FOSTER
Environmental Services

February 5, 1997

0714

Site: Westlake Landfill
ID #: MOD079900932
Break: 3.4
Other: OU #2
2-5-97

Mr. Steven Kinser, Remedial Project Manager
U.S. Environmental Protection Agency
Superfund Branch
Region VII
726 Minnesota Avenue
Kansas City, KS 66101

RE: SOPS FOR THE WEST LAKE LANDFILL OPERABLE UNIT 2, BRIDGETON, MO

Dear Mr. Kinser:

Enclosed are three copies of a Quality Assurance Plan and Standard Operating Procedures (SOPs) for TriMatrix Laboratories. The documents are submitted by Foster Environmental Services on behalf of Laidlaw Waste Systems, Inc.

Also included are three copies of Pace Analytical's SOPs for hardness and sulfide analysis. These SOPs were inadvertently omitted from the previous SOP package.

Should you have any questions please feel free to call me at (609) 492-6747.

Sincerely,

Diane Foster

cc: Doug Borro, Laidlaw Waste Systems, Inc.
Ward Herst, Golder Associates Inc.

40241207
SUPERFUND RECORDS

P.O. Box 1245 • Beach Haven, New Jersey 08008 • (609)492-6747

STANDARD OPERATING PROCEDURE

• TOTAL HARDNESS

(TITRIMETRIC mg/L as $CaCO_3$)

SOP Number:	HO-I-037
Author:	Bruce Brown
Effective Date:	January 31, 1997
Supersedes:	none

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Approvals:

Bruce Brown
Laboratory Supervisor

2-3-97
Date

Quality Assurance Officer

2/3/97
Date

I. PURPOSE

This laboratory standard operating procedure is used for the determination of total hardness by titration.

II. SCOPE AND APPLICATION:

This SOP can be used to determine total hardness in surface, drinking, saline and ground waters, industrial and domestic waste. To avoid large titration volumes, use sample aliquots of less that 25mg/L CaCO3 when possible.

III. SAFETY INFORMATION

A. Wear lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with samples.

B. Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.

C. Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

IV. RESPONSIBILITIES

A. ANALYST

1. All analysts are responsible for adherence to this SOP.

2. All analysts are responsible for notifying the section Supervisor/Manager of any required revisions to this SOP.

B. DEPARTMENT SUPERVISOR / MANAGER

1. The Department Supervisor / Manager is responsible for ensuring adherence to this SOP.

2. The Department Supervisor / Manager is responsible for performing an annual review of this SOP.

C. **QUALITY ASSURANCE OFFICER**

1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to the laboratory general manager and corporate quality assurance department.

2. The QAO is responsible for ensuring that all revisions to this SOP are implemented.

3. The QAO is responsible for determining distribution of and maintaining document control of this SOP.

IV. REVIEWS / REVISIONS

This SOP will be reviewed on an annual basis at a minimum. Revisions will be incorporated at the time of the review. The revised SOP will be distributed to appropriate personnel and the previous version replaced.

V. DISTRIBUTION

Distribution of this SOP will be determined by the QAO.

VI. SAMPLE HANDLING AND PRESERVATION

All samples should be collected in 250mL plastic or glass containers. Samples should be preserved with HNO3 to a pH of less than 2, and stored at 4deg C. samples can be stored for 6 months.

VII. INTERFERENCE

Excessive amounts of heavy metals can interfere with this analysis. A sodium cyanide solution(poison) will minimize this interference. Alternative ICP analysis is recommended in place of sodium cyanide solution.

VIII. APPARATUS AND REAGENTS

A. EDTA Titrant: Dissolve 16.9g of NH4Cl in 143mL of conc. NH4OH in a 250mL volumetric flask, then add 1.25g of Mg EDTA and dilute to the mark. Store for approximately one month.

NOTE: When this solution fails to elevate the sample pH to 10, discard and prepare fresh.

