

METHOD 9071B

n-HEXANE EXTRACTABLE MATERIAL (HEM) FOR SLUDGE, SEDIMENT, AND SOLID SAMPLES

1.0 SCOPE AND APPLICATION

1.1 Method 9071 may be used to quantify low concentrations of oil and grease in soil, sediments, sludges, and other solid materials amenable to chemical drying and solvent extraction with n-hexane. "Oil and grease" is a conventional pollutant under 40 CFR 401.16 and generally refers to substances, including biological lipids and mineral hydrocarbons, that have similar physical characteristics and common solubility in an organic extracting solvent. As such, oil and grease is an operationally defined parameter, and the results will depend entirely on the extracting solvent and method of extraction. Method 9071 employs n-hexane as the extraction solvent with Soxhlet extraction and the results of this method are appropriately termed "n-hexane extractable material (HEM)." Section 1.2 lists the type of materials that may be extracted by this method. In the context of this method, "HEM" is used throughout this method and for operational purposes, may be considered synonymous with "oil and grease" within the limitations discussed below.

1.2 Specifically, Method 9071 is suitable for extracting relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, biological lipids, and related materials.

1.3 Method 9071 is not recommended for measuring materials that volatilize at temperatures below 85°C. Petroleum fuels from gasoline through #2 fuel oil may be partially lost during the solvent removal process.

1.4 Some crude oils and heavy fuel oils may contain materials that are not soluble in n-hexane, and recovery of these materials may be low.

2.0 SUMMARY OF METHOD

2.1 A representative portion of wet (as received) waste is acidified with concentrated HCl and chemically dried with magnesium sulfate or sodium sulfate. Magnesium sulfate monohydrate is used to dry acidified sludges as it will combine with 75% of its own weight in water in forming $MgSO_4 \cdot 7H_2O$. Anhydrous sodium sulfate is used to dry soil and sediment samples.

2.2 After drying, the HEM is extracted with n-hexane using a Soxhlet apparatus. The n-hexane extract is then distilled from the extract and the HEM is desiccated and weighed.

2.3 When necessary, a separate sample portion is evaluated for percent solids, and the dry weight fraction may be used to calculate the dry-weight HEM concentration of the soil, sediment, or waste.

3.0 DEFINITIONS

3.1 n-Hexane extractable material (HEM, oil and grease): Material that is extracted from a sample using n-hexane and determined by this method. This material includes relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.

3.2 Refer to Chapter One for additional definitions.

4.0 INTERFERENCES

4.1 This method is entirely empirical, and duplicate results having a high degree of precision can be obtained only by strict adherence to all details. The rate of cycling and time of extraction in the Soxhlet apparatus must be consistent and length of time required for drying and cooling extracted materials must be the same in order to generate consistent results. It is important that the procedures be performed as directed due to the varying solubilities of the different greases and heavy mineral oils.

4.2 Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts that could affect the results. All solvents and reagents used in the analysis should be demonstrated to be free from interferences by processing a method blank with each analytical batch. Specific selection of reagents, solvent washes, or purification of solvents may be required. Use of plastic measuring devices, and/or plastic tubing attachments must be avoided.

4.3 Glassware should be cleaned by washing with hot tap water with detergent, rinsing with tap water and reagent water, and rinsing with solvent. Glassware may also be baked at 200-250°C for 1 hour. Boiling flasks that are used to contain the extracted residues may be dried in an oven at 105-115°C and stored in a desiccator until used. Depending on the project DQOs, strict adherence to the washing and handling procedures cited above may not be necessary as long as the laboratory can demonstrate that alternative cleaning procedures yield acceptable method performance and meet method blank acceptance criteria.

4.4 A gradual increase in weight may result due to the absorption of oxygen; a gradual loss of weight may result due to volatilization. Extracted residues should be maintained in a desiccator during cooling and prior to weighing. Extracted residues should be weighed as soon as possible after cooling.

4.5 The presence of non-oily extractable substance such as sulfur compounds, organic dyes, and chlorophyll, may result in a positive bias. For the purpose of this method, all materials extracted and retained during this procedure are defined as HEM.

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 a 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 to 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.

