UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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SUBJECT Guidance on Petroleum Refinery Waste Analyses for Land Treatment Permit Applications

FROM John Skinner, Director
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TO Hazardous Waste Permit Branch Chiefs,
Regions I-X

Introduction

The purpose of this memo is to provide permit writers guidance on evaluating petroleum refinery waste analyses submitted in land treatment permit applications. A list of Appendix VIII hazardous constituents suspected to be present in petroleum refinery wastes and a special analytical method for refinery wastes are provided.

Background

The general Part B information requirements specified under §270.14(b) require the submittal of (1) chemical and physical analysis data on the hazardous wastes to be handled at the facility including all data that must be known to treat, store, or dispose of wastes properly in accordance with Part 264, and (2) a copy of the waste analysis plan. In addition, the specific information requirements under §270.20 require an owner/operator of any facility that includes a land treatment unit so submit "a list of hazardous constituents reasonably expected to be in, or derived from, the wastes to be land treated based on waste analyses performed pursuant to §264.13." Also, §270.20(a) stipulates that the description of the treatment demonstration plan must include a list of potential hazardous constituents in the waste.

Because the design and management of a land treatment unit is based on the goal of attaining treatment of hazardous constituents (i.e., constituents listed in Appendix VIII), it is very important that the presence of these constituents in the

land treated wastes be accurately identified and quantified. This is best achieved through a comprehensive waste analysis for all Appendix VIII constituents. However, due to the cost and analytical difficulties associated with these analyses, many applicants have submitted requests to conduct analyses for some subset of Appendix VIII, which are "reasonably expected to be in or derived from the wastes to be land treated." To date, the majority of wastes proposed for land treatment have been petroleum refinery wastes, specifically the listed wastes K048-K052.

The evaluation of these Appendix VIII subsets for each land treatment application has been difficult due to the lack of published information on specific organic compounds in refinery wastes, and also due to the variability of waste characteristics within the refinery industry. However, OSW has gathered sufficient information from EPA research studies, in-house waste studies and analyses, and refinery process evaluations to develop a conservative list of hazardous constituents that are suspected to be present in petroleum refinery wastes. This list is provided in Attachment 1. This list should be used by permit writers as a guide in determining which constituents may and may not be eliminated from consideration when completing waste analyses for a land treatment permit application. Additional explanation of the derivation and use of this list is provided below.

Derivation and Use of List

The list of hazardous constituents suspected to be present in refinery wastewater and sludge characteristics from the following sources: (1) literature, particularly EPA research reports; (2) in-house waste analyses completed by EPA research laboratories; (3) preliminary data from the OSW refinery waste study; and (4) an evaluation of petroleum refinery processes. Although these four sources were used, the data base on specific hazardous organic constituents in sludges was still limited. Considerable weight was placed on wastewater data as indicators of sludge characteristics (e.g., API separator sludge).

Also, the list in Attachment 1 is a generic list developed by combining waste analysis data on all five listed refinery wastes (K048-K052). Due to the lack of extensive data, no attempt was made to differentiate between the characteristics of these five refinery wastes. Until sufficient information is available to allow development of separate lists for each waste, the

attached list should be considered applicable to dissolved air flotation float (K048), slop oil emulsion solids (K049), heat exchanger bundle cleaning sludge (K050), API separator sludge (K051), and leaded tank bottoms (K052).

To compensate for the limited data base and variability among refineries, the attached list is purposely comprehensive. It includes a total of 89 hazardous constituents or groups of constituents (e.g., trichlorobenzenes). All of these constituents have been identified as possibly being present in the above referenced wastes. Many of the compounds on the list may be present at low concentrations and others may not be present at all in certain wastes at some refineries.

The permit writer should use the attached list as a guide to the Appendix VIII constituents that should be addressed in the up-front waste analyses and waste analysis plans for Part B applications that propose land treatment of petroleum refinery wastes. A permit applicant may further refine this list by providing detailed evidence that certain hazardous constituents cannot be present in the listed wastes at that particular refinery. In most cases, however, waste analysis data on the constituents listed in Attachment 1 will be necessary to make this showing.

