		SERIOUSNESS		
		Major	Moderate	Minor
	Major	$10,000–$50,000	$5,000–$25,000	$2,000–$13,000
CONDUCT	Moderate	$5,000–$10,000	$2,500–$5,000	$500–$3,000
	Minor	$500–$7,500	$500–$2,500	$250–$1,250

(g) The Department shall determine the seriousness of the violation as major, moderate or minor as set forth in (g)1 through 3 below.

1. Major shall include:

i. Any violation of any effluent limitation that is measured by concentration or mass for any discharge exceeding the effluent limitation as follows:

(1) By more than 50 percent for a hazardous pollutant;

(2) By more than 100 percent for a non-hazardous pollutant; or

(3) Any discharge of a pollutant that has caused imminent endangerment to human health, welfare or to the environment; or

ii. The greatest violation of a pH effluent range in any one calendar day which violation deviates from the midpoint of the range by more than 50 percent of the midpoint of the range excluding the excursions specifically excepted by a NJPDES/SIU issued permit with continuous pH monitoring; or

iii. Any other violation not included in (g)1i or ii above which either:

(1) Has caused or has the potential to cause serious harm to human health or the environment; or

(2) Seriously deviates from the requirements of the Water Pollution Control Act or of any rule, pretreatment standards, effluent limitation, administrative order or permit issued pursuant thereto; serious deviation shall include, but not be limited to, those violations that are in complete contravention of the requirement, or if some of the requirement is met, which severely impair or undermine the operation or intent of the requirement.

2. Moderate shall include:

i. Any violation, other than a violation of an effluent limitation identified in (g)2ii or iii below, which has caused or has the potential to cause substantial harm to human health or the environment;

ii. Any violation of an effluent limitation which is measured by concentration or mass of any discharge exceeding the effluent limitation as follows:

(1) By 20 to 50 percent for a hazardous pollutant; or

(2) By 40 to 100 percent for a non-hazardous pollutant;

iii. The greatest violation of a pH effluent range in any one calendar day which violation deviates from the midpoint of the range by at least 40 percent but no more than 50 percent of the midpoint of the range excluding the excursions specifically excepted by a NJPDES/SIU issued permit with continuous pH monitoring; or

iv. Any violation, other than a violation of an effluent limitation identified in (g)2ii or iii above, which substantially deviates from the requirements of the Water Pollution Control Act or of any rule, pretreatment standards, effluent limitation, administrative order or permit issued pursuant thereto; substantial deviation shall include, but not be limited to, violations that are in substantial contravention of the requirements or which substantially impair or undermine the operation or intent of the requirement.

3. Minor shall include:

i. Any violation, other than a violation of an effluent limitation identified in (g)3ii or iii below, not included in (g)1 or 2 above;

ii. Any violation of an effluent limitation which is measured by concentration or mass for any discharge exceeding the effluent limitation as follows:

(1) By less than 20 percent for a hazardous pollutant; or

(2) By less than 40 percent for a non-hazardous pollutant; or

iii. The greatest violation of a pH effluent range in any one calendar day which violation deviates from the midpoint of the range by less than 40 percent of the midpoint of the range excluding the excursions specifically excepted by a NJPDES/SIU issued permit with continuous pH monitoring.

(h) The Department shall determine the conduct of the violator as major, moderate or minor as follows:

1. Major shall include any intentional, deliberate, purposeful, knowing or willful act or omission by the violator;

2. Moderate shall include any unintentional but foreseeable act or omission by the violator; or

3. Minor shall include any other conduct not included in (h)1 or 2 above.

(i) The Department may move from the midpoint of the range, to an amount not greater than the maximum amount nor less than the minimum amount in the range, on the basis of the following factors:

1. The compliance history of the violator;

i. No violations of the same effluent limitation and discharge point at all in the two years immediately preceding the pending violation shall result in a reduction equal to 25 percent of the midpoint.

ii. No serious or fewer than four lesser violations of the same effluent limitation and discharge point in the two years immediately preceding the pending violation shall result in a reduction equal to 10 percent reduction of the midpoint.

iii. One isolated serious violation or four or more lesser violations of the same effluent limitation and discharge point in the two years immediately preceding the date of the pending violation shall result in an increase equal to 10 percent of the midpoint.

iv. Any violation(s) which caused a person to become or remain in significant noncompliance or two or more isolated serious violations where such violations are of the same effluent limitation and discharge point in the two years immediately preceding the date of the pending violation shall result in a 25 percent increase from the midpoint;

2. Where the nature, timing and effectiveness of any measures taken by the violator to mitigate the effects of the violation for which the penalty is being assessed results in compliance within 30 days of receipt of the notice of violation from the Department;

3. Any unusual or extraordinary costs or impacts directly or indirectly imposed on the public or the environment as a result of the violation;

4. Any impacts on the receiving water, including stress upon the aquatic biota, or impairment of receiving water uses, such as for recreational or drinking water supply, resulting from the violation; and

5. Other specific circumstances of the violator or violation.

New Rule, R.1997 d.106, effective May 5, 1997.
See: 28 N.J.R. 720(a), 28 N.J.R. 2779(a), 28 N.J.R. 3040(a), 28 N.J.R. 3494(a), 28 N.J.R. 4697(a), 29 N.J.R. 1691(c).
Former section recodified to N.J.A.C. 7:14–8.18.
Administrative correction.
See: 29 N.J.R. 2664(a).
In (f), changed range for Major/ Major from $40,000 – $50,000 to $10,000 – $50,000 and changed range for Minor/Minor from $500 – $1,250 to $250 – $1,250.

7:14–8.17 Civil administrative penalty for failure to implement an approved industrial pretreatment program

(a) The Department may assess a civil administrative penalty against any delegated local agency pursuant to this section for each violator who fails to implement its approved industrial pretreatment program as required by the Federal Act, the State Act, or the Water Pollution Control Act, and for violations of any rule, administrative order, or permit issued pursuant thereto.

(b) Each violation of any provision of the Federal Act, the State Act, the Water Pollution Control Act, or any rule, administrative order, or permit issued pursuant thereto, shall constitute an additional, separate and distinct violation.

(c) The Department may assess a civil administrative penalty for violations described in this section at the midpoint of the following ranges except as adjusted pursuant to (e) below:

1. For failure to implement any of the following pretreatment program requirements, the civil administrative penalty shall be in an amount up to $10,000:

i. Give public notice to indirect users which meet or have met the significant non-compliance criteria as defined by 40 CFR Part 403.8(f)(2)(vii);

ii. Ensure public participation and notification;

iii. Perform RCRA notification pursuant to 40 C.F.R. Part 403; or

iv. Submit required major program modifications.

2. For failure to implement any of the following pretreatment program requirements, the civil administrative penalty shall be in an amount up to $20,000:

i. Identify and locate indirect users;

ii. Perform data management and recordkeeping;

iii. Sample the treatment works as required by the conditions of the IPP; or

iv. Submit a "40 CFR Part 403" annual report, and/or the "CWEA" annual report pursuant to N.J.S.A. 53:10A–14.2.

3. For failure to implement any of the following pretreatment program requirements, the civil administrative penalty shall be in an amount up to $50,000:

i. Inspect indirect users;

ii. Issue a permit to those facilities required to receive such a document;

iii. Sample indirect users;

iv. Initiate enforcement actions in accordance with an approved enforcement response plan and/or the pretreatment program as approved, including any subsequent amendments thereto;

v. Develop and enforce local discharge limitations;

vi. Review reports and identify violations; or

vii. Secure and maintain program resources.

