwater. Outfall 004 does not receive once through cooling water so the 5 mg/l TOC limit is probably not applicable. In addition, this limit appears to have been established specifically for once through cooling water as a default requirement that would both verify the water quality and eliminate the need for other limits. The new permit, however, does include other limits (TSS and oil & grease) as well as the TOC limit. Outfall 004 is equipped w/ and oil/water separator and the oil and grease monitoring requirements and limits will ensure that it is operated/maintained as designed. We do not feel that the default 5 mg/l TOC limit for once through cooling water is required for this outfall. The 110 mg/l TOC limit may be more appropriate for stormwater that is sent to the oil/water separator and ultimately discharged. What are your thoughts on this? [redacted]

Could you go into specific detail about the steam condensate (processes, purpose, whether or not it comes into contact, if it is re-circulated within the system, ect.) so that I can get a better idea of how exactly to characterize it?

Also in referencing the "004 Drainage Details" word document attachment you sent on 1/20/10, what type of wastewater can be attributed to Source #3 and #4? When and how much flow can be attributed to these sources?

6. 002 The monitoring waiver for hex chrome, total chrome, and phenolics has been extended. However, the effluent limitations for each have significantly decreased compared to the previous permit. The BAT calculations for phenolics, total chrome and hex chrome do not appear to factor in all ARG processes. We have process #1, #2, #54 (2 units), #21, #23, #24, #27, #28, and #12 from the list in Appendix A to Part 419. Also, why are crude distilling & desalting considered the same process for the calculation of these limits whereas they are considered separate processes for the purpose of determining the process configuration factor. What are your thoughts on this?

[redacted]

   a. 002 average monthly hex chrome decreased from 0.195 to 0.11 lbs/day.
   b. 002 daily max. hex chrome decreased from 0.429 to 0.24 lbs/day.
   c. 002 average monthly total chrome decreased from 3.08 to 1.3 lbs/day.
   d. 002 daily max. total chrome decreased from 5.3 to 3.7 lbs/day.
   e. 002 average monthly total phenolics decreased from 1.17 to 0.34 lbs/day.
   f. 002 daily max. total phenolics from 2.6 to 0.68 lbs/day.

7. 002 A 1x/week fecal coliform sampling requirement and 200 colony per 100 ml geometric average monthly limit has been added to the permit in response to the concentrations found during permit application testing. Analytical data from the previous permit application did not show significant coliform levels. As such, ARG is currently gathering analytical data in an effort to pinpoint the source for the coliforms. It is our ultimate goal to find a definitive source and eliminate it if possible. If we are successful and reduce the coliforms to a very low level we would like to eliminate the

new sampling/testing obligations at such time we can demonstrate that the potential to pollute is eliminated. Is it possible to amend the permit to reflect those changes during the course of the 5-year permit period rather than revisiting the issue in another 5 years?

[redacted]

8. The flow rates 0.1978 mgd (137.36 gpm) for 002 and 0.015995 mgd (11.11 gpm) for 004 were used for calculating limits. What are these flows based on? [redacted] The ARG Facts sheet states that total phenolics limit is ELG based. Is this the case or is it water quality based? [redacted]

10. PWS Parameter Evaluation
    a. Is "flow @ PWS" the flow of Tuna creek @ the state line? [redacted] Is "Bckg" the pollutant background concentration at the state line? [redacted]
    c. Why is the flow rate for 002 & 004 listed @ 0.33074 mgd rather than 0.213795 mgd? [redacted]
    d. Is the "allowable discharge" the maximum concentration of each pollutant that can be present in ARG's discharge that will still allow the concentration of each pollutant in the Tuna creek (at the state line) to be less than the listed "criteria"? [redacted]

Pesek, Adam

From: Balog, David
Sent: Thursday, March 25, 2010 12:35 PM
To: Pesek, Adam
Subject: RE: ARG - GW Remediation tie in

I never got back to you on this, my bad!

Rick told me you can go ahead & answer his inquiry, w/o worry of the legal matters surrounding this site. I think your approach sounds fine, we'd want to know what the expected effluent quality would be like if they sent the contaminated GW through the treatment plant, and we'd want some sampling of the contaminated GW itself to see what's in it. We'd just list this additional waste source at the top of page 2 of the permit.

So if you haven't already, can you go ahead & reply to Jason's email?