Analytical Methods

To assist in the analysis for specific organic constituents in petroleum refinery wastes, OSW has developed a column cleanup procedure which is provided in Attachment 2. This draft method is used specifically to separate semivolatile aliphatic, aromatic, and polar compounds in the waste matrix. The method should be used only by experienced residue analysts. Volatile compounds are determined using method 8240 with PEG (tetraglyme) Extraction. Test method 3050 should be used for all metal analyses. These methods are described in SW-846.

Relationship to Delisting and Listing Efforts

Finally, the attached list is consistent with the waste analysis information that EPA has requested from delisting petitioners. Many petroleum refinery operators who are preparing Part B applications for land treatment facilities also have submitted delisting petitions to the Agency for one or more of their wastes. It is important that the waste analysis data requested by the Agency for permitting and delisting be consistent, although there may be differences in the extent of data necessary in certain cases. Therefore, the list of Appendix VIII constituents provided in Attachment 1 is also being used in refinery delisting actions. Additional information on non-Appendix VIII constituents, however, is being collected as part of OSW's new waste assessment and listing efforts for petroleum refineries. These compounds, which are listed at the end of Attachment 1 for your information, may be added to Appendix VIII in the future. Although it is not required at this time, permit applicants should be encouraged to provide information on these waste constituents.

If you have any questions on the listing of specific hazardous constituents in Attachment 1 or on the recommended test methods, please contact Ben Smith (382-4791) of the Waste

Identification Branch. Other questions pertaining to the use of the above guidance in permitting land treatment facilities should be directed to Mike Flynn (382-4489) of the Land Disposal Branch.

Attachments

cc: Jack Lehman
Fred Lindsey
Ken Shuster
Eileen Claussen
Matt Straus
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ATTACHMENT 1

Appendix VIII Hazardous Constituents Suspected to be Present in Refinery Wastes

**Acetonitrile (Ethanenitrile)
**Acrolein (2-Propenal)
**Acrylonitrile (2-Propenenitrile)
Aniline (Benzenamine)
Antimony
Arsenic
Barium
Benz (c) acridine (3,4-Benzacridine)
Benz (a) anthracene (1,2-Benzanthracene)
**Benzene (Cyclohexatriene)
Benzenethiol (Thiophenol)
Benzidine (1,1-Biphenyl-4,4'diamine)
Benzo(b)fluoranthene (2,3-Benzofluoranthene)
Benzo(j)fluoranthene (7,8-Benzofluoranthene)
Benzo(a)pyrene (3,4-Benzopyrene)
**Benzyl chloride (Benzene, (chloromethyl)-)
Beryllium
Bis (2-chloroethyl) ether (Ethane, 1,1'-oxybis (2-chloro-))
Bis (2-chloroisopropyl) ether (Propane, 2,2'-oxybis (2-chloro-))
**Bis (chloromethyl) ether (Methane, oxybis (chloro))
Bis (2-ethylhexyl) phthalate (1,2-Benzenedicarboxylic acid, bis (2-ethylhexyl) ester)
Butyl benzyl phthalate (1,2-Benzenedicarboxylic acid, butyl phenylmethyl ester)
Cadmium
Carbon disulfide (Carbon bisulfide)
p-Chloro-m-cresol
**Chlorobenzene (Benzene, chloro-)