(d) The Department may assess a civil administrative penalty in accordance with (c) above at any time. The assessment shall be based on the Department's evaluation of the delegated local agency's pretreatment program requirements. Furthermore, the Department may require a delegated local agency to adequately respond to findings based on an inspection conducted by the Department, the Department's review of the delegated local agency's 40 CFR Part 403 annual report, or the IPP on-site audit conducted by the Department.

(e) The Department may adjust the amount determined pursuant to (c) above to assess a civil administrative penalty from the midpoint of the range to an amount not greater than the maximum amount nor less than the minimum amount in the range on the basis of the following factors:

1. The compliance history of the violator;

2. The nature, timing and effectiveness of any measures taken by the violator to prevent future similar violations;

3. Any unusual or extraordinary costs or impacts directly or indirectly imposed on the public or the environment as a result of the violation; and/or

4. Other specific circumstances of the violator or violation.

(f) When the Department determines that the violator has gained an economic benefit from a violation, the Department may, in addition to any other civil administrative penalty assessed pursuant to this subchapter, include as part of a civil administrative penalty, under (c) above, the economic benefit (in dollars) which the violator has realized as a result of not complying, or by delaying compliance.

New Rule, R.1997 d.106, effective May 5, 1997.
See: 28 N.J.R. 720(a), 28 N.J.R. 2779(a), 28 N.J.R. 3040(a), 28 N.J.R. 3494(a), 28 N.J.R. 4697(a), 29 N.J.R. 1691(c).

7:14–8.18 Severability

If any provision of this subchapter or the application thereof to any person or circumstances is held invalid, such invalidity shall not affect other provisions or applications, and to this end, the provisions of the subchapter are declared to be severable.

New Rule, R.1989 d.282, effective June 5, 1989.
See: 21 N.J.R. 373(a), 21 N.J.R. 1530(a).
Amended by R.1991 d.378, effective August 5, 1991.
See: 23 N.J.R. 1089(a), 23 N.J.R. 2366(a).
Section recodified from 8.14.
Recodified from 7:14–8.16 by R.1997 d.106, effective May 5, 1997.
See: 28 N.J.R. 720(a), 28 N.J.R. 2779(a), 28 N.J.R. 3040(a), 28 N.J.R. 3494(a), 28 N.J.R. 4697(a), 29 N.J.R. 1691(c).

Case Notes

Penalty found appropriate for failure to provide self-monitoring reports, failure to construct treatment works and continued excessive discharge of pollutants. Lentine Aggregates v. Dept. of Environmental Protection, 4 N.J.A.R. 117 (1981), affirmed per curiam Dkt. No. A–3424–80 (App.Div.1982).

APPENDIX A

DEP LABORATORY METHODS

Method No. 010: pH (Electrometric)

Method No. 012: Total Residue

Method No. 013: Volatile and Ash Content of Total Residue

Method No. 032: Phenols

Method No. 036: Oil and grease

Method No. 100: Metals

pH (ELECTROMETRIC)

N.J. SLUDGE METHOD NO. DEP 010

1.0 Scope and Application

1.1 This method is applicable to the determination of pH in municipal and industrial sludges.

2.0 Summary of Method

2.1 A representative sample of sludge is thoroughly mixed and analyzed for pH electrometrically using either a glass electrode in combination with a reference electrode or a combination electrode.

2.2 The calibration of the pH electrode meter system is adjusted and checked with buffer solutions.

3.0 Sample Handling and Preservation

3.1 Upon collection, samples shall be refrigerated or iced at 4°C.

4.0 Limitations

4.1 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode or applying a correction factor from a table or graph provided by the pH meter manufacturer.

4.2 Coatings of oil material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with dilute hydrochloric acid (1 ml concentrated hydrochloric acid diluted to 10 ml with water) may be necessary to remove any remaining film.

NOTE 1: It may be necessary to centrifuge an oily sludge to obtain an aqueous phase for true pH determination.

4.3 Temperature effects on the electrometric measurement of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source is the change of pH inherent in the sample at various temperatures. This error is sample dependent and cannot be controlled; it should therefore be noted by reporting both the pH and temperature at the time of analysis.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory should maintain a current awareness file of OSHA rules regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should be made available to all personnel involved in the chemical analysis.

6.0 Apparatus

6.1 pH Meter, laboratory or field model, with an accuracy of ± 0.05 unit. A wide variety of instruments are commercially available with various specifications and optional equipment.

6.2 Glass pH electrode.

6.3 Reference electrode—a fiber junction, calomel, silver-silver chloride or other electrode of constant potential may be used. (Do not use gel filled electrodes).

6.4 Glass combination electrode.

6.5 Magnetic stirrer and TFE coated stirring bar.

6.6 Thermometer with at least one degree calibrations or less.

NOTE 2: Temperature compensator may be used instead of a thermometer.

6.7 Dispersion Device, homogenizer, blender, or other apparatus capable of disintegrating large particles.

7.0 Reagents

7.1 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial venders. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

8.0 Calibration

8.1 At a minimum, each instrument must be calibrated at pH 7.0 before each use and after each set of 10 samples. The accuracy of the system must be checked and recorded daily at approximately pH 4 and 9 or 10 with appropriate certified buffers. The three values must agree within 0.05 pH units of the assigned values.

8.1.1 If the values do not agree within 0.05 pH units, correct the problem before proceeding.

9.0 Procedure

9.1 Dilute, if required, with distilled water to achieve fluidity and/or to dissolve any inorganic buffer salts that may be present.

9.2 Disperse sample, if necessary, with a homogenizer or blender to disintegrate large particles.

9.3 Calibrate the meter and electrode system as described in Section 8.

9.4 Bring the sample temperature within 2°C of the buffer solution.

9.5 Rinse or gently wipe the electrodes with distilled or deionized water after each sample or buffer and gently blot them with a clean dry tissue. Immerse them into the sample beaker and stir gently at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH to the nearest 0.1 unit and temperature to the nearest degree.

10.0 Precision and Accuracy—No data are available.

11.0 References

11.1 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA 6[00]/4–79–020, March, 1979.

TOTAL RESIDUE

N.J. SLUDGE METHOD NO. DEP 012

1.0 Scope and Application

1.1 This method is designed to measure the residue content of municipal and industrial sludges over a range of 1–75% W/W.

2.0 Summary of the Method

2.1 A representative portion of the sample is weighed and dried to constant weight in an oven at 104 ± 1°C. The remaining solids are weighed and calculated as % W/W total residue of the original sample.

3.0 Sample Handling and Preservation

3.1 Upon collection, samples shall be placed in a wide mouth, air tight, polyethylene or glass container and refrigerated or iced to 4°C.

4.0 Limitations

4.1 Rapid weighing of the sample, before and after drying, is essential to obtain accurate results.

5.0 Safety

5.1 The drying oven should be placed in a hood or supplied with a vent to remove noxious odors.

6.0 Apparatus

6.1 Pan balance, electronic, capable of weighing to ± 0.01 gram.

6.2 Weighing dishes, aluminum pan, porcelain dish or equivalent.

Note 1: Use a porcelain dish if proceeding to N.J. Sludge Method No. DEP 013 or for highly alkaline samples.

6.3 Oven, mechanical or gravity convection capable of being regulated at 104 ± 1°C, or equivalent.

6.4 Steam bath (optional).

6.5 Desiccator, with indicating desiccant.

7.0 Reagents—none.

8.0 Procedure

8.1 Tare the weighing dish, using a pan balance, to the nearest 0.01 gram and record as W1.

Note 2: If used, two aluminum pans should be seated together to provide a more rigid support for the sample.

8.2 Shake the covered sample container vigorously, disperse sample, if necessary, with a homogenizer or blender to disintegrate large particles.