David G. Balog, P.E. | Environmental Engineering Mgr.
Department of Environmental Protection
Northwest Regional Office - Water Management
230 Chestnut Street | Meadville, PA 16335
Phone: 814.332.6328 | Fax: 814.332.6121

-----Original Message-----
From: Pesek, Adam
Sent: Monday, March 15, 2010 8:31 AM
To: Balog, David
Subject: ARG - GW Remediation tie in

Dave,

The question below looks like a question for you, more so on legal issues that could arise due to the CO&A association with Crompton. Permitting wise, it wouldn't complicate stuff much, as PENTOX modeling would be redone with additional sampling for the GW received, and R.P. could be determined based on WL source distribution, specifically mass balance of intake concentrations of both wastestreams. and no additional loading to ELG parameters at 002.

What are your thoughts of this proposal?

-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Friday, March 12, 2010 10:01 AM
To: Pesek, Adam
Subject: RE:

Adam,
Yesterday we held our monthly in-house wastewater compliance meeting and a question arose that I wanted to get your thoughts on. As part of our future site-wide remediation activities, we may need to actively pump certain recovery wells located throughout the refinery. We may want to direct this mix of groundwater and recovered petroleum product to out wastewater treatment plant. What provisions would have to be made in the permit to facilitate this?
Thanks,
Jason

Jason L. Goodling
Environmental Manager
American Refining Group
77 North Kendall Ave.
Bradford, PA 16701
(P) 814-368-1223
(F) 814-368-1427
jgoodling@amref.com

From: Pesek, Adam [mailto:apesek@state.pa.us]
Sent: Thursday, March 04, 2010 10:18 AM
To: Jason Goodling
Subject: RE:

Your interpretation appear to be correct. Makes sense if you think about it. If you can comply with the .18 allowance factor on every individual day when you exceed 12000 mgd and your normal loadings also comply, then your monthly average would of course be in compliance as well when all daily loadings are averaged.

-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Thursday, March 04, 2010 9:51 AM
To: Pesek, Adam
Subject: RE:

Adam,
Based on your explanation for the use of the monthly stormwater allowance factor I think we applied it incorrectly (more conservatively in the past). I interpret your explanation to mean that the a stormwater allowance factor (either daily or monthly) should be applied to ***each given day*** during which the flow rate exceeds 12,000 gallons/day if accompanied by proof that the excess flow was stormwater related.

For the purpose of determining compliance with the current 004 daily TSS loading max (6 lbs/day) we would use the 0.28 lbs/1000 gallons to generate the final daily loading number (for flows in excess of 12,000 gal/day). This is simple calculation that we've used in the past.

In turn, for determining compliance with the current 004 monthly average TSS daily loading max (4 lbs/day) we should apply the 0.18 lbs/1000 gallon allowance factor to ***each individual day*** in the month during which the flow exceeded 12,000 gallons (and was stormwater related). All stormwater-corrected daily loadings in a given month would be then summed with the loading values for all other days during the month and divided by the total number of days. The resulting value would represent the monthly average.

We used the monthly allowance factor differently (incorrectly) in the past. In short, we only used the allowance factor if the average monthly flow rate exceeded 12,000 gallons/day. As such, we experienced months during which several individual days exceeded 12,000 gallons/day and the daily stormwater allowance factor pulled us into compliance, but the monthly average loading was out of compliance b/c we didn't apply the allowance factor since the average monthly flow was less than 12,000 gallons. This caused us to report at least one deviation in our DMR's.

Please let me know if I'm interpreting your email correctly. If so, we'll reapply the correct calculations to the month(s) for which we reported violations to determine if violations actually occured.

Thanks Adam,
Jason

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(P) 814-368-1223

(F) 814-368-1427
jgoodling@amref.com

From: Pesek, Adam [mailto:apesek@state.pa.us]
Sent: Thursday, March 04, 2010 8:19 AM
To: Jason Goodling
Subject: RE:

Jason,

See attached for calculation of Monthly Average Loading. The stormwater allowance factor calculation should be used for each individual daily average loading where 12000 gal/day flow rate is exceeded. When a stormwater allowance factor is used the calculation should be submitted with the monthly DMR when it was used. In addition, proof that the excess flow rate was stormwater on that day should be provided.

The calc: total daily loading (average daily loading) - (gallons over 12000/1000 X .18) = final daily loading
Monthly average loading would then be the sum of final daily loadings recorded that month divided by number of samples (or days sampling was conducted that month).