**Chloroform (Methane, trichloro-)
**Chloromethane (Methyl chloride)
2- Chloronapthalene (Naphthalene, beta-chloro-)
2-Chlorophenol (Phenol, o-chloro-)
Chromium
Chrysene (1,2-Benzphenanthrene)
Cresols (Cresylic acid) (Phenol, methyl-)
**Crotonaldehyde (2-Butenal)
Cyanide
Dibenz(a,h)acridine (1,2,5,6-Dibenzacridine)
Dibenz(a,j)acridine (1,2,7,8-Dibenzacridine)
Dibenz(a,h)anthracene (1,2,5,6-Dibenzanthracene)
7H-Dibenzo(c,g)carbazole (3,4,5,6-Dibenzcarbazole)
Dibenzo(a,e)pyrene (1,2,4,5-Dibenzpyrene)
Dibenzo(a,h)pyrene (1,2,5,6-Dibenzpyrene)
Dibenzo(a,i)pyrene (1,2,7,8-Dibenzpyrene)
**1,2-Dibromoethane (Ethylene dibromide)
Di-n-butyl phthalate (1,2-Benzenedicarboxylic acid, dibutyl ester)
*Dichlorobenzenes
**1,2-Dichloroethane (Ethylene dichloride)
**trans-1,2-Dichloroethene (1,2-Dichlorethylene)
**1,1-Dichloroethylene (Ethene 1,1-dichloro-)
**Dichloromethane (Methylene chloride)
**Dichloropropane
Dichloropropanol
Diethytl phthalate (1,2-Benzenedicarboxylic acid, diethyl ester)
7,12-Dimethyl-benz(a)anthracene
2,4-Dimethylphenol (Phenol, 2,4-dimethyl-)
Dimethyl phthalate (1,2-Benzenedicarboxylic acid, dimethyl ester)
4,6-Dinitro-o-cresol
2,4-Dinitrophenol (phenol, 2,4-nitro-)
2,4-Dinitrotoluene (Benzene, 1-methyl-2,4-dinitro-)
Di-n-octyl phthalate (1,2-Benzenedicarboxylic acid, dioctyl ester)
**1,4-Dioxane (1,4-Diethylene oxide)
1,2-Diphenylhydrazine (Hydrazine, 1,2-diphenyl-)
**Ethyleneimine (Azridine)
**Ethylene oxide (Oxirane)
Fluoranthene (Benzo (j,k) fluorene)
**Formaldehyde
Hydrogen sulfide (Sulfur hydride)
Indeno (1,2,3-cd)pyrene (1 10(1,2-phenylene)pyrene)
Lead
Mercury
Methanethiol (Thiomethanol)
3-Methylchlolanthrene (Benz(j)aceanthrylene, 1,2-dihydro-3-methyl-)
**Methyl ethyl ketone (MEK) (2-Butanone)

Naphthalene
Nickel
p-Nitroaniline (Benzenamine, 4-nitro-)
Nitrobenzene (Benzene, nitro-)
4-Nitrophenol (Phenol,pentachloro-)
Pentachlorophenol (Phenol, pentachloro-)
Phenol (Benzene, hydroxy-)
Pyridine
Selenium
*,**Tetrachloroethanes
**Tetrachloroethylene (Ethene, 1,1,2,2-tetra chloro-)
**Toluene (Benzene, methyl-)
*Trichlorobenzenes
*,**Trichloroethanes
**Trichloroethene (Trichloroethylene)
*Trichlorophenols
Vanadium

* If any of these groups of compounds are found, the specific isomers listed in Appendix VIII should be identified.

** Use Test Method 8240 for these volatile compounds.

*** Use Test Method 3050 in SW-846 for all metals; see Attachment 2 for semivolatile organic compounds.

Non-Appendix VIII Constituents of Concern (may be added to App. VIII)

| | |
|---|---|
| Cobalt | Indene |
| 1-Methylnapthalene | 5-Nitro acenaphthene |
| Styrene | Quinoline |
| Hydroquinone | Phenanthrene |
| Anthracene | Pyrene |

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ATTACHMENT 2

Column Cleanup of Petroleum Wastes

Introduction

The following procedure is intended for application to the analysis of semivolatile organic compounds in oily waste samples. Its application is necessary in those cases where

the conventional cleanup procedures (Methods 3510, 3520, 3540, 3550) fail to provide suitable detection limits (approximately 10ppm) for the semivolatile compounds specified in Attachment 1. Analysis of the cleaned-up extracts should be performed according to Method 8270, a capillary GC/MS technique.

It should be noted that this procedure is in draft form. It may be modified as more experience is gained.