8.3 Immediately, transfer a mixed sample aliquot to the dish such that the final residue weight is at least 1 gram and will provide adequate drying in 16–24 hours.

8.4 Reweigh the dish to the nearest 0.01 gram and record the weight as W2.

Note 3: Rapid transfer and weighing is essential to prevent loss of moisture during this step.

8.5 Transfer the dish containing the sample to a convection oven, operating at 104 ± 1°C and dry the contents to constant weight.

Note 4: A steam bath may be used to reduce the sample volume provided the sample is subsequently dried in the convection oven at 104°C for at least an hour and then brought to constant weight as specified above.

8.6 Remove the dish from the oven and place in a desiccator until cool. Reweigh to the nearest 0.01 gram and record weight as W3.

Note 5: Rapid weighing is essential to prevent the adsorption of moisture from the air.

Note 6: If volatile residue or ash residue analysis is to be performed on the sample, place the weighed sample in a desiccator and proceed directly with N.J. Sludge Method No. DEP 013.

9.0 Calculations

9.1 To determine the percent total residue by weight in the sample, use the following equation:

$$\%\ W/W\ \text{total residue} = \frac{W3-W1}{W2-W1} \times 100$$

Where:
W1 = weight of the original empty dish, in grams (see 8.1);
W2 = weight of the original dish plus the sample, in grams (see 8.4); and,
W3 = weight of the original dish plus the sample residue, in grams (see 8.6).

10.0 Precision and Accuracy—No data are available.

11.0 References

11.1 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, EPA 600/4–79–020, March 1979.

VOLATILE AND ASH CONTENT OF TOTAL RESIDUE

N.J. SLUDGE METHOD NO. DEP 013

1.0 Scope and Application

1.1 This method is applicable to sludge and provides an approximation of the organic material contained in municipal and industrial sludge over a range of 1–75% W/W. It is used in conjunction with the procedure for the determination of Total Residue, N.J. Sludge Method No. DEP 012.

2.0 Summary of the Method

2.1 The residue from N.J. Sludge Method No. DEP 012, is ignited at 550°C in a muffle furnace. The loss in weight

on ignition is reported as volatiles and the resulting solids are reported as ash.

3.0 Sample Handling and Preservation—See N.J. Sludge Method No. DEP 012.

4.0 Limitations

4.1 The method is empirical and approximates the organic content of the sludge due to the volatilization of organic matter. Mineral salts may decompose and give high results for organic volatiles.

5.0 Safety

5.1 The muffle furnace and drying ovens should be placed in a hood or supplied with a vent to remove noxious odors.

Note 1: Sludges containing relatively large amounts of nonvolatile hydrocarbons may present a potential hazard when placed in a muffle furnace at 550°C. These samples may be placed in a cold muffle furnace and brought up to 550°C slowly to avoid spontaneous ignition.

6.0 Apparatus

6.1 Muffle furnace, capable of being regulated at 550 ± 50°C.

7.0 Reagents—none.

8.0 Procedure

8.1 Place the weighed residue and dish from N.J. Sludge Method No. DEP 012, in a muffle furnace preheated to 550 ± 50°C.

Note 2: Do not use an aluminum pan for this procedure.

8.2 Ignite the sample for 60 minutes ± 5 minutes at 550 ± 50°C.

8.3 Remove the sample from the furnace with crucible tongs and after allowing the pan to cool partially in the air, place in a desiccator for at least one hour.

8.4 Reweigh the dish to ± 0.01 gram and record the weight as W4.

Note 3: If subsequent analyses are to be performed on the resultant residue, store the residue in a desiccator.

9.0 Calculations

9.1 To determine the volatile content of the residue, use the following equation:

$$\%\ W/W\ \text{Volatile residue} = \frac{(W3-W4)}{W3-W1} \times 100$$

Where:
W1 = weight of the original dish, in grams (determined in DEP 012, 8.1);
W3 = weight of the original dish plus the sample residue, in grams (determined in DEP 012, 8.6); and,
W4 = weight of the original dish plus the ignited sample, in grams (determined in DEP 013, 8.4).

9.2 To determine the ash content of the residue, use the following equation:

$$\%\ W/W\ \text{Ash residue} = \frac{W4-W1}{W3-W1} \times 100$$

Where:
W1 = weight of the original dish, in grams (determined in DEP 012, 8.1);
W3 = weight of the original dish plus the sample residue, in grams (determined in DEP 012, 8.6); and,
W4 = weight of the original dish plus the ignited sample, in grams (see DEP 013, 8.4).

10.0 Precision and Accuracy—No data are available.

11.0 References

11.1 Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th ed., New York, 1975.

PHENOLS
N.J. SLUDGE METHOD NO. DEP 032

1.1 Scope and Application

1.1 This method is designed to determine the amount of phenolic compounds in municipal and industrial sludges.

1.1.1 The range of the method can be increased, if necessary, either by taking a smaller sample in step 9.2.3 or by taking a smaller aliquot in step 9.5.1.

1.1.2 The range of the method can be lowered, if necessary, by increasing the sample size taken in step 9.2.3.

2.0 Summary of Method

2.1 A representative portion of the sludge sample is mechanically dispersed in water to aid in solubilizing the phenolics, the pH is adjusted to pH 12.0–12.5 with sodium hydroxide. The alkaline sample is made to a known volume with water. A portion of the sample is filtered to remove insolubles. The filtrate is extracted with "Freon" † 113 to remove interferences. The extracted sample is heated to remove the extractant, cooled to room temperature and then adjusted to pH 3 with phosphoric acid. A known portion of the acidic solution, after treatment with copper sulfate solution, is distilled to remove steam-distillable phenolics from the sample matrix. The steam-distillate is reacted with 4–aminoantipyrine at pH 10.0 ± 0.2 in the presence of potassium ferricyanide to form a reddish-brown colored antipyrine dye. The absorbance of the aqueous dye solution is measured directly at 510 nm. The concentration of phenolic compounds, as phenol (C_6H_5OH), in the sample is expressed in terms of mg/kg on the "dry weight" basis.

† Registered U.S. Patent Office

3.0 Sample Handling and Preservation

3.1 Upon collection, samples shall be placed in a wide mouth polyethylene or glass container and refrigerated or iced to 4°C.

4.0 Limitations

4.1 Addition of sodium hydroxide to the sample causes heavy metals to precipitate. If this precipitate is not removed, an emulsion forms during the "Freon" 113 extraction step which causes an inefficient separation of the two phases. Filtration prior to extraction removes the precipitate and the extraction step proceeds without difficulty as little or no emulsion is formed.

4.2 The "Freon" 113 extraction step is necessary to eliminate substances which steam distill over with the phenolics and cause turbidity which interferes with the photometric determination. The "Freon" 113 extraction step normally eliminates the need for redistillation to remove turbid materials as required in the referenced methods (12.1, 12.2 and 12.3).

4.3 Phosphoric acid and copper sulfate are added after extraction and prior to distillation to eliminate interference due to hydrogen sulfide and sulfur dioxide. The use of $CuSO_4$ during the distillation of an acidic sample permits the formation of cupric sulfide without subsequent decomposition to H_2S. The acid solution also prevents the precipitation of cupric hydroxide which acts as an oxidizing agent toward phenols.

4.4 The phenols are distilled at a nearly constant rate from the non-volatile impurities. The rate of volatilization of the phenols is gradual, so that the volume of the distillate must equal that of the sample being distilled. It is for the above reason that the distillation is carried out in two steps.

