71677

Subject	Number	Page
FORMS USED IN RI ACTIVITIES	SA-6.4	25 of 37
	Revision 1	Effective Date 08/10/88

ATTACHMENT C-1

GROUNDWATER LEVEL MEASUREMENT SHEET

Project Name: _____
Project No.: _____
Personnel: _____
Date: _____

LOCATION

Municipality: _____
County: _____
State: _____
Street or Map Location (If Off-Site) _____

WEATHER CONDITIONS

Temperature Range: _____
Precipitation: _____
Barometric Pressure: _____

Equipment No.: _____
Equipment Name: _____
Latest Calibration Date: _____

Tidally-Influenced: [ ] Yes [ ] No

Well or Piezometer Number	Date/Time	Elevation of Reference Point (Feet)*	Water Level Indicator Reading (Feet)*	Adjusted Depth (Feet)*	Groundwater Elevation (Feet)*

* All elevations to nearest 0.01 foot.

ATTACHMENT C-2
PUMPING TEST DATA SHEET

PUMPING TEST DATA SHEET — *NUS CORPORATION*

PROJECT NAME: ______ MEASURED WELL: ______
PROJECT NO.: ______ DATE: ______ PUMPING WELL: ______
GEOLOGIST: ______ CHECKED: ______ TEST NO. ______
DISTANCE FROM PUMPING WELL(ft.)(r): ______ PUMP SETTING, FEET BELOW MONITORING POINT. ______
STATIC H_2O LEVEL (ft.)(s_o): ______ MONITORING POINT: ______
TIME PURGE START OR STOP (t_o): ______ ELEVATION OF MONITORING POINT (ft. above MSL) ______

TIME	(t) MIN. SINCE PUMP START OR STOP	WATER LEVEL MEASUREMENTS (ft.)			(s) DD Or RECOVERY (ft.)	PUMPING RATE (Q) GPM	REMARKS
		READING	CORRECTION	DTW			

DRAFT

AR300535

ATTACHMENT C-3

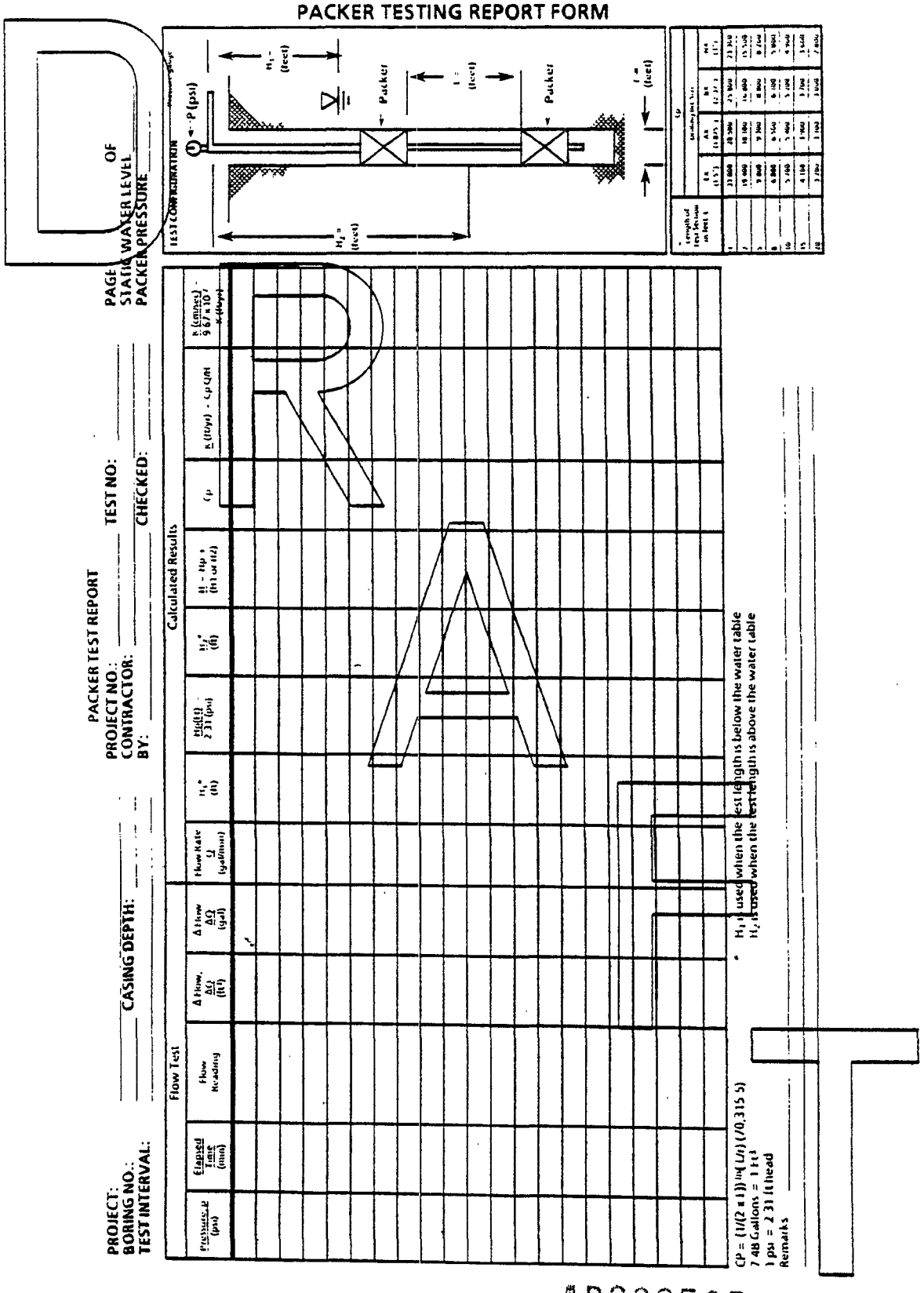
HYDRAULIC CONDUCTIVITY TESTING DATA SHEET — **NUS CORPORATION**

PROJECT NAME: ______ WELL/BORING NO.: ______
PROJECT NO.: ______ GEOLOGIST: ______
WELL DIAMETER: ______ SCREEN LENGTH/DEPTH: ______ TEST NO.: ______
STATIC WATER LEVEL (Depth/Elevation): ______ / ______ DATE: ______
TEST TYPE (Rising/Falling/Constant Head): ______ CHECKED: ______
METHOD OF INDUCING WATER LEVEL CHANGE: ______ PAGE ___ OF ___

TIME	ELAPSED TIME (min. or sec.)	MEASURED DEPTH TO WATER (ft.)	CORRECTION	DEPTH TO WATER (ft.)	DRAWDOWN OR HEAD (ft.)	REMARKS

vac 3/88

ATTACHMENT C-4
PACKER TESTING REPORT FORM



ATTACHMENT C-5

BORING LOG — **NUS CORPORATION**

PROJECT: ..... BORING NO.: .....
PROJECT NO.: ..... DATE: ..... DRILLER: .....
ELEVATION: ..... FIELD GEOLOGIST: .....
WATER LEVEL DATA: .....
(Date, Time & Conditions) .....

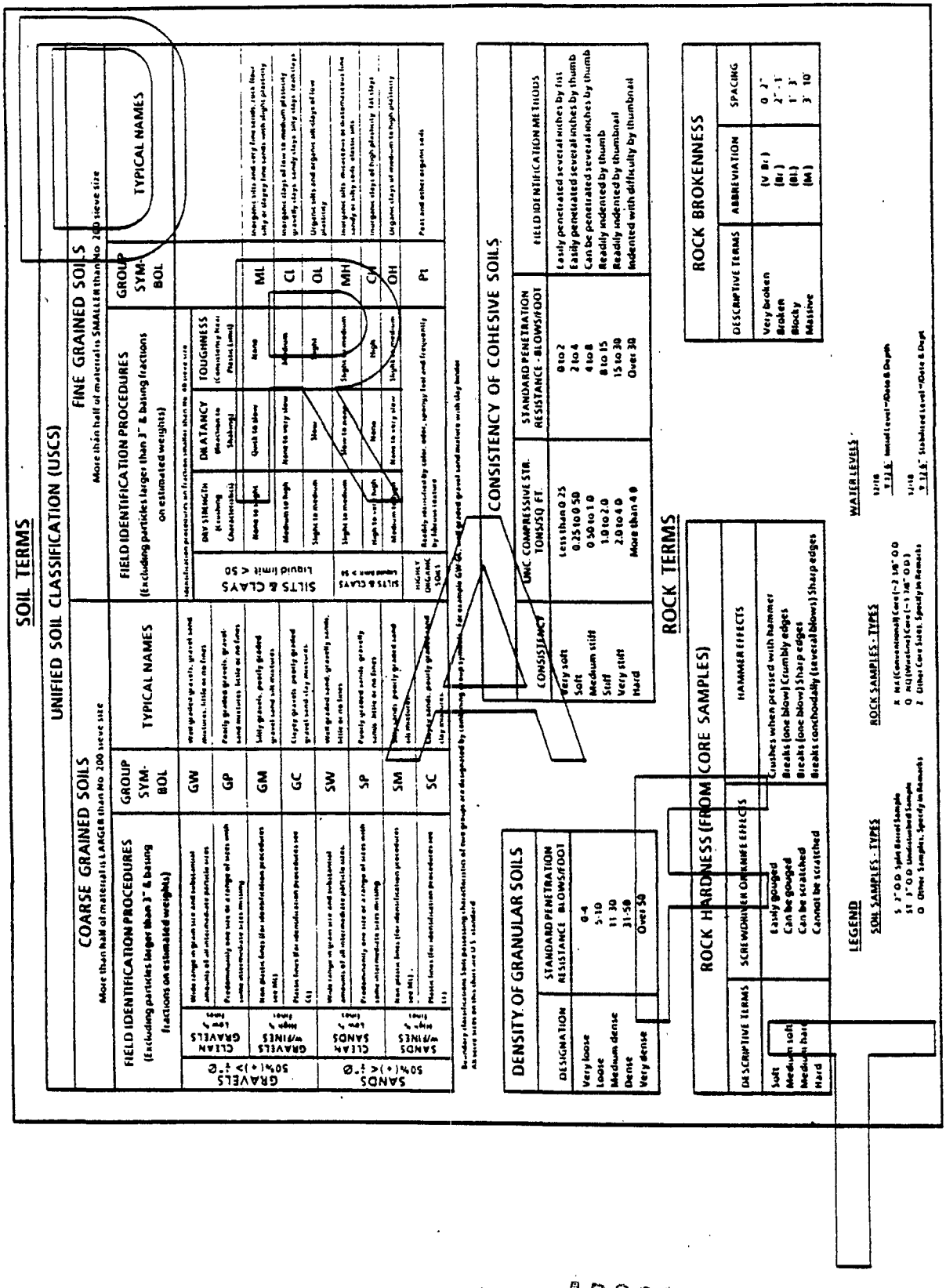
SAMPLE NO. & TYPE OR RQD	DEPTH (ft.) OR RUN NO.	BLOWS/6" OR RQD (%)	SAMPLE RECOVERY SAMPLE LENGTH	LITHOLOGY CHANGE (Depth,ft.) OR SCREENED INTERVAL	MATERIAL DESCRIPTION: SOIL DENSITY/ CONSISTENCY OR ROCK HARDNESS	MATERIAL DESCRIPTION: COLOR*	MATERIAL DESCRIPTION: MATERIAL CLASSIFICATION	BOREHOLE SCREEN SKS	REMARKS