Cleanup Techniques

It is anticipated that after a sample is subjected to conventional extraction procedures (Methods 3510, 3520, 3540, and 3550) or after dilution, a cleanup step may be required to remove matrix interferences and yield acceptable detection limits for compounds of interest. Determination as to whether an extract needs to be cleaned can usually be provided by either examination of the sample itself or by knowledge of the particular waste stream that was sampled. It is also possible to estimate whether or not the extract is suitably clean for GC/MS analysis. An aliquot of the methylene chloride extract can be evaporated to dryness and the total amount of material in the aliquot weighed. In general, if the extract contains less than a few milligrams of material per millilitre of solvent, it is probably clean enough for capillary CG/MS. If it contains more materials, it will likely require additional preparation.

In most instances, some type of cleanup technique will be necessary in order to achieve suitably low detection limits for the target compounds. If much aliphatic material exists in the sample it will mask the compounds of interest. Mere dilution will not remedy the situation as detection limits are raised by the dilution.

If acidic compounds such as phenols are suspected of being present in the sample, a separate fraction containing these acids can be created using the organic extract obtained above. Methods 3530, a base/neutral acid cleanup extraction technique, may be applicable to the cleanup of certain sample types. Modifications to Methods 3530 are as follows:

a) In Section 7.6, the organic and aqueous phases are both treated as containing compounds; and

b) Section 7.15 will not be necessary.

The aqueous phase, when transferred to organic solvent after Section 7.13, will contain acidic compounds. The organic phase contains basic and neutral compounds. In most instances, the acidic fraction will be clean enough for CG/MS analysis. The base/neutral extract, however, may require further cleanup. Thus, a cleanup procedure has been devised for base/neutral extracts that minimizes the interferences caused by high concentrations of aliphatic and polymeric materials.

Although the cleanup procedure is thoroughly described in the next section, one generally proceeds as follows. The sample is subjected to cleanup by placing a representative aliquot of the sample on an alumina column and successively eluting with hexane, methylene chloride, and diethyl ether to yield 3 fractions containing the aliphatic (hexane fraction), aromatic (methylene chloride fraction) and polar compounds (ether fraction). The methylene chloride fraction is then concentrated to about 1 ml. and then is analyzed by GC/MS for the compounds of interest. The hexane concentrate can be screened by GC/MS to determine if compounds were eluted into the hexane fraction. However, this usually will not be required. If polar compounds are of interest, the ether fraction is also analyzed.

Quantitation of the semivolatile constituents in Attachment 1 is to be performed using the reverse search technique. Additionally, tentative identification should be attempted for the ten organic compounds detected at the highest concentrations. Identifications should be made via a forward search of the EPA/NIH mass spectral library. Concentrations should be approximated by comparison of the compound response to that of the closest eluted internal standard. A procedural blank, matrix spike, and duplicate should be analyzed for every batch of samples.

Accuracy and precision control charts should be maintained for indicator constituents. The percent recoveries of spiked surrogate standards for a given sample type should be plotted versus sample identification number. Table 1 contains a list of the surrogate compounds to be employed for the analysis of semivolatile organic compounds, and recovery limits. Recovery limits are based upon obtaining a final extract sufficiently clean, such that the surrogate compounds should be present at 50 ppm or higher in the extract. If dilution of the sample is still required, detection of the surrogates may be difficult

and the associated recoveries imprecise or non-existant. Such samples should be spiked with higher surrogate levels and resubjected to the cleanup procedure.

Table 1. Surrogate Standards for Semivolatile Organic Compound Analysis

| | Recovery Limits |
|---|---|
| Acid surrogates | |
| phenol-d5 | 40-115% |
| 2-fluorophenol | |
| 2,4,6-tribromophenol | |
| Base/neutral surrogates | |
| nitrobenzene-d5 | |
| 5-fluorobiphenyl | 50-120% |
| terphenyl-d14 | |
| acridine-d9 | |
| pyrene-d10 | |

The precision control chart should consist of the percent difference for indicator constituent concentration determined in duplicate samples of a given sample type versus sample identification numbers.

Column Clean Up of Petroleum Wastes

Scope and Application

This method is used to cleanup samples containing high levels of aliphatic hydrocarbons, such as wastes from petroleum refining. It is used specifically to separate aliphatics, aromatics, and polar compounds in the waste matrix. This method is applicable to API separator sludges, rag oils, slop oil emulsion, and other oily wastes derived from petroleum refining. This method is recommended for use only by or under close supervision of experienced analysts.