4.5 The term "phenolics" as used in this method includes those hydroxy derivatives of benzene and its condensed nuclei which can be determined by the specified conditions of this method. Certain para-substituted phenols are excluded from the determination as they do not react with the colorimetric reagent. Other phenols may also be excluded if they (1) do not form water soluble phenolates at pH 12 and are extractable by "Freon" 113 and (2) do not steam distill during the distillation step.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA rule regarding the safe handling of the chemicals specified in this method. A reference file of Material Data Handling Sheets should be made available to all personnel involved in the chemical analysis.

6.0 Apparatus

6.1 Pan balance, capable of weighing to ± 0.1 gram.

6.2 Tekmar Tissumizer homogenizer, or equivalent, consisting of:

Tissumizer motor	# SDT–1810
Tissumizer shaft and generator	# SDT–182EN
Thyristor regulator	# TR–5T
Stand	# R–1821

NOTE 1: Blenders may not be an equivalent substitute.

6.3 Magnetic stirrer and TFE coated stirring bar.

6.4 pH Meter, laboratory or field model, with an accuracy of ± 0.05 unit. A wide variety of instruments are commercially available with various specifications and optional equipment.

6.5 Glass pH electrode.

6.6 Reference electrode—a fiber junction, calomel, silver-silver chloride or other electrode of constant potential may be used. (Do not use gel filled electrodes).

6.7 Glass combination electrode.

6.8 Filter, funnel, Buchner.

6.9 Filter discs, glass fiber, 7.0 cm, Whatman 943AH grade, or equivalent.

6.10 Separatory funnel, 1–liter capacity with TFE stopcock, Lab–Glass Co., Cat. No. LG–8371T–110, or equivalent.

6.11 Hotplate.

6.12 Ice-water bath.

6.13 1–liter distillation apparatus as shown in figure 1. Fisher Scientific Co., Cat. No. 9–126B, or equivalent.

6.14 Heating mantle, 1000 mL size, Glass–Col, or equivalent.

6.15 Retaining pan, stainless-steel mixing bowl, 3 qt. capacity.

6.16 Cenco–Lerner Lab–Jack, or equivalent.

6.17 500–mL volumetric flask, Class A, MCA type, marked at the 450 mL level.

6.18 Spectrophotometer, with 1.0 cm absorption cells.

7.0 Reagents

7.1 Sodium hydroxide (NaOH), 50% solution, reagent. Fisher Scientific Co., Cat. No. So–S–254, or equivalent.

7.2 "Freon" 113 ("F–113"; 1,1,2–trichloro–1,2,2–trifluoro–ethane).

NOTE 2: 250 mL of the solvent should leave no measureable residue on evaporation; distill if necessary.

7.3 Phosphoric acid (H_3PO_4), concentrated, reagent grade.

7.4 Copper sulfate ($CuSO_4$) solution.

Dissolve 100 g of reagent grade copper sulfate ($CuSO_4 .5H_2O$) in reagent water and dilute to 1 liter volume. Store in glass container.

7.5 Ammonium chloride (NH_4Cl) solution, 2%.

Dissolve 20 g of reagent grade ammonium chloride in reagent water and dilute to 1 liter volume. Store in glass container.

7.6 Ammonium hydroxide (NH_4OH) solution, concentrated, reagent grade.

7.7 4–Aminoantipyrine solution, 2%. Prepare fresh daily.

Dissolve 2.0 g of 4–aminoantipyrine crystals in reagent water and dilute to 100 ml volume. Store in glass container.

7.8 Potassium ferricyanide ($K_3Fe(CN)_6$) solution, 8%. Prepare fresh weekly.

Dissolve 8.0 g of reagent grade potassium ferricyanide in reagent water and dilute to 100 ml volume. Store in glass container.

7.9 Phenol (C_6H_5OH), reagent grade.

7.10 Phenol Stock Solution. Prepare fresh monthly and store at 4°C in a low actinic bottle. (1.0 mL = 1.0 mg).

Weigh out 1.000 g (± 0.001 g) of reagent grade phenol crystals and transfer quantitatively to a clean 1–liter volumetric flask which contains about 800 mL of reagent water using reagent water to aid in the transfer. Make the flask to volume with reagent water and mix the contents thoroughly. May be kept for 3 days in 4°C refrigerator.

NOTE 3: CAUTION—Use extreme caution in handling reagent grade (100%) phenol as it is very caustic. Wash off spills with copious amounts of cold water. Wear appropriate gloves and eye protection when handling the crystals.

7.11 Phenol Standard Solution. Prepare fresh on day of use (1.0 mL = 0.10 mg).

Transfer a 25.0 mL (pipet) aliquot of the Phenol Stock Solution (1.0 mL = 1.0 mg) to a clean 250–mL volumetric flask which contains about 100 mL of reagent water. Make the flask to volume with reagent water and mix the contents thoroughly. Use within 2 hours after preparation.

7.12 Reagent water, distilled or deionized.

7.13 Boiling stones, Hengar granule.

7.14 "Chromerge", or equivalent—chromic acid dissolved in concentrated H_2SO_4.

NOTE 4: CAUTION—Use care in preparation and handling. Wear appropriate gloves and eye protection.

8.0 Calibration

8.1 Spectrophotometer Calibration

8.1.1 Prepare a series of 100 mL phenol standards in clean, dry 150–mL beakers according to the following schedule:

Phenol Standard Solution (1.0 mL = 0.10 mg phenol)	Reagent Water	Phenol
	mL	mg
0.0	100.0	0.00
1.0	99.0	0.10
2.0	98.0	0.20
3.0	97.0	0.30
4.0	96.0	0.40
5.0	95.0	0.50
7.0	93.0	0.70
10.0	90.0	1.00

NOTE 5: All solutions must be at room temperature.

NOTE 6: Use an automatic laboratory grade 100–mL buret to add the water to the beaker and a 10–mL buret to add the phenol standard to the water.

8.1.2 Develop and measure the color, immediately and without delay, in the series of standards according to the procedure given in steps 9.5.2–9.5.8.

8.1.3 Calculate the factor (F) according to the following directions.

8.1.3.1 Determine the individual factor (f) for each standard in the series to the nearest 0.1 unit using 1.0 cm cells according to the following formula:

$$\frac{C}{A} \times 1000 = f$$

Where: C = mg of phenol present in the standard solution.
A = absorbance of standard solution in a 1.0 cm cell at 510 nm.

8.1.3.2 Determine the average factor for the seven individual standard solutions and record it as the factor (F) to the nearest whole number for the 1.0 cm cell.

8.1.3.3 A plot of absorbance vs. mg phenol (per 100 mL volume) on rectilinear coordinate graph paper should yield a straight line which passes through the origin.

9.0 Procedure

9.1 Determine % W/W total residue, NJ Sludge Method No. DEP 012.

9.2 Sample Preparation

9.2.1 Shake the covered sample container vigorously several times to ensure mixing.

9.2.1.1 Break up large particles with a spatula and remix.

9.2.2 Tare a clean, dry 250–mL beaker on a pan balance to the nearest 0.1 gram, record as W1.

9.2.3 Transfer, with a metal spatula 18–22 g of the well-mixed sample, (be sure to pick up the sample from at least two different spots within the sample container), weighed to the nearest 0.1 g, to the beaker, record as W2.

9.2.4 Add about 150 mL of reagent water to the beaker.

9.2.5 Use the Tekmar homogenizer to disperse the sludge sample into the water. Homogenize for 1–minute, first at a low speed setting, with the bottom of the probe just off the beaker bottom. The speed setting may be increased to increase the efficiency of the dispersion as long as no sample spills from the beaker.

9.2.6 Turn off homogenizer and let any large undispersed particles settle for 1 minute.

9.2.7 Decant slowly the dispersed sample into a clean 1–liter beaker. Retain all large particles in the 250–mL beaker for further dispersion.