REMARKS _____

BORING _____

PAGE ____ OF ____

ATTACHMENT C-5 (CONTINUED)



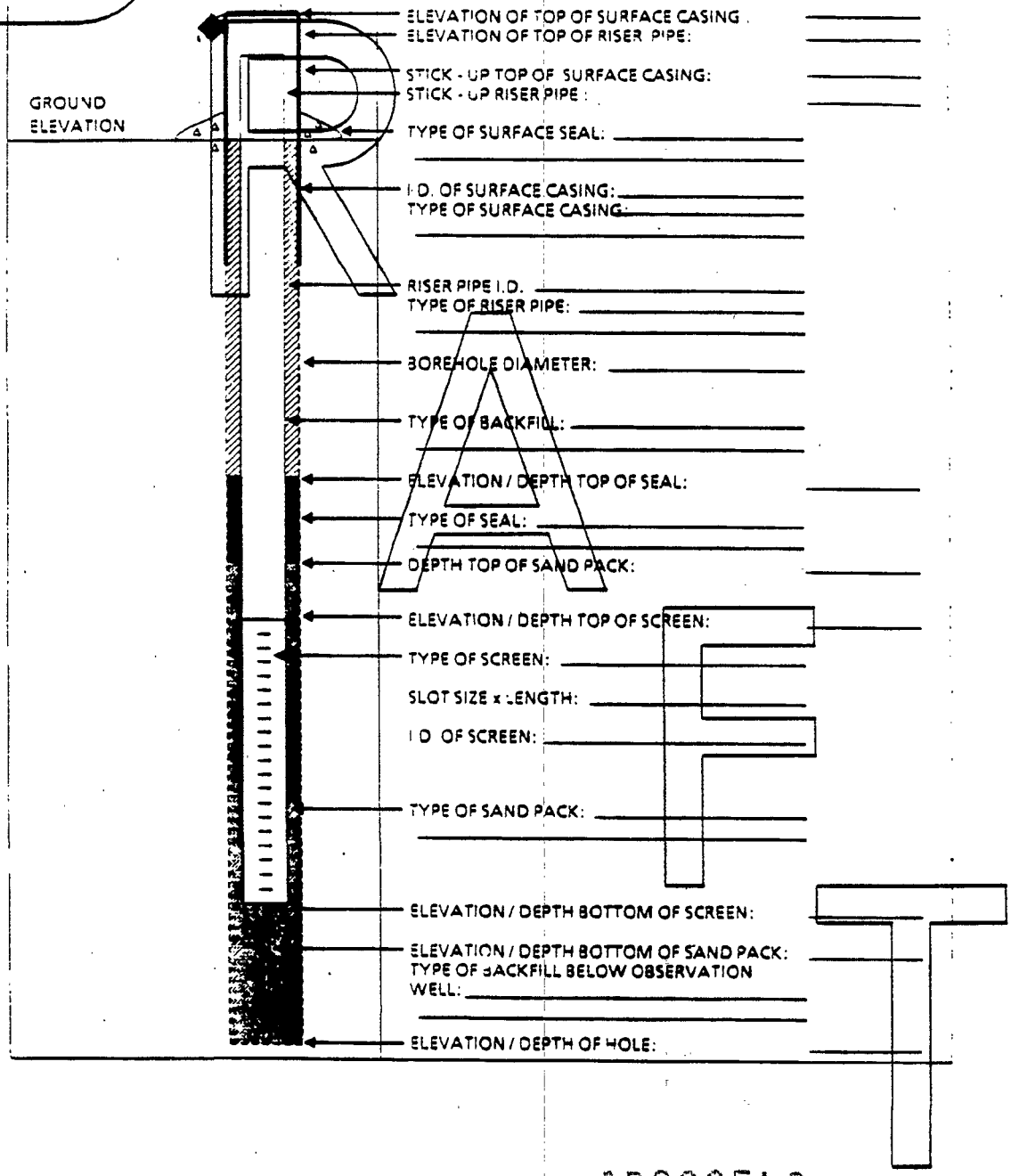
ATTACHMENT C-6

NUS CORPORATION
A Halliburton Company

BORING NO. _____

OVERBURDEN MONITORING WELL SHEET

PROJECT _____ LOCATION _____ DRILLER _____
PROJECT NO. _____ BORING _____ DRILLING METHOD _____
ELEVATION _____ DATE _____ DEVELOPMENT METHOD _____
FIELD GEOLOGIST _____



ATTACHMENT C-7

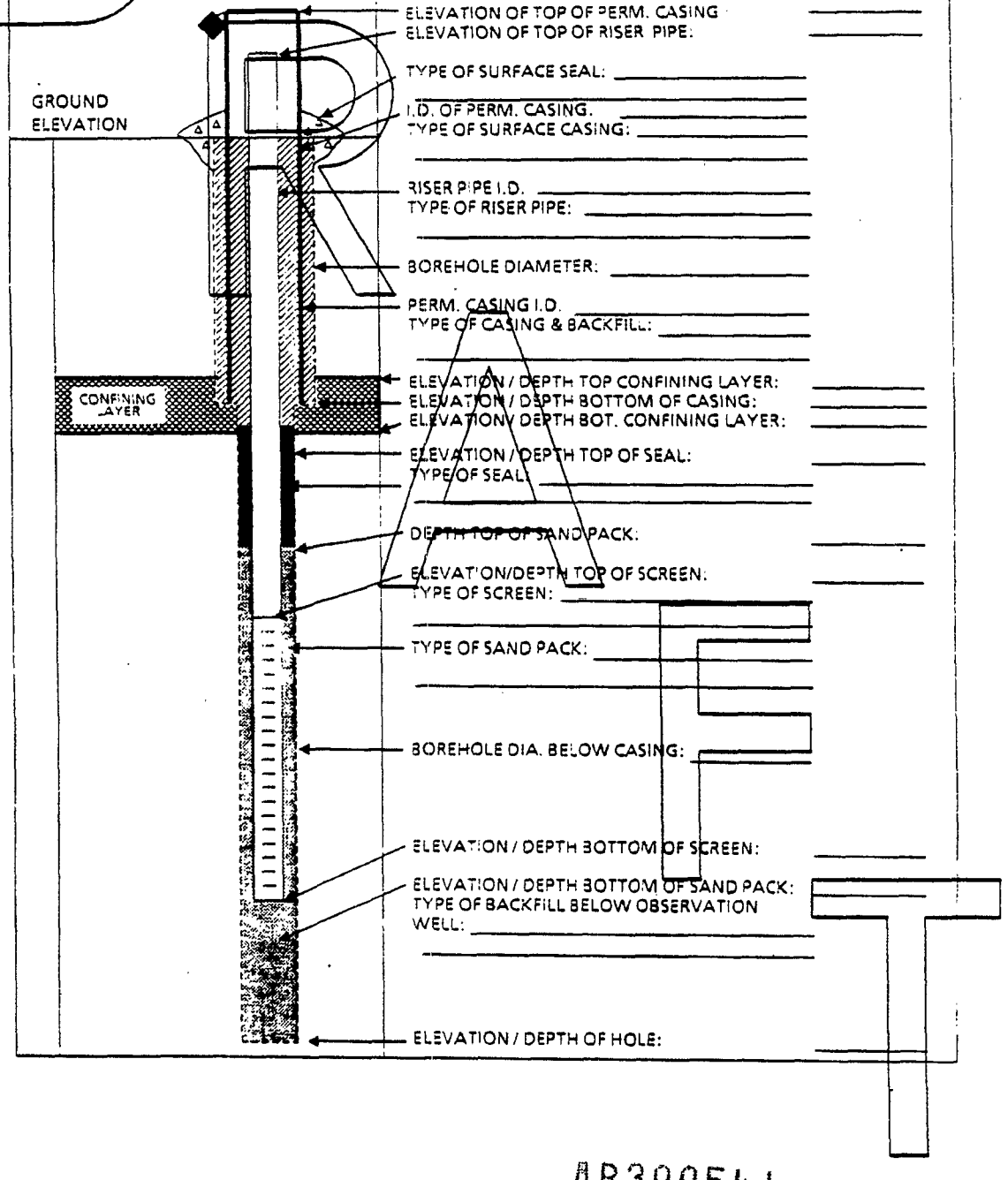
NUS CORPORATION

BORING NO. _____

CONFINING LAYER
MONITORING WELL SHEET

5.87

PROJECT _____ LOCATION _____ DRILLER _____
PROJECT NO. _____ BORING _____ DRILLING METHOD _____
ELEVATION _____ DATE _____ DEVELOPMENT METHOD _____
FIELD GEOLOGIST _____