In looking into the other questions you raised in our telephone conversation yesterday about the proposed limitations in draft permit:

TOC at 004 would have an concentration allowance factor for stormwater flow exceeding the 12000 gallon/day design flow. with proof that it is stormwater
TSS should have a constant concentration limit of 40 mg/l monthly average regardless of flow rate. TSS, TOC, Oil & Grease would all have monitor and report for loading because loading is not specified in the ELG for this waste stream and TSS is a technology based concentration limit.

-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Wednesday, March 03, 2010 3:53 PM
To: Pesek, Adam
Subject: RE:

Adam,
I've got another question for you. This one is in regards to how the monthly stormwater allowance factors should be applied. Using the existing 004 outfall as an example, the monthly TSS stormwater allowance factor is 0.18 lbs/1,000 gallons in excess of 12,000 gallons. We've interpreted this to mean that the monthly stormwater allowance factor is only used if the average monthly discharge rate is greater than 12,000 gallons/day regardless if there were individual days w/ flow rates greater than 12,000 gallons during the month. Do you know if this is correct or if the Department has any guidance on this calculation?
Thanks,
Jason

Jason L. Goodling
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jgoodling@amref.com

From: Pesek, Adam [mailto:apesek@state.pa.us]
Sent: Monday, March 01, 2010 8:17 AM
To: Jason Goodling
Subject: RE:

Good morning Jason,

I was not in the office on Friday, so my apologies for not getting back to you sooner. I have never received feedback from EPA headquarters so I referenced United Refining's NPDES Permit for how they handle a similar wastestream. I am proposing to permit this outfall as "once through cooling water" as defined and found in the ELGs. 002 will now receive additional loading for ELG parameters as it will have the loading once allocated to 004. 004 will now have limits for TSS, Oil and Grease, TOC, and pH. Stormwater allowance factors will be included for flow over 0.012 MGD. Flows below the 0.012 must be able to consistently meet the TOC limit of 5 mg/l. as a daily maximum. Sampling frequency is also proposed to be reduced to 1/week from the current 3/week.

A copy of the proposed draft permit should be available sometime soon after results of the additional sampling requested is received.

Adam J. Pesek| Environmental Engineering Specialist
Department of Environmental Protection
Northwest Regional Office
230 Chestnut Street | Meadville, PA 16335
Phone: 814.332.6331 | Fax: 814.332.6121
apesek@state.pa.us

-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Friday, February 26, 2010 8:38 AM
To: Pesek, Adam
Subject: RE:

Adam,
We would be willing to decrease the flow rate for the sake of increasing the limit, but if that isn't possible the 0.5 mg/l limit would work for us. On another note, were you able to reach any conclusions regarding the permitting of 004 outfall?

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From: Pesek, Adam [mailto:apesek@state.pa.us]
Sent: Thursday, February 25, 2010 2:47 PM
To: Jason Goodling
Subject: RE:

Jason,

If it was based solely on water quality modeling, the limit would be around 1.1 to 1.5 mg/l at your projected flow rates. However, the Department is hesitant to exceed the 0.5 mg/l limit based on similar discharges effluent data, consideration of source water concentration, and implementation of the required BMPs that are found in the general permit (will be in special condition in new permit).

Adam

-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Thursday, February 25, 2010 1:54 PM
To: Pesek, Adam
Subject: RE:

Adam,
What would the acceptable flow rate be if the limit was 1.0 mg/l? We anticipate that our flow rate will be ~100-150 gpm.

Jason L. Goodling
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From: Pesek, Adam [mailto:apesek@state.pa.us]
Sent: Wednesday, February 24, 2010 2:12 PM
To: Jason Goodling
Subject: RE:

Jason,

Through the Department's TRC Calculator Spreadsheet, I came up with a 0.5 mg/l limit to be acceptable for flow rates under 459 GPM or 27560 gal/hr. Let me know if this is an attainable rate.

Adam

Adam J. Pesek | Environmental Engineering Specialist
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-----Original Message-----
From: Jason Goodling [mailto:jgoodling@amref.com]
Sent: Wednesday, February 24, 2010 12:20 PM
To: Pesek, Adam
Subject:

Adam,
Our largest tank capacity is ~1.7 million gallons.

Have a good day,
Jason

Jason L. Goodling
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