9.2.8 Repeat steps 9.2.4–9.2.7 as needed, to completely disperse the sample. Normally, this step will be repeated 4–5 times.

9.2.9 Quantitatively rinse all residue from the homogenizer probe into the beaker using several reagent water rinses. The homogenizer may be turned "on" for a fraction of a second several times to remove water from the probe. Do this while the probe is inserted in the empty beaker.

9.2.10 Add a magnetic stirring bar to the dispersed sample in the liter beaker, stir the contents and measure the sample pH (meter standardized with pH 7 buffer; use temperature compensation).

9.2.11 Add dropwise 50% NaOH solution to bring solution to pH 12.2–12.5. Heavy metal ions will form a precipitate.

9.2.12 Transfer the alkaline solution quantitatively to a 1–liter volumetric flask using reagent water to aid in the transfer and to make the flask to volume. Mix the contents thoroughly.

9.2.13 Let the solids formed settle for 5–10 minutes and then filter about 600 mL of the supernatent solution through a 7.0 cm glass fiber filter (on a 7.0 cm Buchner funnel) into a 1–liter suction flask. Do not wash the filter cake. Use a dry funnel and suction flask for this step. Discard the filter residue.

9.3 Sample Extraction

9.3.1 Transfer the filtrate to a dry 1–liter separatory funnel.

9.3.2 Add 50 mL (graduated cylinder) of "Freon" 113, stopper the funnel and shake the contents vigorously for 1 minute to extract interferences into the "Freon" 113. Carry out extractions in front of well-ventilated laboratory hood. The separatory funnel stem must be dry before use. Vent the funnel, after the extraction, through the top stopper, not through the stopcock. Keep the emulsion in the funnel.

9.3.3 Swirl the funnel contents gently, let the "Freon" 113 settle for about 1–2 minutes and then drain the bottom "Freon" 113 layer to a waste solvent jar.

9.3.4 Repeat steps 9.3.2 and 9.3.3 three times more to extract the solution with a total of 200 mL of "Freon" 113.

9.3.5 Drain the extracted alkaline water layer back to a clean, dry 800–mL beaker.

9.3.6 Heat the solution (in a hood) to 60°C (thermometer) with occasional stirring to remove residual "Freon" 113. Stir the hot solution on magnetic stirrer at moderate rate for 1 minute to completely remove all of the "Freon" 113.

9.3.7 Cool the solution to room temperature (thermometer in an ice-water bath).

9.3.8 Measure out 500 mL (graduated cylinder) of the above solution to an 800–mL beaker and adjust the solution to pH 3.0–3.1 by the dropwise addition of concentrated phosphoric (H_3PO_4) acid while stirring the solution with a magnetic stirrer.

9.3.9 Proceed now directly to step 9.4, without delay.

9.4 Sample Distillation

NOTE 7: IMPORTANT, if a white residue (probably a copper salt) remains on the interior of the distillation flask after the normal cleaning treatment, it can be removed by rinsing the flask with warm 1+1 nitric acid (caution) followed by rinsing with reagent water to remove the residue and the acid.

9.4.1 Transfer, without rinsing the beaker, the extracted, acidified solution to a clean phenol distillation apparatus (see Figure 1).

9.4.2 Add 5 mL pipet of copper sulfate ($CuSo_4$) solution, add 12–15 boiling stones and then stopper the retort flask.

NOTE 8: Do not use glass beads as they cause excessive bumping.

9.4.3 Place a clean, dry 500–mL special volumetric flask under the condenser and turn on the positioned heating mantle. Be sure cooling water is flowing through the condenser.

9.4.4 Let the solution come to a full boil, distill 450 mL of the sample into the volumetric flask and then stop the distillation at this point by turning off the heating mantle and lowering it from the distillation flask. Use the 450 mL graduation mark on the special volumetric flask to determine the distillate volume. The heating mantle is connected directly into a 110 volt line, not into a Variac, in order to reduce the time of distillation.

9.4.5 Remove carefully, when boiling ceases, the stopper from the retort flask and add 50 mL (graduated cylinder) of reagent water to the flask.

9.4.6 Restopper the apparatus, reposition the heating mantle and reheat the solution to a boil again. Continue the distillation until a total of 500 mL of distillate has been collected in the volumetric flask.

9.4.7 Just as 500 mL volume is collected, turn off the heating mantle and lower it from the retort flask to stop the distillation. The distillate should be clear (no turbidity or oil droplets), essentially odorless and essentially colorless.

9.4.8 Mix thoroughly the contents of the stoppered volumetric flask by shaking and then proceed directly to step 9.5 without delay.

9.5 Colorimetric Procedure–Direct Photometric

9.5.1 Transfer 100 mL (pipet) of the mixed distillate (from step 9.4.8) to a clean dry 150–mL beaker. Prepare a blank from 100 mL (pipet) of reagent water and carry it through the same steps as the sample. If necessary, a smaller aliquot (pipet) of the sample distillate plus enough reagent water (pipet) to make a total volume of 100 mL is transferred to a 150–mL beaker.

9.5.2 Add 5.0 mL (pipet) of ammonium chloride (NH_4Cl) solution and mix with a clean glass stirring rod.

9.5.3 Calibrate the pH meter (combination electrode) with pH 7 buffer. Be sure to wash off buffer from the electrode with reagent water.

9.5.4 Measure pH of sample solution and adjust it to pH 10.0 ± 0.2 by dropwise addition of concentrated ammonium hydroxide (NH_4OH) solution (in a hood) from a medicine dropper while mixing the solution with the glass rod.

9.5.5 Remove pH electrode from the solution. Rinse off the electrode into a waste beaker, not into the sample solution.

9.5.6 Add 2.0 mL (pipet) of 4–aminoantipyrine solution (4–AAP) to the sample and mix promptly; followed immediately by 2.0 mL (pipet) of potassium ferricyanide solution ($K_3Fe(CN)_6$) and again mixed immediately. Treat each sample (and BLANK) in the series with the two reagents, as above, before proceeding to the next in the series.

9.5.7 Let the solution stand for 15 minutes, after mixing, to develop the color completely.

9.5.8 Measure the absorbance (A) of the sample solution (vs. the BLANK set at 0.000 absorbance) in a 1.0 cm absorption cell with the spectrophotometer set at 510 nm wavelength. Rinse the cell 2 times with reagent water and 2 times with acetone between samples. Use vacuum to aspirate the sample, water and acetone from the cell.

10.0 Calculations

10.1 Determine the amount (mg/kg) of phenolics in the sample on a dry weight basis, use the following equation:

$$\text{mg/kg phenolics} = \frac{A(F)(100000)}{V(W2-W1)(\%S)}$$

Where:

A = absorbance of sample solution (see 9.5.8) in 1.0 cm cell;
F = factor as determined (see 8.1.3.2);
V = mL volume of distillate (see 9.5.1), usually 100 mL;
W1 = weight of the original empty beaker, in grams (see 9.2.2);
W2 = weight of the original empty beaker plus the sample, in grams (see 9.2.3); and
%S = percent W/W total residue of sample (see 9.1) as determined by N.J. Sludge Method No. DEP 012.

Report all results to nearest mg/kg.

10.1.1 If the absorbance in the 1.0 cm cell in step 9.5.8 is less than 0.010A, then report the mg/kg value as "less than" the calculated value using 0.010A.

10.1.2 If the absorbance in the 1.0 cm cell in step 9.5.8 is greater than 1.000A, repeat steps 9.5.1–9.5.8 using a smaller aliquot of the distillate.