6.0 EQUIPMENT AND SUPPLIES

6.1 Soxhlet extraction apparatus.

6.2 Heating mantle - explosion-proof, with temperature control.

6.3 Boiling flask - 125-mL or appropriate size.

6.4 Analytical balance - capable of weighing 0.1 mg.

6.5 Vacuum pump, or other vacuum source.

6.6 Paper extraction thimble for Soxhlet apparatus.

6.7 Glass wool or small glass beads to fill thimble.

6.8 Grease-free, non-absorbent cotton - To remove possible interferences, each batch of cotton should be washed with n-hexane. Solvent washing may not be necessary if the laboratory can demonstrate that the unwashed cotton does not affect the performance of the method or that the concentration of HEM in the sample is so high that low contaminant concentration is insignificant.

6.9 Beakers - 100- 150-mL.

6.10 pH paper.

6.11 Porcelain mortar and pestle.

6.12 Extraction flask - 150-mL or appropriate size.

6.13 Waterbath or steam bath-explosion-proof - capable of maintaining a temperature of at least 85°C .

6.14 Distilling apparatus - For removing n-hexane from extract.

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

6.14.2 Distillation adapter (used to attach distilling head and to the waste collection flask for recovery of solvent).

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

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

6.15 Desiccator - Cabinet or jar type, capable of holding boiling flasks during cooling and storage.

6.16 Tongs - for handling the boiling flasks.

6.17 Glass fiber filter paper - Whatman No. 40 or equivalent.

6.18 Boiling chips - Silicon carbide or fluoropolymer.

7.0 REAGENTS

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

7.3 Concentrated hydrochloric acid (HCl).

7.4 Magnesium sulfate monohydrate. Prepare $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ by spreading a thin layer in a dish and drying in an oven at 150°C overnight. Store in a tightly sealed glass container until used.

7.5 Sodium sulfate, granular, anhydrous (Na_2SO_4). Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Store in a tightly sealed glass container until used.

7.6 n-Hexane. Purity of 85%, 99.0% minimum saturated C_6 isomers, residue less than 1 mg/L. Boiling point, 69°C .

7.7 Hexadecane($\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$)/stearic acid ($\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$). 1:1 spiking solution. Prepare in acetone at a concentration of 2 mg/mL each.

Weigh 200 ± 2 mg of stearic acid and 200 ± 2 mg hexadecane into a 100 mL volumetric flask and fill to the mark with acetone. The total concentration of this stock is 4000 mg/L (ppm) HEM. This standard may be used for spiking samples and preparing laboratory control samples. Store in a glass container with a fluoropolymer-lined cap at room temperature. Shield from light.

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

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 A minimum of 100 grams of sample should be collected using a metal spatula, spoon, or equivalent device. Samples should be collected into a pre-cleaned wide-mouth glass container fitted with a TFE-lined screw cap.

8.2 When practical (i.e., when the sample matrix allows the complete mixing of sample and acid such as with a pourable sludge or sediment), the sample should be preserved to a pH < 2 by adding 1 mL of concentrated HCl per 100 gram of sample and cooled to 4 ± 2 °C. If acidification is not practical (as with a dry soil), the addition of the HCl is not required and the sample should be cooled to 4 ± 2 °C. The laboratory must be notified so that the sample can be acidified prior to analysis.

8.3 A holding time has not been established for HEM in solids, but it is recommended that the sample be analyzed as soon as possible.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

9.2 Employ a minimum of one method blank per analytical batch or twenty samples, whichever is more frequent, to verify that all reagents, solvents, and equipment are contamination free. Prepare the method blank from 5 g of inert matrix such as pre-cleaned sand or similar material, and carry it through the analytical process.

9.3 Run one matrix duplicate and matrix spike sample every twenty samples or analytical batch, whichever is more frequent. Matrix duplicates and spikes are brought through the whole sample preparation and analytical process.

9.4 The performance of the method should be evaluated by the use of a Laboratory Control Sample (LCS). The LCS is prepared by spiking an inert matrix (as pre-cleaned sand or similar material) with an appropriate volume of spiking solution (Sec. 7.7) and carrying it through the analytical process.

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 $\pm 10\%$ (i.e., ± 0.2 mg) at 2 mg and $\pm 0.5\%$ (i.e., ± 5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

11.0 PROCEDURE

11.1 Determination of Sample Dry Weight Fraction

11.1.1 When it is necessary to report the HEM on a dry weight basis, determine the dry weight fraction using a separate aliquot of sample, as discussed below. The aliquot used for this determination cannot be used to evaluate HEM.

11.1.2 Weigh 5-10 gram (\pm 0.01 gram) of the sample into pre-weighed crucible. Determine the weight of the wet sample by subtracting the weight of the crucible.