ATTACHMENT C-8

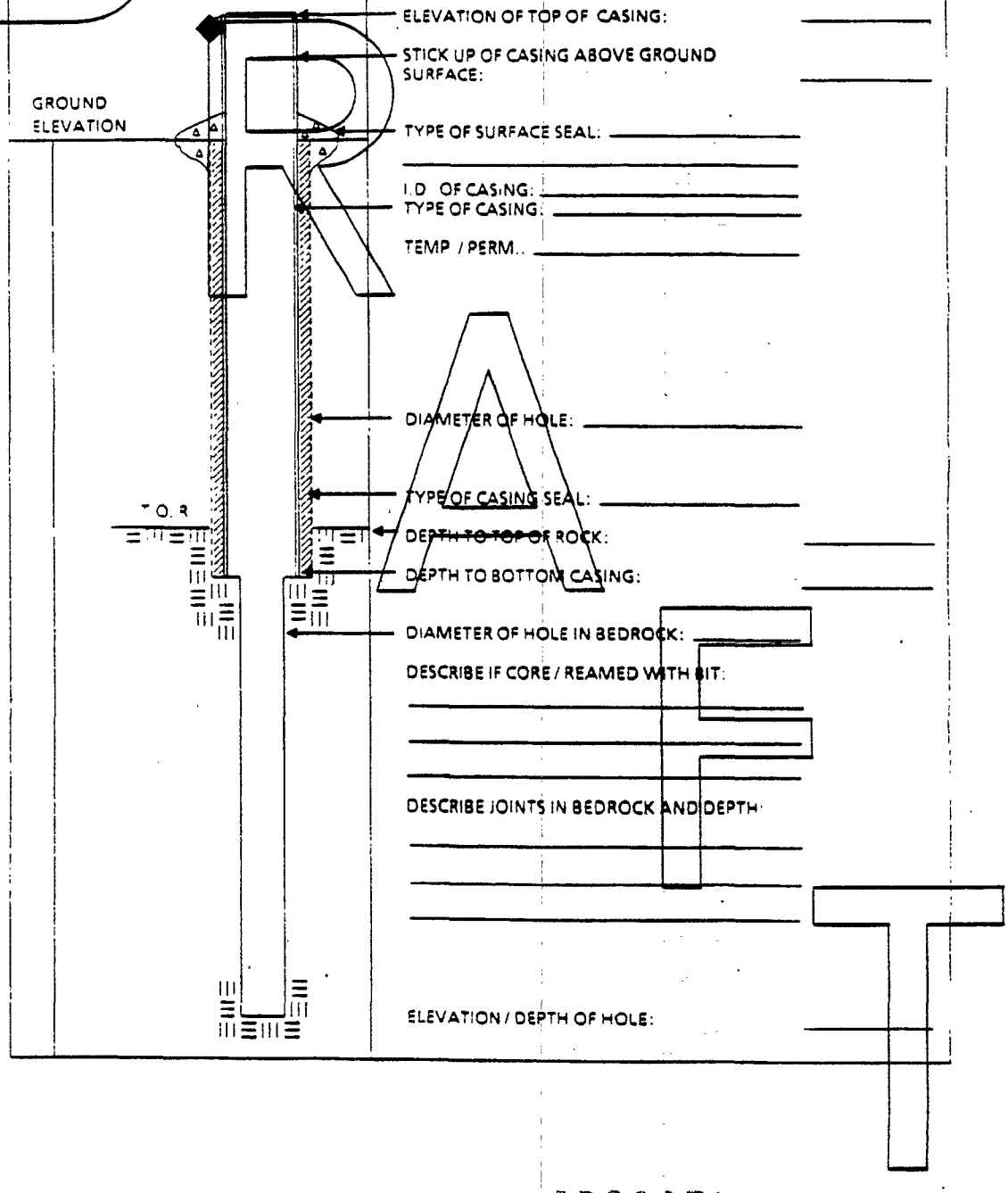
NUS CORPORATION
A Halliburton Company

BORING NO _____

BEDROCK
MONITORING WELL SHEET
OPEN HOLE WELL

PROJECT _____ LOCATION _____
PROJECT NO. _____ BORING _____
ELEVATION _____ DATE _____
FIELD GEOLOGIST _____

DRILLER _____
DRILLING METHOD _____
DEVELOPMENT METHOD _____



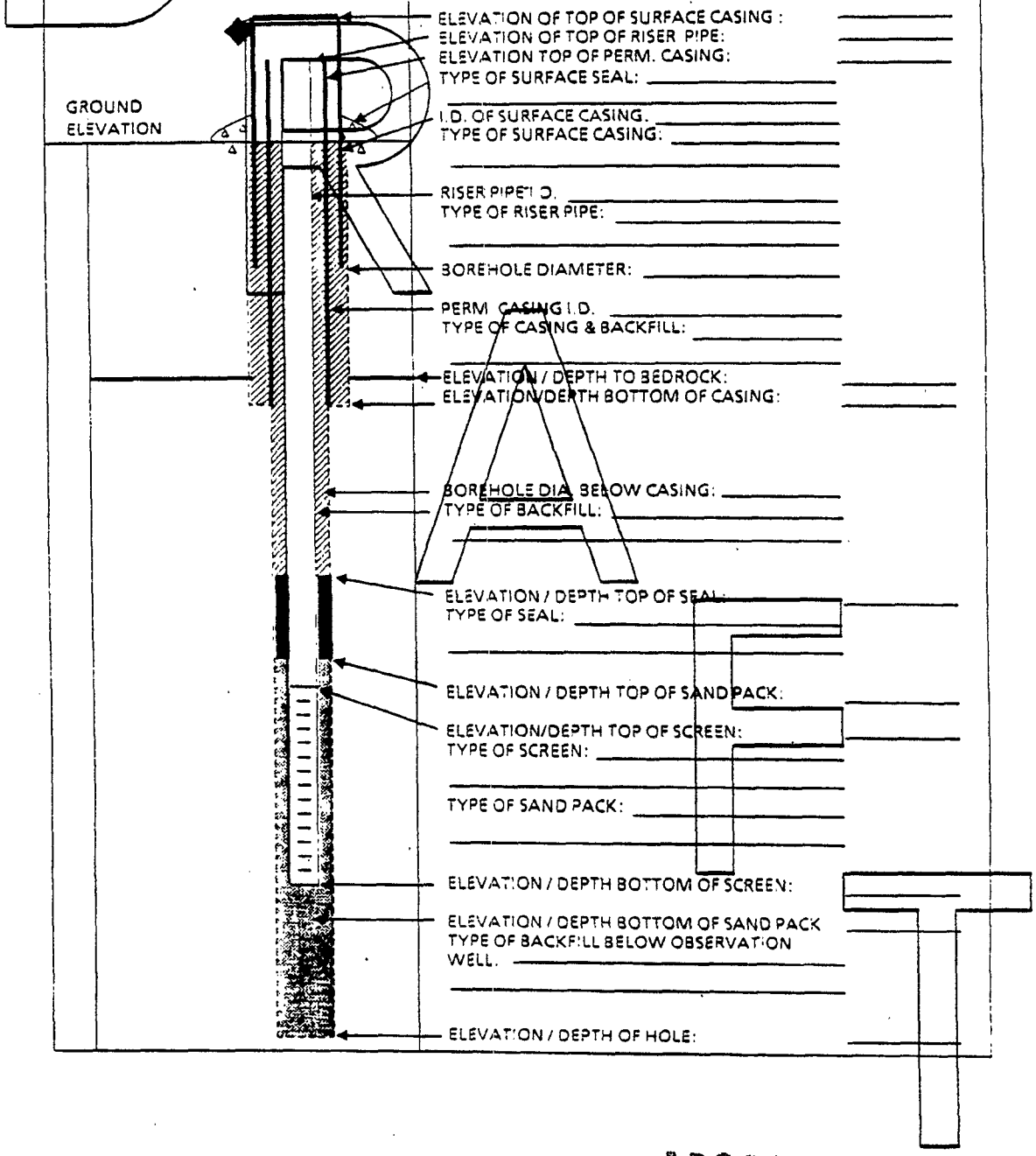
ELEVATION OF TOP OF CASING: _____
STICK UP OF CASING ABOVE GROUND SURFACE: _____
TYPE OF SURFACE SEAL: _____
I.D OF CASING: _____
TYPE OF CASING: _____
TEMP / PERM.. _____
DIAMETER OF HOLE: _____
TYPE OF CASING SEAL: _____
DEPTH TO TOP OF ROCK: _____
DEPTH TO BOTTOM CASING: _____
DIAMETER OF HOLE IN BEDROCK: _____
DESCRIBE IF CORE / REAMED WITH BIT: _____
DESCRIBE JOINTS IN BEDROCK AND DEPTH _____
ELEVATION / DEPTH OF HOLE: _____

ATTACHMENT C-9

BORING NO : _____

BEDROCK
MONITORING WELL SHEET
WELL INSTALLED IN BEDROCK

PROJECT _____ LOCATION _____ DRILLER _____
PROJECT NO. _____ BORING _____ DRILLING METHOD _____
ELEVATION _____ DATE _____ DEVELOPMENT METHOD _____
FIELD GEOLOGIST _____



ATTACHMENT C-10

NUS CORPORATION
A Halliburton Company

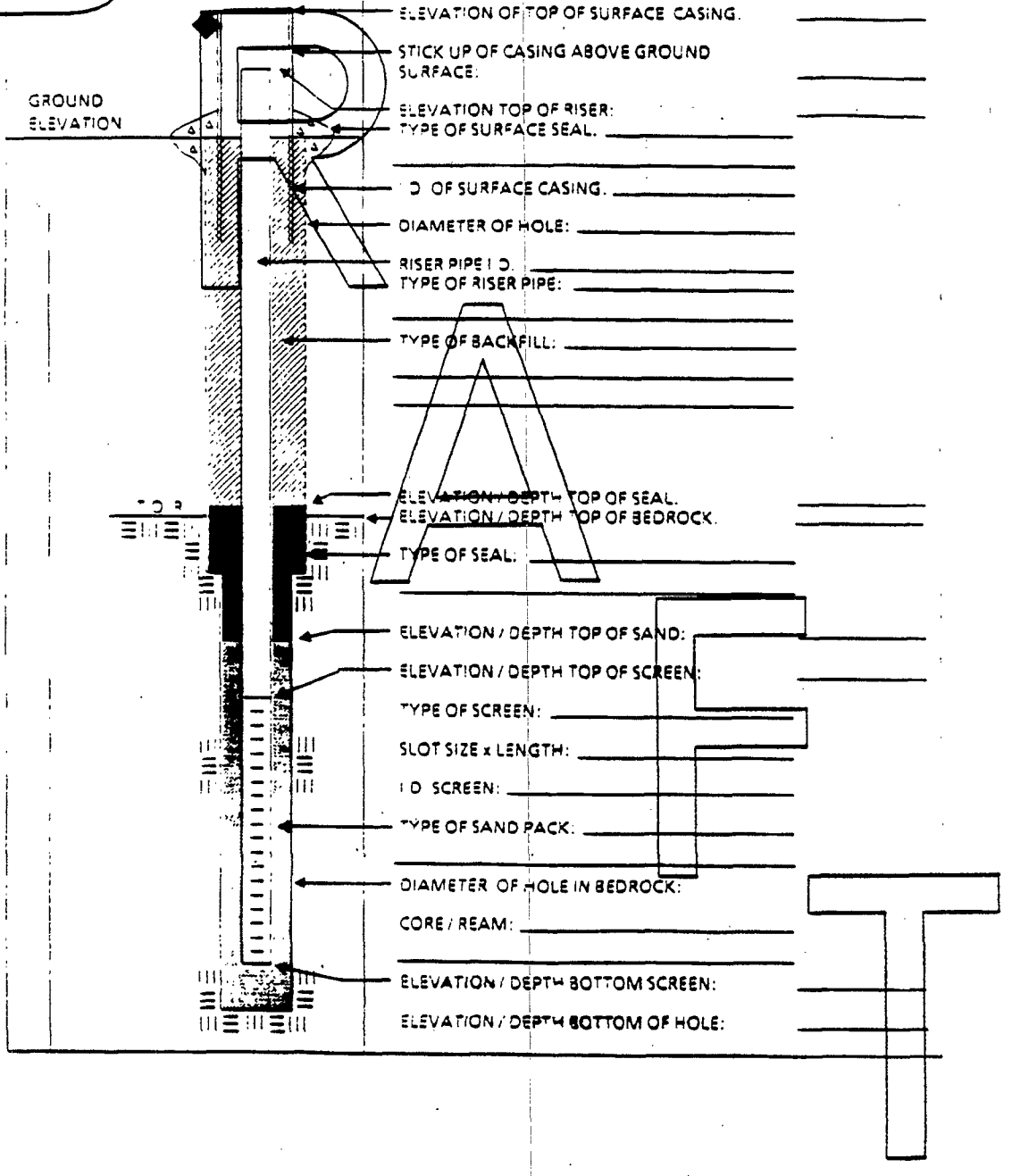
BORING NO _____

BEDROCK MONITORING WELL SHEET

WELL INSTALLED IN BEDROCK

PROJECT _____ LOCATION _____
PROJECT NO _____ BORING _____
ELEVATION _____ DATE _____
FIELD GEOLOGIST _____

DRILLER _____
DRILLING METHOD _____
DEVELOPMENT METHOD _____



ATTACHMENT C-11

TEST PIT LOG — NUS CORPORATION

PROJECT: TEST PIT NO.:
PROJECT NO: DATE:
LOCATION:
FIELD GEOLOGIST:

DEPTH (ft.)	LITHOLOGY CHANGE (Depth, ft.)	MATERIAL DESCRIPTION (Soil Density / Consistency, Color)	USCS	REMARKS

Test Pit Cross Section and / or Plan View

REMARKS

PHOTO LOG

TEST PIT

PAGE OF

ATTACHMENT D-1

EQUIPMENT CALIBRATION LOG

Instrument (Name/Model No./Serial No.): _____ Date Purchased _____

Manufacturer _____

Calibration Date	Initial Settings	Standard/Gas Used	Procedure	Adjustments Made	Final Settings	Signature	Comments

NUS CORPORATION WASTE MANAGEMENT SERVICES GROUP	STANDARD OPERATING PROCEDURES	Number SA-6.5	Page 1 of 7
		Effective Date 08/10/88	Revision 1
		Applicability WMSG	
		Prepared Earth Sciences	
Subject FIELD REPORTS		Approved A. K. Bomberger, P.E.	

TABLE OF CONTENTS

1.0 PURPOSE

This procedure describes the periodic field reports which are required to be filled out during the conduct of Remedial Investigation (RI) field studies. These reports on the progress of field assignments are not to be confused with the forms associated with boring and well installation, sampling, sample custody and equipment maintenance described in Procedure SA-6.4.

These reports serve several purposes:

- To maintain a written record of major events/accomplishments/problems related to the field work.
- To allow ongoing monitoring of the actual progress of field tasks in comparison to the planned schedule, and to allow timely corrective action (if required).
- To inform Site Managers of progress/accomplishments for inclusion in The Monthly Project Tracking System.

2.0 SCOPE

The reports described herein are to be used during field investgiations, but do not replace or take precedence over project-specific or subcontractor-specific required reports. Additional reporting may particularly be required at enforcement-lead sites.

3.0 GLOSSARY

None

4.0 RESPONSIBILITIES

Field Operations Leader - responsible for assuring that the appropriate reports are completed in the required time-frame. Responsibilities for filling out individual reports are identified within the description of the reports (see below).

5.0 PROCEDURES

5.1 PROGRAM DESIGN

The primary means of recording onsite activities is the site logbook (see Procedure SA-6.3) and other field logbooks (e.g. geologists notebook, health and safety officer's logbook, sample logbooks). However, these logbooks and notebooks usually contain extremely detailed information which is required for data interpretation or documentation, but not for tracking and reporting of progress. Furthermore, the field logbooks remain onsite for extended periods of time and are thus not accessible for review by project management. The reports described in this procedure are, in essence, simplified summaries of the logbooks, which are designed to provide only the information needed by project management to keep informed of the progress of field activities.

5.2 DAILY ACTIVITIES REPORT

5.2.1 Description

The Daily Activities Report documents the activities and progress for each day's field work. This report is filled out on a daily basis whenever there are drilling, test pitting, well construction, or other related activities occurring which involve subcontractor personnel. These sheets summarize the work performed and form the basis of payment to subcontractors. (see Attachment A).

5.2.2 Responsibilities

It is the responsibility of the rig geologist to complete the report and obtain the driller's signature acknowledging that the times and quantities of material entered are correct.

5.2.3 Submittal and Approval

At the end of the shift, the rig geologist submits the Daily Activities Report to the Field Operations Leader (FOL) for review and filing. The Daily Activities Report is not a formal report and thus requires no further approval. The reports are retained by the FOL for use in preparing the site logbook and weekly Field Summaries, and are submitted to the Site Manager weekly along with the Weekly Field Summary.

5.3 WEEKLY FIELD SUMMARY

5.3.1 Description

The Weekly Field Summary is an abstract of the Site Logbook, summarizing the major activities onsite for a particular week (Sunday through Saturday). It should be organized on a day-by-day basis, and contain the following information at a minimum (see Attachment B):

- Date (week ending)
- Personnel onsite (contractor, subcontractors, visitors)
- Weather conditions encountered during the week
- Site activities
- Number and type of samples collected (including C.O.C. form numbers)
- Issues impacting progress of the project.

5.3.2 Responsibilities

The Field Operations Leader or responsible individual onsite if not the FOL (e.g., geophysics team leader, sampling team leader) is responsible for completing the Weekly Field Summary at the end of each week of ongoing site activity, or at the completion of an activity (if no further activity will take place during that week).

5.3.3 Submittal and Approval

The summary, along with Daily Activities Reports, Health & Safety Officer's Reports, and any other documentation, must be delivered or sent to the Site Manager at the end of each week.

DAILY ACTIVITIES RECORD - FIELD INVESTIGATION — NUS CORPORATION

PROJECT NAME: _____ PROJECT NO.: _____
CLIENT: _____ LOCATION: _____
DATE: _____ ARRIVAL TIME: _____ DEPARTURE TIME: _____
CONTRACTOR: _____ DRILLER: _____
BORING NO.: _____ NUS REPRESENTATIVE: _____

ITEM (1)	ORIGINAL QUANTITY (2) ESTIMATE	QUANTITY (2) TODAY	PREVIOUS TOTAL (2) QUANTITY	CUMULATIVE QUANTITY (2) TO DATE
1. Mobilization/Demobilization	Job			
2. Overburden Drilling/Sampling, minimum 6-inch	100 ft.			
3. Overburden Drilling, 10-inch	250 ft.			
4. Overburden Drilling 14-inch	450 ft.			
5. Bedrock Drilling 6-inch	530 ft.			
6. Bedrock Drilling 10-inch	650 ft.			
7. Bedrock Drilling 14-inch	150 ft.			
8. Temporary 6-inch Steel Casing	250 ft.			
9. Temporary 10-inch Steel Casing	200 ft.			
10. Temporary 14-inch Steel Casing	250 ft.			
11. Permanent 6-inch Steel Casing	1,250 ft.			
12. Permanent 10-inch Steel Casing	400 ft.			
13. PVC Well Construction/Installation	1,120 ft.			
14. Mine Void Sealing	8			
15. Boring Backfilling	NA			
16. Well Development	24 hrs.			
17. Test Borings	200 ft.			
18. Test Pit Excavation	50 hrs.			
19. Standby	20 hrs.			

COMMENTS: _____

(1) AS LISTED IN SPECS
(2) INCLUDE QUANTITY AND UNITS
(Ex. 20 ft., 6 hrs.)

APPROVED BY:

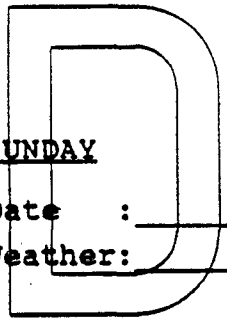
_____
NUS FIELD REPRESENTATIVE

_____
DRILLER OR REPRESENTATIVE

ATTACHMENT A

ATTACHMENT B
PAGE 1 OF 2

WEEKLY FIELD SUMMARY REPORT



SUNDAY

Date : _____ Personnel _____ _____

Weather: _____ Onsite _____ _____

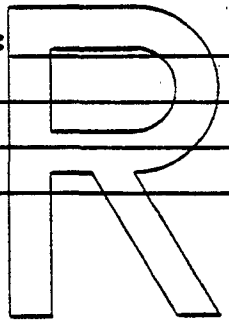
_____ _____

Site Activities: _____

_____

_____

_____



MONDAY

Date : _____ Personnel _____ _____

Weather: _____ Onsite _____ _____

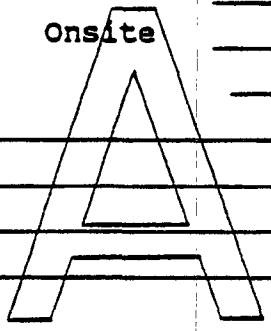
_____ _____

Site Activities: _____

_____

_____

_____



TUESDAY

Date : _____ Personnel _____ _____

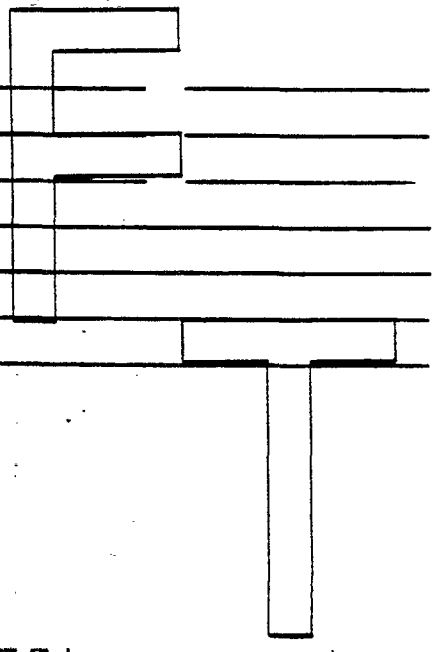
Weather: _____ Onsite _____ _____

Site Activities: _____

_____

_____

_____



ATTACHMENT B
PAGE 2 OF 2

WEDNESDAY
Date :_____ Personnel_____ _____
Weather:_____ Onsite _____ _____
_____ _____

Site Activities:_____
_____
_____
_____

THURSDAY
Date :_____ Personnel_____ _____
Weather:_____ Onsite _____ _____
_____ _____

Site Activities:_____
_____
_____
_____

FRIDAY
Date :_____ Personnel_____ _____
Weather:_____ Onsite _____ _____
_____ _____

Site Activities:_____
_____
_____
_____

SATURDAY
Date :_____ Personnel_____ _____
Weather:_____ Onsite _____ _____
_____ _____

Site Activities:_____
_____
_____

The Weekly Field Summary is an internal informational document and is not subject to project management review or approval.