11.0 Precision and Accuracy—No data are available.

12.0 References

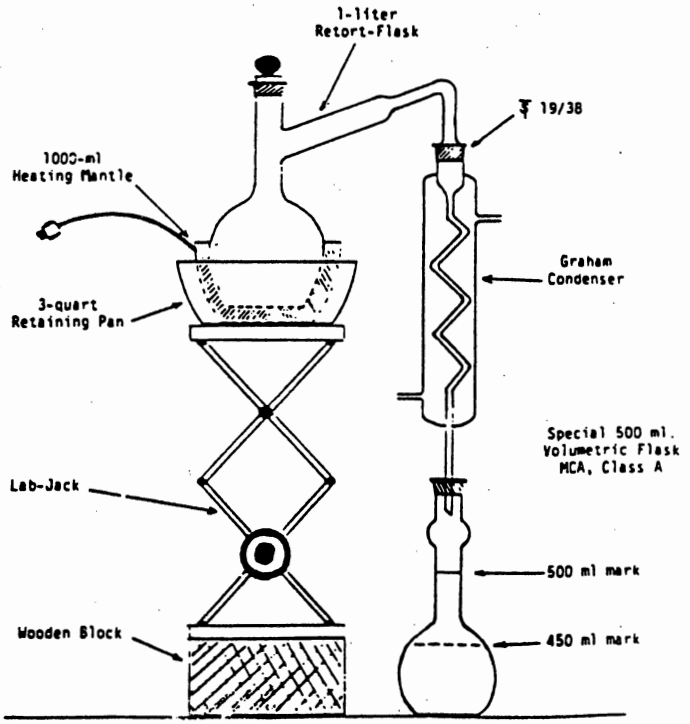
12.1 Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Cincinnati, 1974, pp. 241–242.

12.2 1974 Annual Book of ASTM Standards (Part 31), American Society for Testing and Materials, Philadelphia, 1974, Method D 1783–70 (Reapproved 1974).

12.3 Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th ed., New York, 1975, Method 510.

Figure 1

Distillation Apparatus



OIL AND GREASE

N.J. SLUDGE METHOD DEP 036

1.0 Scope and Application

1.1 This method is designed to determine the amount of oil and grease in municipal and industrial sludges in the range of 0 = 10% W/W oil and grease.

2.0 Summary of Method

2.1 This method defines two extraction procedures, one applicable to all sludges and one which may be used for sludge samples with a low percent total residue.

2.1.1 For all sludge samples, provided the detection limit of 0.5% can be achieved, a representative portion of the sludge sample is manually dispersed in a limited volume of water and then acidified with concentrated hydrochloric acid. The acidified sample slurry is dehydrated with the addition of magnesium sulfate monohydrate. After solidification, the dry sample is ground to a powder. Oil and grease is extracted from the powdered sample in a soxhlet extraction apparatus, using "Freon" † 113 as the extractant.

2.1.2 For sludge samples containing less than ten percent W/W total residue, the sample may be manually dispersed and acidified with concentrated hydrochloric acid. The oil and grease is extracted from the sample in a separatory funnel using "Freon" 113 as the extractant.

2.2 The "Freon" 113 is removed by distillation and the amount of residual extracted oil and grease, after drying, is determined gravimetrically. Results are reported as % W/W oil and grease on the dry 100% solids basis.

† Registered U.S. Patent Office.

3.0 Sample Handling and Preservation

3.1 Upon collection, samples shall be refrigerated or iced at 4°C.

4.0 Limitations

4.1 Any filterable "Freon" 113 soluble substances, such as elemental sulfur and certain organic dyes and nitrobodies, will be extracted and calculated as oil and grease.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential

health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA rule regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets should be made available to all personnel involved in the chemical analysis.

6.0 Apparatus

6.1 Pan balance, capable of weighing to ± 0.1 gram.

6.2 Glass stirring rod, heavy duty.

6.3 Boiling stones, Hengar granule.

6.4 Desiccator, with indicating silica-gel or calcium sulfate desiccant.

6.5 Finger cots, rubber, large, Fisher Scientific Co., Cat. No. 10–001C, or equivalent.

6.6 Balance, analytical, capable of weighing to ± 0.1 mg.

6.7 Hot water/steam bath.

6.8 Connecting tube, condenser, and solvent receiver.

6.9 For soxhlet extraction only (see 8.2).

6.9.1 Mortar and pestle, glass, 16 oz. capacity. Do not use porcelain as it is difficult to clean.

6.9.2 Soxhlet extraction assembly, consisting of:

Flask, 250 ml capacity, flat-bottom, with 24/40 joint; Fisher Scientific Co., Cat. No. 09–559B, or equivalent;

Extraction tube, with 55/50 joint, Fisher Scientific Co., Cat. No. 09–558C, or equivalent;

Condenser, Allihn-type with 55/50 joint, Fisher Scientific Co., Cat. No. 09–557C, or equivalent; and

Soxhlet cellulose extraction thimble, 43 mm diameter x 123 mm long, mfged. by Whatman, or equivalent.

6.9.3 Glasswool, washed with "Freon" 113.

6.9.4 Heating mantle, designed for flat bottom flask, 250–ml size.

6.9.5 Variable autotransformer, 120V output with 0–100 scale.

6.9.6 Forceps, metal, approx. 10 inch length.

6.10 For separatory funnel extraction only (see 8.3).

6.10.1 Separatory funnel, 50 ml with TFE stopcock.

6.10.2 Drying column-Chromatographic column, 19 mm ID, coarse frit filter disc.

6.10.3 Flask, 250 ml capacity, flat-bottom, with 24/40 joint; Fisher Scientific Co., Cat. No. 09–559B, or equivalent.

7.0 Reagents

7.1 Hydrochloric acid (HCl), concentrated.

7.2 Indicating pH paper for low pH measurement.

7.3 "Freon" 113 ("F–113"; 1,1,2–trichloro–1,2,2–trifluoro–ethane).

NOTE 1: 250 ml of the solvent should leave no measurable residue on evaporation; distill if necessary.

7.4 For soxhlet extraction only (see 8.2).

7.4.1 Magnesium sulfate monohydrate ($MgSO_4H_2O$).

Dry a thin layer of laboratory grade magnesium sulfate heptahydrate ($MgSO_47H_2O$), crystal, in an oven at 105–110°C for 48 hours.

NOTE 2: Stir and break up lumps frequently during the drying process.

NOTE 3: Caution, do not attempt to substitute magnesium sulfate, anhydrous, powder for the monohydrate as too much heat will be generated during the procedure and the resulting mass will be difficult to pulverize.

7.4.2 Reagent Water, distilled or deionized.

7.5 For separatory funnel extraction only (see 8.3).

7.5.1 Sodium sulfate-(ACS) Granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

8.0 Procedure

8.1 Determine % W/W total residue, N.J. Sludge Method No. DEP 012, if necessary.

8.2 Soxhlet extraction-applicable to all sludge samples, provided the required detection limit can be achieved.

8.2.1 Shake the covered sample container vigorously, disperse sample, if necessary, with a homogenizer or blender to disintegrate large particles.

8.2.2 Tare a clean, dry 250 ml beaker on a pan balance to the nearest 0.1 mg, record as W1.

8.2.3 Transfer, with a metal spatula 18–22 grams of the well-mixed sludge sample, (be sure to pick up the sample from at least two different spots within the sample container), weighed to the nearest 0.1 mg, to the beaker, record as W2.