11.1.3 Place the crucible with the wet sample in an oven overnight at 105°C. Remove crucible from oven and place in a desiccator to cool. Weigh. Determine dry weight of sample by subtracting the weight of the crucible. Determine the dry weight fraction of the sample as follows:

NOTE: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

$$\text{dry weight fraction} = \frac{\text{g of dry sample}}{\text{g of sample}}$$

11.2 Sample Preparation

11.2.1 Sludge/Waste Samples

11.2.1.1 Weigh out 20 ± 0.5 grams of wet sample into a 150-mL beaker.

11.2.1.2 If the sample has not been acidified, acidify to a $\text{pH} \leq 2$ with approximately 0.3 mL concentrated HCl.

11.2.1.3 Add 25 grams $\text{Mg}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (Sec. 7.4) and stir to a smooth paste.

11.2.1.4 Spread paste on sides of beaker to facilitate evaporation. Let stand about 15-30 min or until material is solidified.

11.2.1.5 Remove solids and grind to fine powder in a mortar.

11.2.1.6 Add the powder to the paper extraction thimble.

11.2.1.7 Wipe beaker and mortar with pieces of filter paper moistened with n-hexane and add to thimble.

11.2.1.8 Fill thimble with glass wool (or glass beads).

11.2.2 Sediment/Soil Samples

11.2.2.1 Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

11.2.2.2 Blend 10 grams of the sample with 10 grams of anhydrous sodium sulfate (Sec. 7.5) as described in Section 11.2.1. Transfer homogenized paste to an extraction thimble and cover with glass wool or glass beads. The extraction thimble must drain freely for the duration of the extraction period.

11.3 Extraction

11.3.1 Set-up the Soxhlet apparatus containing the extraction thimble and sample and attach a 125-mL boiling flask containing 90 mL of n-hexane. Add boiling chips. Adjust the heating control on the heating mantle so that a cycling rate of 20 cycles/h is obtained. Extract for a period of 4 hrs.

11.3.2 Tare a clean 250-mL or appropriate sized boiling flask as follows:

11.3.2.1 Dry the flask in an oven at 105-115°C for a minimum of 2 h.

11.3.2.2 Remove from the oven and immediately transfer to a desiccator to cool at room temperature.

11.3.2.3 When cool, remove from the desiccator with tongs and weigh immediately on a calibrated balance.

11.3.3 At the end of the 4 h extraction period, filter the extract through grease-free cotton, into the pre-weighed boiling flask (Sec. 11.3.2). Use gloves to avoid adding fingerprints to the flask.

11.3.4 Rinse flask and cotton with n-hexane and add to the 250-mL boiling flask.

NOTE: If the extract is clear and no suspended particles are present, the filtration step may be omitted.

11.3.5 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. A heating mantle may also be used. Adjust the temperature of the heating device to complete the distillation in less than 30 minutes. Collect the solvent for reuse or appropriate disposal.

11.3.6 When the distillation is complete, remove the distilling head. Immediately remove the flask from the heat source and wipe the outside to remove excess moisture and fingerprints. To remove solvent vapor, sweep out the flask for 15 sec with air by inserting a glass tube that is connected to a vacuum source.

11.3.7 Cool the boiling flask in a desiccator for 30 min and weigh. Determine the gain in weight of the boiling flask by subtracting the weight of the boiling flask (Sec. 11.3.2) from the final boiling flask weight.

12.0 DATA ANALYSIS AND CALCULATIONS

Calculate the concentration of HEM in the sample as follows:

$$\text{HEM (mg/kg wet weight)} = \frac{\text{gain in weight of flask(mg)} \times 1000}{\text{weight of wet solid(g)}}$$

NOTE: If it is necessary to report the results on a dry weight basis, divide the result obtained above by the dry weight fraction calculated in Sec. 11.1.3. Report the results as mg/kg HEM dry weight. If it is necessary to report the results as a percentage of the wet or dry weight, divide the wet-weight concentration or dry weight concentration by 10,000 and report the result as % HEM wet or dry weight.

13.0 METHOD PERFORMANCE

In a preliminary study designed to find a suitable replacement for Freon-113, three EPA contract laboratories evaluated a total of 28 solid samples derived from various industrial and commercial processes for oil and grease. This study evaluated a total of six solvents, including n-hexane, to determine which of the alternative solvents produced results most closely with that of Freon-113. In this study, each waste was Soxhlet-extracted in triplicate using Freon-113 and each of the alternative solvents. Based on the overall results, n-hexane was judged to be the best alternative solvent. The data provided in Table 1 compare the results for Freon-113 and n-hexane for each waste. For a complete discussion of this study, refer to reference 1 in Section 16.0.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable Federal, state and local rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer

discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Preliminary Report of EPA Efforts to Replace Freon for the Determination of Oil and Grease, United States Environmental Protection Agency, Office of Water, EPA-821-93-009. June 1993.
2. Method 1664, Revision A: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Table 1, and a flow diagram of the method procedure.