6.0 REFERENCES

Ebasco Services Incorporated; REM III Field Technical Guideline No. 13.02. October 30, 1987.

Ebasco Services Incorporated; REM III Field Technical Guideline No. 2.06. June 2, 1986.

Ebasco Services Incorporated; REM III Field Technical Guideline No. 13.03. October 30, 1987.

Ebasco Services Incorporated; REM III Field Technical Guideline No. 13.01. October 29, 1987.

7.0 RECORDS

Attachment A - Rig Shift Report
Attachment B - Weekly Field Summary Report (2 pages)

NUS CORPORATION WASTE MANAGEMENT SERVICES GROUP	STANDARD OPERATING PROCEDURES	Number SA-6.6	Page 1 of 27
		Effective Date 01/01/88	Revision 0
		Applicability WMSG	
		Prepared Earth Sciences	
Subject: MANAGEMENT OF SAMPLING AND PREPARATION OF REQUIRED FORM		Approved A. K. Bomberger, P.E.	

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

1.0 PURPOSE

The purpose of this procedure is to describe the method used in planning and managing sample shipments to the EPA Contract Laboratory Program (CLP).

2.0 SCOPE

This procedure applies to all NUS staff involved in preparation of the Project Operations Plans (POP) Plan (FSAP), and personnel involved in RI field work, involving collection of samples for off-site chemical analysis.

3.0 GLOSSARY

Authorized Requestor (AR) - The EPA contact person(s) in the Regional Sample Control Center through which CLP's analytical services must be accessed.

Contract Laboratory Program (CLP) - A system of contractor-run laboratories providing analytical services and support for EPA's Superfund program. Data produced from this program is subject to rigorous QA/QC and documentation procedures to ensure its admissibility as evidence in any EPA enforcement proceedings.

Deputy Project Officer (DPO) - Appointed by the EPA Regional Administrator for each region, the EPA's DPO has partial responsibility for monitoring the laboratory contractors actually located in the region. Additional duties currently include resolution of problems in laboratory operations and laboratory site evaluations.

Environmental Monitoring and Support Laboratory/Las Vegas (EMSL/LV) and National Enforcement Investigations Center (NEIC) - Current responsibilities of EMSL/LV and NEIC include methods development, QA, and automated data transfer.

Laboratory Services Manager (LSM) - The ARCS III PMO Manager responsible for all ARCS III laboratory analytical services, including ARCS III subcontractor laboratories and submission of samples to CLP.

National Enforcement Investigations Center (NEIC) - The EPA unit responsible for developing guidance and providing technical assistance to EPA enforcement efforts.

RAS Sample - A quantity of soil, water or sediment, taken from the field at a single point at a single time and submitted for a set of Routine analytical Service (RAS) analyses. One sample collected and submitted for both organic and inorganic analysis would be counted as two RAS samples.

Regional Laboratory Services Coordinator (RLSC) - The ARCS III person responsible for coordination of ARCS III Laboratory analytical services. The RLSC is in general the single point of contact for the EPA Regional Sample Control Center (RSCC). The RLSC will usually be an employee of the lead firm, but will coordinate laboratory services for all sites, regardless of which ARCS III team member firm is performing site work.

Regional Sample Control Center (RSCC) - The EPA regional offices which serve as the central contact with the CLP for each region. The RSCC coordinates the level of regional sampling activities to correspond with monthly allocations of CLP capacity, places all requests for CLP analyses, coordinates sampling and sample shipment, and resolves any problems that may arise concerning the samples.

Repository Authorized Requestor (RAR) - The ARCS III personnel (one for each region) recognized by the Sample Management Office (SMO), through whom all requests for sample containers must be forwarded to the CLP Sample Bottle Repository. The RAR is usually the Regional Laboratory Services Coordinator (RLSC).

Routine Analytical Services (RAS) - Offered through CLP, for the determination of common organic and inorganic parameters and dioxin. The nature of these services is specified in contracts with each laboratory. For a detailed description of these services, see the "User's Guide to the Contract Laboratory Program" (Reference 1 of this guideline).

Sample Bottle Repository - A contractor-operated, centralized source for the most commonly-used sizes of pre-cleaned and QC-tested sampling containers for CLP samples.

Sample Management Office (SMO) - The contractor-operated office through which CLP receives analytical requests from the regions. Duties of SMO include sample scheduling and tracking, Special Analytical Services (SAS) subcontracting, laboratory invoice processing, maintenance of CLP records and management reporting, and NPO (National Program Office at EPA Headquarters) management and administrative support.

Special Analytical Services (SAS) - Analyses requiring special protocols or handling (e.g., high-hazard, non-routine parameters, enhanced detection limits) are available through this option. Individual contracts for these services are solicited, awarded and administered by SMO. For a description of these services, see Reference 1 of this guideline.

Traffic Report (TR) - Documentation used to track CLP samples from the field to the laboratory. Separate versions exists for inorganic and organic samples. One traffic report is used per twenty samples.

4.0 RESPONSIBILITIES

Site Manager (SM) - responsible for thorough understanding of the CLP (or non-CLP) requirements and incorporation of these requirements into the POP and project schedule. The SM retains overall responsibility for the success of the sampling and analysis and serves as the prime interface with EPA staff, although certain aspects of sampling (e.g., preparation for sampling and shipment, coordination with RSCC) may be delegated to other project personnel (e.g., Regional Laboratory Services Coordinator and Field Operations Leader).

With regard to sampling, the SM's specific responsibilities include:

- Preparation of EPA-approved POP (including QA/QC protocols and SAS analytical protocols) for CLP analysis;
- Coordination with RAR to order sample containers
- For non-CLP analysis, coordination with the PMO Laboratory Services Manager (LSM) through the Regional Laboratory Services Coordinator (RLSC) to identify the laboratory and analytical protocols, and management of the non-CLP Laboratory's subcontract;
- Obtaining required EPA and NUS document forms, site logbook and sample logbook;
- Assigning and preparing the sampling team.

Field Operations Leader (FOL) - responsible for thorough understanding of CLP (or non-CLP) requirements and retains overall responsibility for the correct collection, bottling, documentation, preservation, and shipment of samples to the analytical laboratories, including notification of RSCC and SMO of sample shipment. Some of these responsibilities may be delegated to a sampling technician.

Field Sampling Technicians - responsible for correctly collecting samples, filling out the required sample documentation, traffic reports and chain-of-custody forms and following the directions of the Project Operations Plan, relevant NUS Procedures, and the FOL regarding sample collection, preservation, and shipment methods.

EPA ~~Remedial Project Manager (RPM)~~ - The designated EPA representative for the work assignment, the RPM is responsible for EPA's activity in all phases of the assignment. With regard to sampling, the RPM is responsible for:

- Assisting with regard to site entry;
- Contacts with the state agencies and responsible parties in the local community;
- Approval of plans, subcontracts, and reports; data validation and data entry.

5.0 PROCEDURES

5.1 OVERVIEW

Sampling and analysis, as conducted in accordance with EPA and NUS procedures and requirements, are extremely complex operations. From 6 to 12 agencies, organizations, or offices are involved in the overall program, and each has its own procedures and requirements. There are at least eight separate and distinct administrative and management activities needed to establish a sampling and analysis program. These are:

1 Planning
2 Logistics
3 Subcontracting
4 Site activities, including sampling, drilling, surveying, test ~~pit excavation~~, boring etc.
5 Packaging and shipping, including documentation
6 Analysis
7 Data Validation
8 Reporting

Activities 1 and 2 shall be covered in detail in the POP and are the responsibility of the SM, FOL, and other staff assigned to the project. Activity 3 should be initiated by the SM, through the NUS Contracting Officer at PMO, during the RI/FS Initial Tasks and Activities.

Activities 4 and 5 are field activities to be conducted by the NUS field personnel. Activity 6 shall be conducted by CLP (not including field analysis, which will be conducted by ~~field personnel~~), and Activity 7 may be conducted by various branches of EPA. Finally, Activity 8 is the responsibility of the NUS contractor for that work assignment.

Frequent communications with the offices and organizations involved are necessary to maintain effective coordination. Throughout the entire operation, quality assurance and quality control requirements must be satisfied in accordance with the Quality Assurance Program Plan. Extensive documentation is needed to assure adequate management tracking of samples through the complex

system and to maintain a chain-of-custody record for litigation purposes. Attachment A presents a summary of the timing of activities for scheduling CLP samples.

5.1.1 Sampling Equipment

Proper and sufficient sampling equipment is a basic necessity for a successful sampling effort. Attachment I contains an equipment checklist which shall be used by the SM or FOL when preparing for a sampling program. To avoid delays in the sampling programs, it is in the interest of the SM to provide this equipment request with sufficient advance notice (usually 2 to 3 weeks minimum).

Additionally, if Special Analytical Services (SAS) are requested, the POP must include specific methods and protocols required for these analyses. These protocols must be approved by EPA before requesting SAS from SMO.

5.2 PLANNING FOR SAMPLING ACTIVITIES

Planning for work assignments involving the collection of samples to be submitted for CLP analyses consists of several major steps:

- Develop Project Operations Plan;
- Schedule CLP Analysis;
- Obtain CLP Sample Bottles;
- Obtain Sample Shipping Coolers, and any other materials required for shipping samples.

The NUS Site Manager (SM) shall communicate regularly with the EPA Remedial Project Manager (RPM) to ensure that site planning activities progress in a smooth and timely fashion, through each of the major steps listed above. In addition, the Regional Laboratory Services Coordinator (RLSC) shall communicate regularly with the EPA Regional Sample Control Center (RSCC) to ensure smooth approval and coordination of the sampling effort. Responsibilities in each step are discussed in turn.

5.2.1 Project Operations Plan

The Project Operations Plan (POP) is the major document outlining all planned sampling activities for a RI/FS, including elements of site-specific quality assurance. For non-RI/FS work assignments which nevertheless involve field work and analysis of samples (e.g., PA/SI, oversight, confirmational sampling for enforcement cases), an equivalent task specific POP will be developed.

The POP must be approved by EPA before CLP sample scheduling procedures can be initiated. The POP must therefore be prepared by the NUS Site Manager (SM) and submitted to the EPA Remedial Project Manager (RPM) at least two months prior to the date that samples will be submitted for CLP analysis. Additionally, if Special Analytical Services (SAS) and analysis are requested, the POP must include specific methods and protocols and the SAS Request Forms required for these analyses. Requirements for SAS should be defined in consultation with chemists, engineers and risk assessment personnel during the development as Data Quality Objectives (DQO's) for inclusion in the Work Plan for the site.