8.2.4 Add 20 ml (graduated cylinder) of reagent water to the sample, if necessary, to fluidize.

8.2.5 Disperse the sample manually into the water, using the flat end of a clean, heavy glass stirring rod, with stirring and mixing to yield a uniform, lump-free slurry (do not homogenize). This step may require several minutes of effort to achieve the uniform finely divided slurry; do not use any additional water in this step.

8.2.6 Add concentrated hydrochloric acid (HCl), approximately one ml at a time, to the dispersed sample while stirring with the glass rod until the slurry is strongly acidic (pH 2 or less) as indicated by the pH paper. Stir the sample 10–15 seconds before testing for acidity.

8.2.7 Wait 10 minutes after the last HCl addition and recheck for acidity using the pH paper. If the sample is strongly acidic (pH 2 or less) proceed to step 8.2.8. If the sample is not strongly acidic, continue the HCl addition as in step 8.2.6 and repeat step 8.2.7 until the acidity holds for at least 10 minutes.

8.2.8 Reweigh the beaker (no stirring rod present) to the nearest 0.1 gram, record as M, determine the amount of total acidic slurry (TAS) that is present by difference from the tare weight (W1) of step 8.2.2 (TAS = M–W1).

8.2.9 Weigh out the magnesium sulfate monohydrate ($MgSO_4$–H_2O) that is at least equal to 1.3 times the total acid slurry weight found in step 8.2.8, (grams $MgSO_4H_2O$ = TAS x 1.3).

8.2.10 Add slowly while stirring with the glass rod the $MgSO_4$–H_2O to the acid slurry. The $MgSO_4H_2O$ will dehydrate the sample slurry to form a solid sample that can be ground to a powder. The oil and grease will be dispersed in the solid sample and heat will be generated by the reaction.

8.2.11 Stir the sample with the glass rod to a smooth paste and, before the paste sets up, spread the paste evenly over the entire inside of the beaker surface to facilitate its subsequent removal after it solidifies. Keep the paste off the bottom of the beaker as much as possible to ease the removal of the solidified sample in step 8.2.13.

8.2.12 Let the sample stand for about ½ hour so it may solidify and cool.

8.2.13 Transfer the solidified sample, using a metal spatula, to a clean glass mortar and grind to a uniform, free-flowing powder. Do not attempt to grind the entire sample at one time.

8.2.14 Transfer the entire powdered sample to a soxhlet cellulose extraction thimble (43 mm diameter X 123 mm long). Tap the thimble gently as it is filled to prevent the presence of voids in the powder. At this point, the thimble and sample can be placed in a clean labeled pint screwcap jar to hold overnight, if necessary.

8.2.15 Transfer one small boiling stone to a clean, dry 250 ml flat bottom extraction flask (24/40 joint) and place in a desiccator to condition for at least 1/2 hour.

8.2.16 Remove the flask from the desiccator, using finger cots, and rapidly weigh to the nearest 0.1 mg; record as W3, and set the flask aside.

8.2.17 Fill the remaining space in the sample-filled thimble with a loosely-packed wad of glasswool (washed with "Freon" 113) to prevent particles from flushing out of the thimble during extraction.

8.2.18 Gently slide the extraction thimble down the inside of the clean, dry extractor tube and assemble it to the condenser and to the tared extraction flask. Be sure good seal is obtained for the ungreased ground glass joint.

8.2.19 Seat the extraction flask in the heating mantle that is controlled by a variable transformer.

8.2.20 Turn on the water flow to the condenser; check for an adequate flow during the extraction procedure.

8.2.21 Slowly transfer about 225 ml (graduated cylinder) of "Freon" 113 to the apparatus by pouring it through the condenser top.

8.2.22 Turn on the heating mantle with the transformer (120 V output) to obtain a reflux rate of 1 cycle/3 minutes ± 15 seconds, maintain reflux for 4 hours.

Note 4: The transformer setting should be noted for future use.

Note 5: The rate and time of extraction in the soxhlet apparatus must be exactly as directed because of the varying solubilities of different greases.

8.2.23 Turn off and remove the hot mantle from the extraction flask at the end of the 4 hour extraction period.

8.2.24 Remove the extraction flask from the apparatus and set aside; remove the thimble from the tube, using a clean, long metal forceps, and let the "Freon" 113 drain back into the tube; transfer the residual "Freon" 113 from the tube to the flask. Discard the thimble and extracted sample. Proceed to step 8.4.

8.3 Separatory funnel extraction-recommended for sludge samples with less than ten percent W/W total residue as determined in N.J. Sludge Method No. DEP 012.

8.3.1 Shake the covered sample container vigorously, disperse sample, if necessary, with a homogenizer or blender to disintegrate large particles.

8.3.2 Tare a clean, dry 250 ml beaker on a pan balance to the nearest 0.1 mg, record as W1.

8.3.3 Transfer approximately 100 grams of the well-mixed sludge sample to the 250 ml beaker, weigh to the nearest 0.1 mg, record as W2.

8.3.4 Add concentrated hydrochloric acid (HC1), approximately one ml at a time, to the dispersed sample while stirring with the glass rod until the slurry is strongly acidic (pH 2 or less) as indicated by the pH paper. Stir the sample 10–15 seconds before testing for acidity.

8.3.5 Wait 10 minutes after the last HC1 addition and recheck for acidity using the pH paper. If the sample is strongly acidic (pH 2 or less) proceed to step 8.3.6. If the sample is not strongly acidic, continue the HC1 addition as in step 8.3.4 and repeat step 8.3.5 until the acidity holds for at least 10 minutes.

8.3.6 Place a clean, dry 250 ml flat bottom extraction flask in a desiccator to condition for at least one hour.

8.3.7 Remove the flask from the desiccator, using finger cots, and rapidly weigh to the nearest 0.1 mg; record as W3, and set the flask aside.

8.3.8 Quantitatively transfer the acidified sample to a 500 ml separatory funnel with a TFE stopcock.

8.3.9 Add 50 ml of "Freon" 113 to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, centrifugation, or other physical methods. Transfer the extract to an Erlenmeyer flask.

8.3.10 Add a second 50 ml volume of "Freon" 113 and repeat the extraction procedure a second time combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

8.3.11 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the tared 250 ml flat bottom extraction flask. Rinse the Erlenmeyer flask and column with 20 to 30 ml of "Freon" 113 to complete the quantitative transfer. Proceed to step 8.4.

8.4 Distill the "Freon" 113 from the flat bottom extraction flask in a 70 ± 5°C hot water bath. Clamp the extraction flask at a 45 degree angle and distill the "Freon" 113 into the solvent recycling apparatus.

Note 6: Carry out the distillation in a hood.

8.5 Place the extraction flask, free of "Freon" 113, on a boiling water/steam bath for 15 minutes. Again, clamping the flask at a 45 degree angle in a hood.

8.6 During the final 1 minute on the steam bath, draw air gently through the flask by means of applied vacuum, using 1/4" OD polyethylene tube which reaches to within 1" from the bottom of the extraction flask. The vacuum removes any heavy "Freon" 113 vapors which could cause high results to be reported if they were not drawn off and removed.

8.7 Wipe off the entire outside of the extraction flask with clean, dry paper towels to remove all traces of water.

8.8 Place the flask in a desiccator and let it cool for exactly 30 minutes.

Note 7: The length of time required for drying and cooling the extracted material cannot be varied. There may be a gradual increase in weight, presumably due to the absorption of oxygen or a gradual loss in weight due to volatilization, if the times are varied.