Summary of Method

Take a 20 mg aliquot of the waste/methylene chloride concentrate from step 7.13 of Method 3530. Dissolve the

aliquot in hexane and spike with 10mg each of d9-acridine, d5-nitrobenzene, d5-phenol, 2-fluorobiphenyl, tribromophenol, d14-terphenyl, 2-fluorophenol, and d10-pyrene. Apply the mixture directly to the alumina column.

The column is eluted sequentially with hexane, methylene chloride, and diethyl either and the corresponding three factions are collected. An aliquot of the CH2Cl2 fraction is evaporated under a gentle stream of nitrogen and weighed to determine the appropriate concentration factors prior to GC/MS. If pyrene or terphenyl is recovered at less than 50%, the procedure should be repeated.

Interferences

Matrix interferences will likely be coextracted from the sample. The extent of these interferences will vary considerably from waste to waste depending on the nature and diversity of the particular waste being analyzed. The use of additional cleanup extractions can be used as necessary for specific compound identification and quantitation.

Apparatus

Glass Column: 30 cm long x 1 cm I.D. with glass frit or glass wool and stop clock.

Aluminum weighing boats: Approximately 2 in. in diameter.

Analytical Balance: Capable of weighing to Ò0.5 mg.

Concentrator Tube, KD, 10 ml

Evaporative Flask, KD, 250 ml

Snyder Column, KD, three-ball micro

Snyder Column, KD, two-ball micro

Steam Bath

Boiling Chips: 10-40 mesh carbarundum. Heat to 450¯C for 5-10 hours.

Syringe: 1 ml glass

50 ml beaker

250 ml beaker

Reagents

Hexane: Distilled in glass (B&J) or equivalent

Methylene Chloride: Distilled in glass (B&J) or equivalent

Diethyl Ether: Distilled in glass (B&J) or equivalent

Alumina: Dried overnight at 130°C, neutral 80-325 MCB chromatographic grade

Sodium Sulfate: Washed with CH2Cl2 and heated to 150°C for 4 hours

Procedure

Weigh out 10.0 gm of alumina and add to the chromatographic column that is filled to about 20 mL with hexane.

Allow the alumina to settle and then add 0.5 gm sodium sulfate.

Let the solvent flow such that the head of liquid in the column is about 1 cm above the sodium sulfate layer. Stop the flow.

Add the aliquot equivalent to 100-200 mg of material.

Start the flow and elute with 13 ml of hexane. Collect the effluent in a 50 beaker. Label this fraction "aliphatics".

Elute the column with 100 ml of methylene chloride and collect the effluent in a 250 ml beaker. Label "aromatics".

Elute the column with 100 ml of diethyl ether and collect the effluent in a 250 ml beaker. Label "polars".

Weigh three sample boats to the nearest 0.5 mg. Reduce the volume of each fraction using the KDs to between 1 and 5 ml. Record the volume of each and place 1/2 of each sample in the respective boat.

Evaporate the liquid in each boat under a gentle stream of nitrogen. Reweigh each boat and record the weight of each fraction.

Calculate the weight of each fraction as a proportion of the total sample. For example, fraction 1 is 56.3 mg, fraction 2 is 25.4 mg, and fraction 3 is 85.0 mg.

Calculate the amount of sample in the fractions and adjust the volumes so injection will permit determination of various components on scale

12.7 mg/2500 ul = 5.1 ug/ul

Dilute each of the three fractions obtained by a ratio so that the sample entering the capillary column does not exceed 2.5 ug. For example, if the calculated weight of the fraction as a proportion of the total sample is 12.7, and the amount of sample in the fractions is 5.1 ug/ul as in the above example, dilute the sample 1:1 with methylene chloride.

Quality Control

Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank sample should be carried through all stages of the sample preparation and measurement. Standard quality assurance practices should be used with this method. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be anlayzed to validate the sensitivity and accuracy of the analysis.