Requirements for notifying EPA of sampling requirements and gaining approval of the POP vary among EPA Regions. The requirements of EPA Region III are outlined below:

- Region III: Region III requires that the SM prepare and submit duplicate copies of the POP one month in advance of planned sampling for CLP analysis. One copy must be sent to the RPM and another copy sent to the RSCC at the Central Regional Laboratory in Annapolis, MD. Following RPM and RSCC review and approval of the POP, the SM is authorized to schedule samples for CLP analysis through the RSCC. Because of some past difficulties in obtaining CLP capacity for SAS samples, Region III requires 6-8 weeks notice in order to schedule these types of samples for CLP analysis.

5.2.2 General Steps in Scheduling CLP Analyses

Following EPA approval of the POP, the Regional Laboratory Services Coordinator (RLSC) contacts the EPA Regional Sample Control Center (RSCC) to schedule samples for CLP analysis. The precise information required by the RSCC in order to schedule sample analyses is discussed in Section 5.2 and on pages 52-62 of the CLP User's Guide (Reference 1 of this Guideline). However, the general steps in initiating this process include:

- RLSC submits request to RSCC for specific CLP RAS analytical support at least one week prior to sampling dates. The RLSC should also request CLP and evidence documentation forms from the RSCC, e.g., Traffic Reports, Chain-of-Custody forms, evidence seals, and sample tags, several weeks in advance of sampling.
- The RSLC submits SAS Request Forms with the POP and to the RSCC between 6-8 weeks prior to the start of sampling.
- RSCC requests Sample Management Office (SMO) to schedule samples for CLP analysis, informing SMO of the sampling requirements identified by the RLSC.
- Initiation of SMO sample scheduling activities with CLP laboratories.
- SMO calls RSCC confirming sample scheduling with CLP laboratories.
- RSCC calls RLSC with information on sample scheduling.

When there is sufficient CLP capacity, the RAS scheduling process usually takes one to three days to complete. If there is a shortage of CLP capacity RAS, sample scheduling can take up to one week. Where CLP capacity is limited, the RSCC may allocate available capacity to another project with a higher regional priority.

Once CLP laboratory assignments have been made, it is important to notify the RSCC immediately of any changes in the sampling plan or schedule. If postponements or cancellations in sampling activities are necessary, this too must be communicated to the RSCC or RPM with reasonable justification for the cancellation. When possible, the RLSC should have a replacement sampling activity to substitute for the postponed or canceled activity to ensure that the assigned CLP capacity is used.

5.2.3 Obtaining CLP Sample Bottles

The CLP Sample Bottle Repository program may be used by any organization scheduling samples through the CLP, and is commonly accessed by regional and NUS contractor clients. One staff member from each region, usually the RLSC, is designated by SMO as a Repository Authorized Requestor (RAR) and only these individuals may place bottle orders through the program using a Sample Bottle Repository Delivery Order (Attachment C). Once designated, the RAR orders bottles

directly from the Repository. Because the Repository can respond only to orders submitted by an SMO-designated RAR, NUS regional staff must contact SMO to request any changes in RAR designees.

CLP clients may obtain eleven types of bottles for use in sampling activities. The Sample Bottle Repository Program provides bottles in numbered lots, packing in protective cardboard containers, that are pre-cleaned and QC-tested to ensure no contamination exists that may affect sample data results. The identification number of the bottle lot used for each sample shall be written on the Traffic Report or other sample document form (e.g., Dioxin Shipment Record, Packing List - see Section 5.3).

There are three types of bottle orders; Routine (fifteen or more working days lead time for delivery), Fast-turnaround (more than three days, but less than fifteen days lead time for delivery), and emergency (three days lead time for delivery). Shall it be necessary to cancel an order, contact the Repository either directly or through the RAR, by telephone. Follow up with a cancellation memo to the repository (see CLP User's Guide, Reference 1 of this guideline) with a copy to the work assignment file.

Some common problems which have been experienced with the bottle repository program include:

- Bottles shipped directly to sampling locations occasionally arrive at local hotels or agencies before sampling crews. Consequently, these bottles are sometimes stored improperly, broken or lost. Shipping the bottles to the nearest Federal Express or other carrier's office, marked "For Pick-Up" will avoid these problems. Alternatively, the bottles may be shipped directly to the contractor's office, laboratory, or other field sampling staging location.

- Bottle types are prepared specifically for the type of analyses specified in the CLP User's Guide (Reference 1 of this guideline). Use the correct bottle for the parameter of interest.

5.2.4 Obtaining Sample Shipping Coolers

The CLP does not provide sample shipping coolers. It is therefore the responsibility of the SM to obtain the required number of coolers through his/her firm prior to sampling activities.

All shipping coolers shall have clearly visible return address labels on the outside. Shipping coolers that are labeled in this manner will be returned to the sampler by the CLP laboratory usually within 14 days following laboratory sample receipt. NUS staff shall be sure that the return address label is distinct from, and not obscured by, other shipping labels.

5.3 CLP SAMPLE SCHEDULING AND COLLECTION

The two keys to using the CLP successfully are first, rapid and effective communication among the sampler, RSCC, and SMO, particularly when changes in the sampling plan are necessary, and, second, accurate completion and routing of all required documentation. The appropriate steps in sample scheduling are collection under the CLP's RAS and SAS programs are summarized below. For more complete information on these activities, consult the CLP User's Guide (Reference 1 of this guideline).

5.3.1 Routine Analytical Services (RAS)

To initiate a RAS request, a SM must request the RLSC to contact the RSCC who will in turn contact the SMO by telephone with a description of the analytical requirements. It is the responsibility of the

SM to maintain a working knowledge of RAS protocols and analytical services. The analytical protocols described in the CLP User's Guide (Reference 1) contain specific information on sample types suited to RAS analysis, target analytes, detection limits, and other information.

The RSCC will require the following information from the SM:

- Name(s), firm name, and telephone number(s) of sampling personnel.
- Name and location of the site to be sampled.
- Number of samples and matrix of each sample to be collected.
- Type of analyses required for each sample; i.e., inorganic, organic, dioxin.
- Cyanide analysis requirement (inorganics only).
- Scheduled sample collection and shipment dates.
- Nature of sampling event (i.e., investigation, monitoring, enforcement, remedial construction).
- Other pertinent information which may affect sample scheduling or shipment (i.e., potential delays due to site access, weather conditions, or drilling or sampling equipment difficulties).

Once the RAS laboratory arrangements have been made, the SMO will confirm the field investigation plans with the RSCC and identify the laboratories to which the samples will be sent. The RSCC will, in turn, pass this information back to the RLSC.

For a more detailed description of how to request RAS, see pp. 52-54 of the CLP User's Guide (Reference 1).

5.3.2 Special Analytical Services (SAS)

Analytical services other than those specified in the RAS analytical protocols may be obtained by requesting Special Analytical Services (SAS). Examples of SAS needs include quick turnaround, multiphase, or non-RAS protocol analyses. Although the RSCC will assist in identifying appropriate SAS protocols, it is the responsibility of the SM and project chemist to select and provide to the laboratory the applicable analytical protocols to be used. These protocols must also be included in the Project Operation Plan (POP) for review by ESD before SAS can be requested. The lead time requirement for requesting SAS samples may be lengthened on the basis of the availability and familiarity of these protocols. In addition to the information required for RAS, the RSCC will require the following information from the RLSC for SAS:

- Specific analyses required, appropriate analytical protocols and required detection limits.
- Matrix spike and duplicate frequency.
- Justification of fast turnaround request, if applicable.
- RI/FS contractor contact person for immediate problem resolution, usually the RLSC or the lead environmental chemist assigned to the project.

Once the RSCC requests SAS by telephone, SMO will initiate SAS subcontracting procedures and assign a sequential SAS number for each sampling activity. If the request is made concurrently with a RAS request, SMO will also issue a Case Number. The RSCC will record both of these numbers (if applicable) and use them to reference the samples. The RLSC must complete a SAS Client Request Form (see Attachment D) and submit it to the RSCC prior to sample scheduling for clarification and confirmation purposes.

Following is a brief summary of SAS procedures. SMs may request assistance from the RLSC or the LSM in choosing appropriate SAS protocols. For a more detailed description of how to request SAS, see pp. 55-59, of the CLP User's Guide (Reference 1).

5.3.3 High Concentration Analyses

The steps in scheduling analytical services for high concentration samples are similar to those described above for SAS. High concentration samples require SAS, not RAS analysis. For a description of this option, see pp. 59-61 of the CLP User's Guide (Reference 1).

Note: Samples no longer travel to EPA EMSL/LV or NEIC for preparation; high concentration samples are now being handled directly by CLP laboratories.

5.3.4 Weekend Shipments

Occasionally, it will be necessary to ship samples on Friday afternoon or evening. If this is the case, the sampler must notify the RSCC ~~and SMO~~ at the latest by 3:00 p.m. eastern standard time, Friday.

5.3.5 Changes in Sampling Plans

Sometimes, due to unforeseen circumstances, it will be necessary to change the sampling plan. This may entail changes in the number of samples, sample matrix, shipment date, or other items. The sampler must notify the RSCC of any changes. Do not ship any samples that differ from those described in the sampling plan without authorization of the RSCC.

5.3.6 Sample Collection, Preservation, and Holding Times

Detailed guidance on approved sampling procedures may be obtained by consulting other Standard Operating Procedures.

Samples requiring preservatives shall be identified and the necessary techniques to maintain sample quality shall be described in the POP. Common preservation techniques may include the addition of acids or other materials to the sample container, or refrigeration of the sample. Refrigerated samples require special packaging (see Section 5.5.1 below).

Regardless of the method of preservation used (if any), strict adherence to holding times is necessary. Holding times represent the maximum amount of time that a preserved sample may be held from the time of sampling until extraction or analysis without compromising the validity of the analytical results. Maximum holding times at the laboratories are specified in the CLP laboratories scopes-of-work. The difference between those times and the total maximum holding times is the time allowed for shipment to the laboratory. If the laboratory receives a sample with less than the allowable laboratory holding time remaining, the laboratory is not contractually liable for analysis within the holding time (although the laboratories will try to meet the maximum holding times). In general, the following shipping frequencies should be followed:

- Samples requiring organics analysis Shall be shipped the same day collected, or on the following day.
- Samples for inorganic analysis may be held until the shipping container is full. Three days is the maximum recommended period for holding of inorganic samples prior to shipping.

Different EPA regions, however, may have different requirements as to holding times for samples in the field. For a detailed description of holding times, packaging, and transportation see the CLP User's Guide (Reference 1), pp. 71-73 and Appendix C of the User' Guide.