8.9 Remove from the desiccator, using finger cots, and rapidly weigh to the nearest 0.1 mg, record as W4.

9.0 Calculations

9.1 To determine the percent W/W oil and grease in the sample on a dry weight basis, use the following equation:

$$\%\ \text{W/W oil and grease} = \frac{W4\text{-}W3}{W2\text{-}W1\ (\%S)} \times 10{,}000$$

Where

W1 = weight of the original empty beaker, in grams (see 8.2.2 or 8.3.2);
W2 = weight of the original empty beaker plus the sample, in grams (see 8.2.3 or 8.3.3.);
W3 = weight of the empty flask, in grams (see 8.2.16 or 8.3.7);
W4 = weight of the empty flask plus the oil and grease extract, in grams (see 8.9); and
%S = percent W/W total residue of sample (see 8.1) as determined by N.J. Sludge Method No. DEP 012.

Report all results to the nearest 0.1%

10.0 Precision and Accuracy

10.1 The following data were obtained during the development of this method.

A composite sample (43.7% solids) was analyzed four times according to the soxhlet extraction procedure contained in this method. The following results were obtained:

Run	1	2	3	4	Avg.	STD. Dev.
% of oil and grease	1.0	1.0	0.8	1.1	1.0	0.13

10.2 The above data indicates that the method, as written, is reasonably precise when a large enough representative sample is taken for analysis. The relative standard deviation of the determination is ± 13%, for a single laboratory.

11.0 References

11.1 Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 14th ed., New York, 1975, Method 502D.

METALS

N.J. SLUDGE METHOD NO. DEP 100

1.0 Scope and Application

1.1 This procedure is applicable to the preparation of sludge samples prior to the determination of metals by atomic absorption spectrometry. This procedure is applicable to both direct aspiration and furnace atomization of the following elemental priority pollutants: arsenic (As), cadmium (Cd), calcium (Ca), chromium (Cr), copper (Cu), lead (Pb), magnesium (Mg), nickel (Ni), potassium (K), and zinc (Zn).

2.0 Summary of Method

2.1 This method defines two digestion procedures, one applicable to all sludges and one which may be used for sludge samples with a low percentage total residue.

2.1.1 For all sludge samples, the sample is digested with nitric acid and hydrogen peroxide and analyzed using atomic absorption methods.

2.1.2 For sludge samples containing less than ten percent W/W total residue, the sample may be treated as an aqueous sample and analyzed using the U.S. EPA procedure for the determination of total metals by atomic absorption found in the Methods for Chemical Analysis of Water and Wastes U.S. EPA (EPA–900/4–79–020).

3.0 Sample Handling and Preservation

3.1 Samples should be maintained at 4°C.

4.0 Limitations

4.1 See Section 5.0 of the Metals–Atomic Absorption Method in the Methods for Chemical Analysis of Water and Wastes, U.S. EPA (EPA 600/4–79–020).

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA rules regarding the safe handling of the chemicals specified in this method. A reference file of Material Data Handling Sheets should be made available to all personnel involved in the chemical analysis.

6.0 Apparatus

6.1 See Section 6.0 of the Metals–Atomic Absorption Method in the Methods for Chemical Analysis of Water and Wastes, U.S. EPA (EPA 600/4–79–020).

7.0 Reagents

7.1 See Section 7.0 of the Metals–Atomic Absorption Method in the Methods for Chemical Analysis of Water and Wastes, U.S. EPA (EPA 600/4–79–020).

7.2 Hydrogen Peroxide (30%).

8.0 Procedure

8.1 Sludge Digestion—applicable to all sludge samples.

8.1.1 Weigh and transfer to a 125–mL conical beaker a representative, 1.0 gram aliquot of a pulverized sample that has been dried in accordance with N.J. Sludge Method No. DEP 012. Record the weight of the sample to the nearest mg and record as D.

8.1.2 Add 5 mL of 1:1 nitric acid to the beaker, and cover it with a watch glass. Heat the contents of the beaker gently so that a reflex action occurs. Continue heating until the volume of the contents is reduced to approximately 2 mL.

8.1.3 Allow the contents to cool, add 4 mL of concentrated HNO_3 and again heat at a gentle reflux until the volume is reduced to approximately 2 mL.

8.1.4 After the second reflux has been completed and the sample has cooled, add 2 mL of concentrated nitric acid, 2 mL of deionized distilled water, and 2 mL of 30% hydrogen peroxide.

8.1.5 Return the beaker to the hot plate for warming to start the peroxide reaction. The reaction is vigorous. Care must be taken to avoid losses with the start of effervescence.

8.1.6 Heat until the volume is reduced to approximately 3 mL.

8.1.7 Continue the addition of 30% hydrogen peroxide in 3 mL increments (do not add more than 3 increments) with warming until the effervescence is minimal or the general sample appearance is unchanged.

8.1.8 Wash any residue from the underside of the watch glass and walls of the beaker into the sample solution and dilute the contents of the beaker to approximately 10.0 mL with deionized distilled water. Filter the contents of the beaker into a 50–mL volumetric flask through Whatman No. 42 paper (or the equivalent). Wash the insoluble residues in the beakers three times with 5 mL portions of 1% nitric acid, and add the washings to the volumetric flasks through the filters.

8.1.9 Dilute the contents of the volumetric flasks to 50 mL with deionized distilled water and analyze by atomic absorption spectrometry as specified in the Section 9.0 of the Metals–Atomic Absorption Method in the Methods for Chemical Analysis of Water and Wastes, U.S. EPA (EPA–600/4–79–020). Record the metal concentration in μg/ml.

8.2 Aqueous Sludge Digestion—if the percent W/W total residue as determined in N.J. Sludge Method No. DEP 012 is less than ten, the following procedure may be used.

8.2.2 Determine percent W/W total residue, N.J. Sludge Method No. DEP 012, if necessary.

8.2.3 Digest an amount of sludge that will give the equivalent of one (1) gram on a dry weight basis and analyze the sample using the method specified in Section 4.1.3 of the Metals–Atomic Absorption Method in the Methods for the Chemical Analysis of Water and Wastes, U.S. EPA (EPA 600/4–79–020).

NOTE 1: The appropriate conversion must be made to report the final result on a dry weight (W/W) basis.

9.0 Calculations

9.1 To determine the amount of metal present in the sample on a dry weight basis when using the procedure in section 8.1 of this method, use the following equation:

$$\text{mg metal/kg sample} = \frac{(A)(V)}{(D)}$$

Where: A = ug/mL of metal in digested sample (see 8.1.9);
V = final volume of processed sample in mL (see 8.1.8); and
D = Weight of dry sample in grams (see 8.1.1).

10.0 Precision and Accuracy

10.1 In an interlaboratory study, Reference 11.4, using a U.S. EPA reference sludge sample, the following data were obtained:

		Interlaboratory Study		
Determination	EPA Reference Value	Number of Participants	Laboratory Average	Laboratory Standard Deviation
1. ARSENIC	16.97	6	6.57	12.8
2. CADMIUM	20.77	13	18.5	2.95
3. CALCIUM	—	10	15300	5800
4. CHROMIUM	204	15	183	38
5. COPPER	1095	14	941	125
6. LEAD	519	14	516	83
7. MAGNESIUM	—	9	3620	2200
8. NICKEL	198	15	165	27
9. POTASSIUM	—	7	775	262
10. ZINC	1323	14	1190	185

11.0 References

11.1 Methods for the Chemical Analysis of Water and Wastes, U.S. EPA (EPA–600/4–79–020), March 1979.

11.2 Test Methods for the Evaluation of Solid Waste, Method 3050, USEPA SW–846, April 1984.

11.3 "Interim Methods for the Analysis of Elemental Priority Pollutants in Sludge", U.S. EPA, Cincinnati, 1978.

11.4 Adelman, H., Jenniss, S.W., and Katz, S.A., "Interlaboratory Analysis of Sewage Sludge", American Laboratory, December 1981.