B. Indicators: See indicators as purchased from the manufacturer.
Calmagite Indicator
Methyl Red

C. Prepare 1+1 HCL in a 500mL volumetric flask.

D. NH4OH solution is prepared by diluting 210mL of NaOH into a 1000mL volumetric flask.

E. Ca standard solution is prepared by slowly dissolving 1.0g of CaCO3 in 1+1 HCl. Using a 500mL flask dissolve the CaCO3 in the 1+1 slowly the add 200mL of reagent grade water, stir to expel CO2 and cool. Add three drops methyl red and adjust to a orange color by 3N NH4OH or 1+1 Hcl as needed. Transfer to a 1000mL flask 0 and dilute to the mark.

IX. PROCEDURE

A. Place 25.0mL of sample in a 100mL -250mL porcelain casserole dish and neutralize with 1N NaOH.

B. Dilute the sample to a total volume of 50mL, then add 1 to 2mL of buffer solution.

C. Add 1 -2 drops of indicator solution or one small scoop if powdered indicator is used, then titrate to a blue-end point.

D. Record the ml of titrant used and calculate as per section X.D.

Note: For samples with <5mg/L hardness, redo analysis using a 100mL of sample.

X. QUALITY CONTROL

A. An LCS should be analyzed every twenty samples or daily per analytical batch.

B. An MS and duplicate should be analyzed every twenty samples or daily analytical batch.

C. Before any analysis begins all titration solution concentrations should be verified if purchased or standardized if prepared.

D. Hardness Calculation

$$\text{mg/L } CaCO_3 = \frac{A * N * 50{,}000}{\text{ml of sample}}$$

Where: A = ml of EDTA titrant used
B = Normality of EDTA titrant

XI. REFERENCE

Methods for the analysis of Water and Wastewater. 1983 and updates, Method 130.2

STANDARD OPERATING PROCEDURE

PREPARATION and ANALYSIS of AQUEOUS SAMPLES for TOTAL SULFIDE

SOP Number:	HO-I-038
Author:	Bruce Brown
Effective Date:	February 01, 1997
Supercedes:	none

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Approvals:

Russell Morgan 2/3/97

Operations Manager Date

2/3/97

Quality Assurance Officer Date

I. PURPOSE

This method is used for the determination of total sulfide released from aqueous samples, groundwater, effluents, and waste matrices. Separation of the acid soluble sulfide is accomplished by distillation under acidic conditions, and trapping the sulfide as H2S, then precipitate ZnS.

II. SCOPE AND APPLICATION

This standard operating procedure measures the total sulfide concentration in aqueous samples. Total sulfide can be measured as the acid insoluble and acid soluble fractions combined. For our purposes we can consider total sulfide as the acid soluble fraction.

III. SAFETY INFORMATION

Wear lab coat and safety glasses with side shields at all times while performing this procedure. Wear gloves to avoid skin contact with the samples and reagents.

1. Should skin or eye contact occur, flush the exposed area(s) with large amounts of water and seek immediate medical attention.
2. Never pipet materials by mouth. Use a rubber bulb or other approved suction device to transfer materials by pipet.

Handle and store all reagents in accordance with the precautions listed on the material safety data sheets (MSDS's).

1. Consult the MSDS for each reagent listed in this procedure before use. The MSDS will provide pertinent information on toxicity, safety precautions and storage conditions.
2. Always consult the label on the reagent bottle for up-to-date information on safety precautions during handling, preferred storage conditions, and expiration date.
3. Label all flasks, vials, etc. with the intended contents prior to filling. Follow established laboratory procedure in completing and affixing labeling information to equipment.

Handle all glass equipment with care, particularly during periods of heating and cooling.

IV. RESPONSIBILITIES

A. ANALYSTS

1. All analysts are responsible for adherence to this SOP.
2. All analysts are responsible for notifying the section Supervisor/ Manager of any required revisions to this SOP.

B. DEPARTMENT SUPERVISOR/MANAGER
   1. The Department Supervisor/Manager is responsible for ensuring adherence to this SOP.
   2. The Department Supervisor/Manager is responsible for performing an annual review of this SOP.