5.4 DOCUMENTATION FOR CLP AND EPA CHAIN-OF-CUSTODY

Requests for analytical services through the CLP must be documented properly. Documentation serves to ensure timely, correct and complete analysis for all requested parameters, provides support data for use in potential enforcement actions, and provides a means by which results may be validated. The CLP User's Guide (Reference 1) provides descriptions of various sample documentation forms and their applicability to CLP analytical requests.

5.4.1 Traffic Reports

All RAS samples must be accompanied by a Traffic Report (TR). TRs are uniquely numbered and come in two varieties: Organic, and Inorganic, (see Attachment E-1, E-2. Following are general guidelines for TRs.

- Use one TR for twenty samples. A sample is a collection of material from a single point at one time and submitted for a single type of analysis (e.g., inorganic or organic). The use of multiple containers does not necessarily mean multiple samples: for example, an organic CL sample may be submitted in three containers for volatile, semi-volatile and pesticide analyses.
- Several spare TR forms shall be brought to the field to replace damaged or improperly completed forms prior to sample shipment.
- The sampler shall complete the following information: Case Number, site name or code, location, analytical laboratory to which the samples are shipped, firm name and sampler's name, dates of samples collection and shipment, number of sample bottles used, sample concentration (e.g., high, medium or low) and matrix.
- Samples for SAS only, (i.e., those for which no RAS is required) will be tracked using a SAS packing List (see Attachment E-3). No TR is to be completed for these samples.
- For samples requiring both RAS and SAS, a TR is used with both the Case number and SAS number entered.
- Samples requiring RAS dioxin analysis only, will be tracked using a Dioxin Shipment Record (see Attachment E-4), not a TR.
- Two copies of the TR go to the laboratory, one to SMO, one to the sampler's files.

Examples of sample TRs are included in Attachment E of this guideline. For a detailed description of these forms and instructions on their usage, see pp. 63-64 of the CLP User's Guide (Reference 1).

5.4.2 Dioxin Shipment Record

Samples destined for the RAS dioxin program must be accompanied by the CLP Dioxin Shipment Record (DSR). Only 2,3,7,8 TCDD is considered a RAS parameter. All other isomers are shipped as SAS parameters. These will be used in lieu of the TR for dioxin samples only. A sample form is included as

Attachment E-4 of this guideline. For a description of this form, see p. 65 of the CLP User's Guide (Reference 1).

5.4.3 SAS Packing List

Samples that require SAS only are to be accompanied by an SAS Packing List (PL) instead of a TR. Do not use this form for RAS-plus-SAS samples. A sample form is included as Attachment E-4 of this guideline. See p. 65 of the CLP User's Guide (Reference 1) for a description of this form.

5.4.4 Sample Identification Tags

Sample identification tags are required for all samples. Check off the desired analytical parameters directly on the tag and attach it securely to the sample container. The tags will be retained by the laboratory as physical evidence that the sample was received, and may be used by EPA in litigation.

Care shall be taken in filling out the sample tag. Improperly completed tags require time-consuming telephone inquiries to verify the actual parameters intended.

These tags may not accurately reflect the most recent CLP protocols. Mercury, for example, is considered part of the CLP metals analysis package, but is a separate parameter on these tags . In requesting metals analysis, be sure to check mercury along with metals.

5.4.5 Chain-of-Custody

In order for analytical results to be introduced as evidence in court, the custody of samples must be maintained and documented at all times. Chain-of-custody begins with the taking of the samples in the field. A detailed description of this requirement may be found on pp. 69-70 in the CLP User's Guide (Reference 1).

It is strongly recommended that a second person or persons be used to verify the accuracy and correctness of the chain-of-custody and all other documentation. The second person shall cross-check the chain-of-custody form with packing lists, TRs, sample tags, and logbooks. This cross-check shall be done prior to shipment.

5.5 NUS Program Sample Documentation

In addition to the required EPA QA, and CLP or non-CLP laboratory documentation of samples, certain standard forms are required for NUS program sample description and documentation. These include the well sampling data sheet (for water samples taken from monitoring wells) and the sample logbook, which contains sample log sheets for all samples collected.

5.5.1 Well Sampling Data Sheet

A well sampling data sheet shall be filled out whenever samples are collected from a monitoring well. This form records information about the well evacuation and other parameters (see Attachment F) which may be necessary for sample validation or interpretation. The well sampling data sheet shall be retained in the sample logbook (see Section 5.5.2), attached to the sample logsheet(s) for that well sampling event.

5.5.2 Sample Logbook

The sample logbook is a 3-ring binder which contains sample log sheets for each sample collected, and also well sampling data sheets. A sample log sheet (Attachment F) is filled out for each and every sample collected. This form records vital information concerning the sample source, sampling methods, sample conditions, and field measurements, and is used for sample validation and report preparation. The sample log sheets are numbered in order when placed in the sample logbook, and the sample number and log sheet page numbers are recorded on the sample logbook table of contents sheet (which is placed at the front of the sample logbook) for easy reference and access.

5.6 SAMPLE SHIPMENT AND NOTIFICATION

5.6.1 Sample Packaging

Samples must be properly prepared for shipment to the recipient laboratory. This preparation includes packaging and labeling sample coolers to comply with current U.S. DOT and commercial carrier regulations. The CLP User's Guide (Reference 1) should be consulted for specific guidance in this area. Specific points to note include:

- Dioxin samples shall be shipped as Poison B, rather than flammable liquid or solid.
- The use of bubble wrap sample bottles, after they have been placed in plastic bags, has proven very successful in reducing breakage. The material may be purchased from GSA, local office suppliers or direct from the manufacturer (e.g., Sealed Air Corporation). Under no circumstances shall earth or ice be used to cushion samples. Vermiculite or similar material shall be used.

Ice or "blue ice" refrigerant packages may be packed in contact with the sample bottle, and the entire package (bottle and ice) overpacked with plastic bags and bubble wrap.

5.6.2 Use of Common Carriers

Where possible, the use of reputable, overnight couriers, such as Federal Express, DHL, Purolater, and Emery, is strongly encouraged.

5.6.3 Shipment Notification

Immediately after shipping, the sampler must notify the RLSC who will inform the RSCC that samples have been collected and shipped. Under certain circumstances, the FOL or SM can contact the RSCC directly to inform of sample shipment or problems. The sampler should be prepared to provide the following information:

- Sampler Name.
- Case Number and/or SAS Number of the project.
- Batch numbers (dioxin only).
- Exact number(s) and matrices of sample(s) shipped.
- Carrier and airbill number(s) for the shipment.

- Method of shipment.
- Any irregularities or anticipated problems with the samples, including special handling instructions, or deviations from established sampling procedures.
- Status of the sampling project (e.g., final shipment, update of future shipping schedule).
- SMO must be notified by 3:00 p.m. eastern standard time Friday, for samples due to arrive on Saturdays. Failure to do so may result in the laboratory not having anyone on hand to accept the samples. In notifying SMO of weekend or any other deliveries, the airbill number is critical.
- Do not write the site name on the airbill. Use the CLP case number or the NUS charge number to maintain confidentiality at the laboratory.

5.7 POST-SAMPLING ACTIVITIES

Following sample collection and shipment activities, and upon return to the NUS office, the SM or designated staff member must meet the specific information requirements of Region III.

5.7.1 Region III Information Requirements

The SM or FOL must complete the EPA Region III sample shipping log for all samples sent through the CLP (Attachment G) and submit it to the RSCC during the week following sample collection.

5.7.2 Receipt of Data from CLP Laboratories

CLP laboratories are required to analyze RAS samples and report the data within either 30 or 40 days (depending on the specific contract). Often the analysis takes longer, depending on the total CLP sample load and other factors. CLP laboratories are required to send the analytical data directly to the region in which the samples were collected. All data must be reviewed and validated by the region or designated validation contractor before release to the SM for use, and this data review process can often take a month to complete. The EPA data review and validation process is shown in Attachment H. As the attachment indicates, at least two months pass between the time samples were collected to the time the SM receives data that is authorized for use.

6.0 REFERENCES

USEPA, 1984. User's Guide to the Contract Laboratory Program. Office of Emergency and Remedial Response, EPA, Washington, D.C. (revision planned for publication in late 1986).

U.S. Environmental Protection Agency, 1983. Method for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1982. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA-600/4-82-029. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

U.S. Environmental Protection Agency, 1980. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600-2/80-018. Municipal Environmental Research Laboratory, Cincinnati,Ohio.

U.S. Environmental Protection Agency, 1980. QAMS 005. Interim Guidelines and Specification for Preparing Quality Assurance Project Plans.

U.S. Environmental Protection Agency, 1984. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. EPA 600/4-84-041.

U.S. Environmental Protection Agency, 1983. SOP for the GC/MS Determination of Volatile Organic Compounds Collected on Tenax. EMSL/RTP-SOP-EMD-020. Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina.

U. S. Environmental Protection Agency, 1981. Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils. EPA 600/4-81-045.

U.S. Environmental Protection Agency, 1985. Groundwater Technical Enforcement Guida Document. Draft - August 1985.