TABLE 1

SOXHLET EXTRACTION OF SOLIDS USING FREON-113 AND N-HEXANE
All concentrations in mg/kg

Facility/ Process	Waste Stream	Solvent: Freon Hexane	Rep No. 1	Rep No. 2	Rep No. 3	Mean Concen- tration	Standard Deviation
Paper Mill	Dewatered Sludge	Freon Hexane	11000 6600	5300 2400	7900 11000	8000 6600	2762 4203
POTW	Sewage Sludge	Freon Hexane	98000 110000	81000 86000	81000 80000	87000 91000	9940 13281
Leather Tannery	Dewatered Sludge	Freon Hexane	11000 21000	12000 15000	12000 19000	12000 18000	732 3201
POTW	Digested Sludge	Freon Hexane	130000 54000	97000 76000	66000 48000	98000 59000	33028 14516
Petroleum Refinery	API Separator Sludge	Freon Hexane	320000 240000	350000 320000	250000 240000	310000 270000	53257 43822
Industrial Laundry	DAF Sludge	Freon Hexane	310000 290000	310000 360000	240000 180000	290000 280000	41717 90819
Fish Oil Plant	Oily Sludge	Freon Hexane	890000 440000	1000000 530000	770000 460000	890000 480000	131249 46318
Coke Plant	Waste Activated Sludge	Freon Hexane	8300 14000	8000 19000	18000 15000	11000 16000	5505 2732
Wood Preserving Plant	Solid Waste	Freon Hexane	150000 140000	140000 130000	140000 130000	140000 130000	3512 6557
Drilling Fluid Supplier	Used drilling mud	Freon Hexane	1300 1300	1600 1200	1300 1600	1400 1400	157 201
Contam. Soils	Kerosene Contaminated Soil	Freon Hexane	2000 2500	1400 3200	1900 2600	1700 2800	352 410
Poultry Plant	Waste Activated Sludge	Freon Hexane	38000 5900	11000 11000	40000 46000	30000 21000	16263 21795
Rolling Mill	Dewatered Scale	Freon Hexane	11000 14000	14000 14000	17000 16000	14000 15000	2884 983
Mayonnaise Plant	Oily Sludge	Freon Hexane	880000 590000	850000 780000	780000 520000	840000 630000	50521 132020
Seafood Plant	Waste Sludge	Freon Hexane	64000 34000	31000	53000 27000	58000 31000	7526 3867