C. QUALITY ASSURANCE OFFICER
   1. The QAO is responsible for conducting periodic laboratory audits to monitor adherence to this and other SOPs. Results of the audit will be reported to Regional Management and Corporate Quality.
   2. The QAO is responsible for determining distribution of and maintaining document control of this SOP.

IV. REVIEWS/REVISIONS

A. This SOP will be reviewed on an annual basis at a minimum.
B. Required revisions will be incorporated at the time of the review.
C. The revised SOP will be distributed to all appropriate personnel and the superseded version replaced.

V. DISTRIBUTION

Distribution of this SOP will be determined by the QAO.

VI. SUMMARY OF METHOD

An aliquot of the waste is acidified in a closed system. The hydrogen sulfide gas generated is purged by nitrogen into a scrubber containing zinc acetate, where zinc sulfide is precipitated. The scrubber solution is then analyzed.

VII. SAMPLE HANDLING AND PRESERVATION

A. Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. The sample should be preserved with 2N Zn Acetate at a rate of 4 drops/100mL of sample. If excess sulfide is present then add Zn acetate until all sulfide precipitates. Analysis should commence as soon as possible, and samples should be kept refrigerated and stored in the dark until analysis begins. Samples can be held up to seven days in 4deg C conditions. When possible samples should be preserved with NaOH to raise the pH in the field.

III. APPARATUS

A. Round-bottom flask: 1000-ml with a two-hole stopper, fitted with a fritted gas-diffusion tube and a gas outlet tube.

B. Stirring apparatus: To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor driven propeller stirrer.

C. Flexible tubing: For connection from nitrogen supply to apparatus.

D. Nitrogen gas: With two-stage regulator.

E. Absorption flasks: 500 ml capacity flasks with glass tube and air stone, and an air outlet tube.

IX. REAGENTS

A. Zinc acetate solution, 2N: Dissolve 220 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 870 ml reagent water; this makes 1 liter of solution.

B. Sulfuric acid, conc. reagent grade.

X. PROCEDURE

A. Measure 250mL of sample into a graduated cylinder. Obtain a weight for the sample. After weighing pour sample into a distillation flask. Record both weight and volume.

B. Assemble distillation apparatus as shown in diagram.

C. With the nitrogen flowing, acidify the sample in the reaction flask with conc. H_2SO_4, and immediately replace the prepared 2-hole stopper tightly. Begin stirring the sample in the reaction flask. Total H2SO4 volume should be 50mL + an amount pre-determined needed to adjust sample pH to 1.

E. After 90 minutes, close off the nitrogen and disconnect the scrubber. *Transfer the solution in the scrubber to a plastic screw-top bottle.*

F. Titration Procedure

1. Place a known amount of standard iodine solution (0.025N) into a 500mL flask. The amount should be estimated to be in excess of the amount of sulfide expected.
2. Add distilled water, if necessary, to bring the volume to approximately 20mL.
3. Add 2 ml of 6 N HCl.
4. Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface if the sample.
5. If the iodine color disappears, add more iodine until the color remains. Record the total number of milliliters of standard iodine used in performing this step and step VII.A.1.
6. Titrate with the reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution) using a starch indicator until the blue color disappears. Record the number of milliliters used.

XI. QUALITY CONTROL

A. Prepare a method blank for every batch of up to 20 samples. If the method blank result is not less than the reporting limit, re-prep a new method blank and all samples in the batch with positive hits.

B. Prepare a laboratory control sample (LCS) for every batch of up to 20 samples. If the LCS recovery does not fall within statistical control limits, re-prep a new LCS and all samples in the batch.

C. Prepare a matrix spiked sample and a sample duplicate for every batch of up to 20 samples. If recovery is not within the control limits established for the LCS, and the LCS recovery is acceptable, flag the data as indicative of possible matrix interference.

Calculations.

$$\frac{\text{mL of I2 - (mL titrant * N titrant) * 32.06g/2eq}}{\text{sample vol.}}$$

XII. REFERENCE

EPA SW-846, *Test Methods for Evaluating Solid Waste*, Method 9030A.