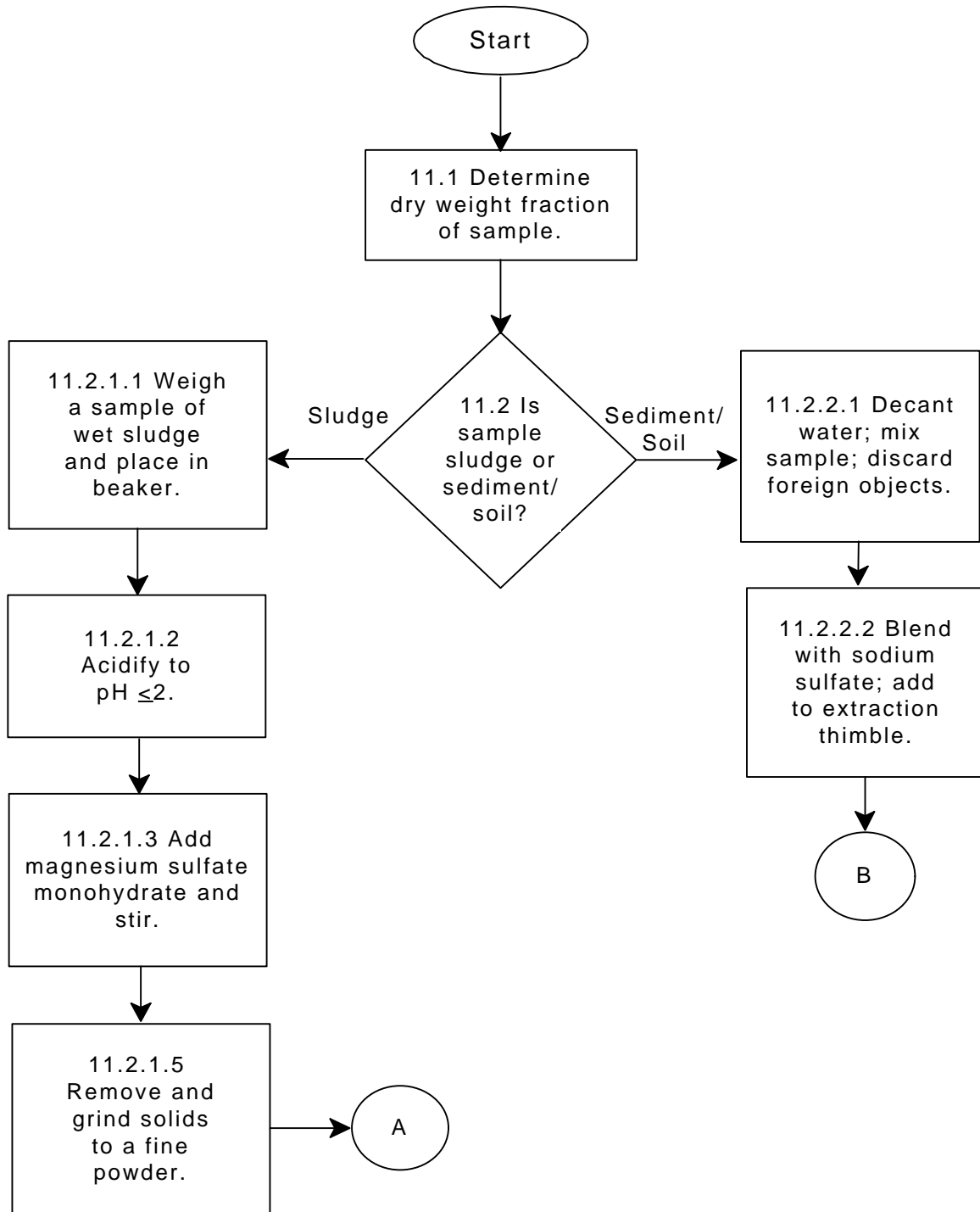
TABLE 1
(CONTINUED)

Facility/ Process	Waste Stream	Solvent: Freon Hexane	Rep No. 1	Rep No. 2	Rep No. 3	Mean Concen- tration	Standard Deviation
Seafood Plant	Oily Sludge	Freon Hexane	400000	410000	430000	410000	16371
			400000	390000	390000	400000	7095
Poultry Plant	DAF Sludge	Freon Hexane	670000	600000	570000	610000	49549
			530000	530000	530000	530000	2449
Railroad Yard	Oily Sludge	Freon Hexane	870000	920000	870000	890000	27906
			850000	840000	830000	840000	6884
Can Manufact Plant	Filter Cake	Freon Hexane	62000	62000	60000	61000	976
			69000	64000	66000	66000	2615
Soup Plant	DAF Sludge	Freon Hexane	600000	590000	610000	600000	10066
			580000	520000	600000	570000	40361
Oily Water Treatment Plant	Oily Sludge	Freon Hexane	76000	75000	70000	74000	3215
			77000	60000	79000	72000	10713
Can Manufact Plant	Oily Sludge	Freon Hexane	94000	88000	94000	92000	3291
			80000	90000	83000	85000	4992
Can Manufact Plant	Filter Cake	Freon Hexane	290000	290000	300000	290000	6217
			290000	290000	290000	290000	2029
Drum Handling Facility	Oily Sludge	Freon Hexane	1200000	1100000	1200000	1200000	57735
			990000	1000000	980000	1000000	27319
Polymer Plant	Dewatered Sludge	Freon Hexane	13000	12000	8200	11000	2524
			8400	6900	9100	8100	1122
Restaurant	Vegetable Oil Waste	Freon Hexane	760000	610000	780000	720000	92060
			1100000	980000	980000	1000000	80064
Leather Tannery	Waste Sludge	Freon Hexane	180000	220000	190000	190000	22140
			240000	270000	210000	240000	31177

Source: Reference 1

METHOD 9071B

n-HEXANE EXTRACTABLE MATERIAL (HEM) FOR SLUDGE, SEDIMENT, AND SOLID SAMPLES



METHOD 9071B

n-HEXANE EXTRACTABLE MATERIAL (HEM) FOR SLUDGE, SEDIMENT, AND SOLID SAMPLES
(Continued)