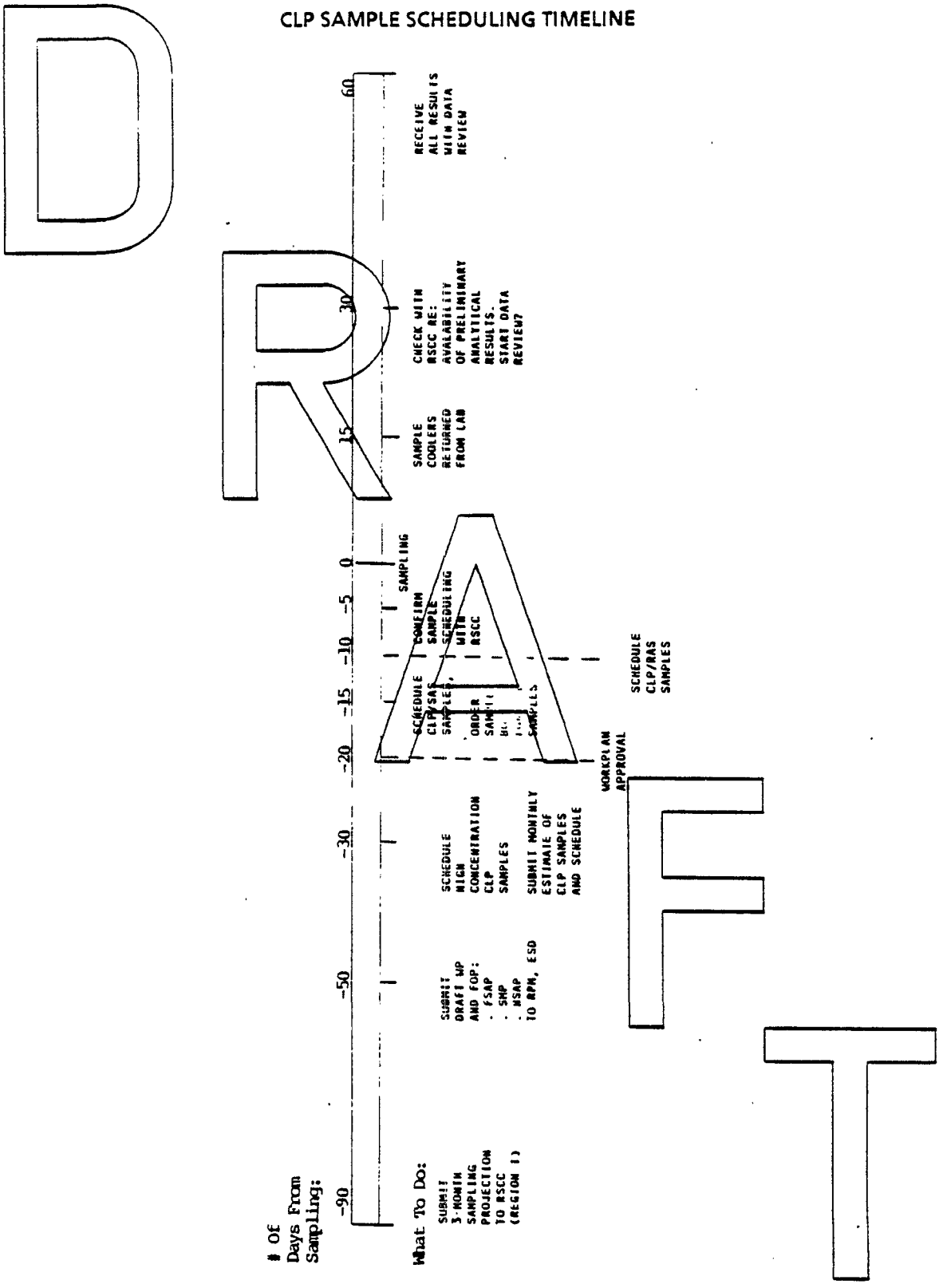
EBASCO Services Incorporated; REM III Field Technical Guideline No. FT-7.04, May 5, 1986.

7.0 ATTACHMENTS

Attachment A - CLP Sample Scheduling Timeline
Attachment B - Three-Month Sample Projection Plan
Attachment C - Sample Bottle Repository Delivery Order
Attachment D - SAS Client Request Form
Attachment E-1 - Inorganic Traffic Report
Attachment E-2 - Organic Traffic Report
Attachment E-3 - SAS Packing List
Attachment E-4 - Dioxin Shipment Record
Attachment F - Well Sample Data Sheet
Attachment G - Sample Shipping Log
Attachment H - EPA Data Review Process

ATTACHMENT A

CLP SAMPLE SCHEDULING TIMELINE



ATTACHMENT B

PLANNED SAMPLING ACTIVITY REQUIRING CLP ANALYSES

Region _____ Site _____ Month/Year of Activity _____ Case _____

Sampling Organization (State, REM, FIT, etc.) _____ Regional Contact _____ Telephone _____

Type of Investigation (RI/FS, Enforcement, etc.) _____ Activity Status (Definite, Conditional or Tentative) _____

Sampling Date(s) _____ Alternate Sampling Date(s) _____

Sample Shipment Date(s) _____ Alternate Shipment Date(s) _____

Routine Analytical Services Required	Media/Concentration: Liquid or Water Low	Med	High	Solid, Soil or Sediment Low	Med	High	Other (SAS) Low	Med	High	Total Low	Med	High
Full HSL Organics												
VOA Fraction Only												
Semi-VOA Fraction Only												
Pesticide/PCB Fraction Only												
Dioxin Only												
HSL Metals & Cyanide												
HSL Metals Only												

Special Analytical Services Required: Specify (Method, QA, Reporting Requirements to be Provided via SMO Client Request Form)

Submittal Status: _____ (Current, 1, 2 or 3 Month Projection)

Notification Status: _____ (Initial Notification or Resubmittal)

Resubmittal Status: _____ (Resubmittal With or Without Changes)

Submitted By: Date: Phone:

Approved By: Date:

Date Notification Received By SMO:

Date Laboratory(ies) Assigned:

ATTACHMENT C

CLP SAMPLE BOTTLE REPOSITORY SUPERFUND DELIVERY REQUEST

Date of Request: _____

Type of Request:
Routine ☐
Fast Turnaround ☐
Emergency ☐

_____
(date/time request called in)

FROM (Name): _____
Affiliation: _____
Telephone: _____
AR Signature: _____

TO: I-Chem Research Corporation
23787-F Eichler Street
Hayward, CA 94545
Phone: 415/782-3905

Ship the following items for arrival by: _____(date)
(If applicable) Ship to arrive no earlier than: _____(date)

Item		Description	No. of Items Per Case	No. of Cases Requested
A	80-oz	amber glass bottle	6	
B	40-mL	glass vial	72	
C	1-L	polyethylene bottle	12	
D	120-mL	wide-mouth glass vial	12	
E	16-oz	wide-mouth glass jar	12	
F	8-oz	wide-mouth glass jar	12	
G	4-oz	wide-mouth glass jar	12	
H	1-L	amber glass bottle	12	
J	32-oz	wide-mouth glass jar	12	
K	4-L	amber glass bottle	4	
L	500-mL	polyethylene bottle	24	

Ship To: _____
(provide street address) _____
Attention: _____
Call before Delivery: _____
(Phone No.) _____

DISTRIBUTION: *White—Repository* *Yellow—Requestor* *Pink—SMO*

ATTACHMENT D - page 1

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

☐ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: _____

B. Representative: _____

C. Telephone Number: _____

D. Date of Request: _____

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: _____

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium or high concentration): _____

3. Purpose of analysis (specify whether enforcement, remedial action, etc.): _____

4. Estimated date(s) of collection: _____

5. Estimated date(s) and method of shipment: _____

ATTACHMENT D - page 2

6. Approximate number of days results required after lab receipt of samples: _____

7. Analytical protocol required (attach copy if other than a protocol currently used in this program): _____

8. Special technical instructions (if outside protocol requirements, specify compound names, ~~CAS~~ numbers, detection limits, etc.): _____

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain of Custody documentation, etc.) If not completed, format of results will be left to program discretion. _____

10. Other (use additional sheets or attach supplementary information, as needed): _____

11. Name of sampling/shipping contact: _____
Phone: _____

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call us at the Sample Management Office.

ATTACHMENT E-1

DRAFT

USEPA CONTRACT LABORATORY PROGRAM
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 ALEXANDRIA, VA 22313
703/557-2490 FTS-557-2490

CASE NO:

SAS NO: (IF APPLICABLE)

INORGANIC TRAFFIC REPORT

(FOR CLP USE ONLY)

① TYPE OF ACTIVITY (CIRCLE ONE)
SUPERFUND—PA SI ESI RIFS RD RA ER NPLD O&M OTHER ______
NON-SUPERFUND—__________ PROGRAM

SITE NAME:

CITY, STATE. SITE SPILL ID:

② REGION NO: SAMPLING COMPANY

SAMPLER. (NAME)

③ SHIP TO:

ATTN:

④ SAMPLING DATE:
BEGIN: ______ END: ______

⑤ DATE SHIPPED: ______ CARRIER: ______

AIRBILL NO: ______

⑥ SAMPLE DESCRIPTION (ENTER IN BOX A)
1 SURFACE WATER
2. GROUND WATER
3. LEACHATE
4. SOIL
5. SEDIMENT
6. OIL (SAS)
7 WASTE (SAS)

DOUBLE VOLUME REQUIRED FOR MATRIX SPIKE/DUPLICATE AQUEOUS SAMPLE

SHIP MEDIUM AND HIGH CONCENTRATION SAMPLES IN PAINT CANS

SEE REVERSE FOR ADDITIONAL INSTRUCTIONS

CLP SAMPLE NUMBER (FROM LABELS)	Ⓐ SAMPLE DESCRIPTION (FROM BOX 1) 1 2 3 4 5 6 7	Ⓑ CONCENTRATION L = LOW M = MED H = HIGH (SAS)	Ⓒ RAS ANALYSIS: TOTAL METALS	CYANIDE	DISSOLVED METALS	HIGH ONLY (SAS): SULFIDE	pH	CORROSIVITY	OXIDANTS	Ⓓ SPECIAL HANDLING	Ⓔ STATION LOCATION

EPA Form 2075-6 (8-87)

WHITE — SMO COPY PINK — CLIENT COPY WHITE — LAB COPY FOR RETURN TO SMO YELLOW — LAB COPY

ATTACHMENT E-2

USEPA CONTRACT LABORATORY PROGRAM
SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 ALEXANDRIA, VA 22313
703/557-2490 FTS-557-2490

CASE NO: | SAS NO: (IF APPLICABLE)

ORGANIC TRAFFIC REPORT

(FOR CLP USE ONLY)

TYPE OF ACTIVITY (CIRCLE ONE) ①
SUPERFUND—PA SI ESI RIES RD RA ER
NPLD O&M OTHER _____
NON-SUPERFUND—_____ PROGRAM

SITE NAME:

CITY, STATE: | SITE SPILL ID:

REGION NO: | SAMPLING COMPANY ②

SAMPLER: (NAME)

SHIP TO: ③

ATTN:

SAMPLING DATE. ④
BEGIN: _____ END: _____

DATE SHIPPED: _____ CARRIER: ⑤

AIRBILL NO:

SAMPLE DESCRIPTION ⑥
(ENTER IN BOX A)
1. SURFACE WATER
2. GROUND WATER
3. LEACHATE
4. SOIL
5. SEDIMENT
6. OIL (SAS)
7. WASTE (SAS)

TRIPLE VOLUME REQUIRED FOR MATRIX SPIKE/DUPLICATE AQUEOUS SAMPLE

SHIP MEDIUM AND HIGH CONCENTRATION SAMPLES IN PAINT CANS

SEE REVERSE FOR ADDITIONAL INSTRUCTIONS

CLP SAMPLE NUMBER (FROM LABELS)	SAMPLE DESCRIPTION (FROM BOX 1) 1 2 3 4 5 6 ⑦	CONCENTRATION L = LOW/MED H = HIGH (SAS) ⑧	RAS ANALYSIS ⑨ VOLATILE	BASE/NEUT /ACID	PESTICIDE /PCB's	SPECIAL HANDLING ⑩	STATION LOCATION ⑪

EPA Form 2075-7 (8-87)

WHITE — SMO COPY PINK — CLIENT COPY WHITE — LAB COPY FOR RETURN TO SMO YELLOW — LAB COPY

ATTACHMENT E-3

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP Sample Management Office
P.O. Box 818 - Alexandria, Virginia 22313
Phone: 703/557-2490 - FTS/557-2490

SAS Number

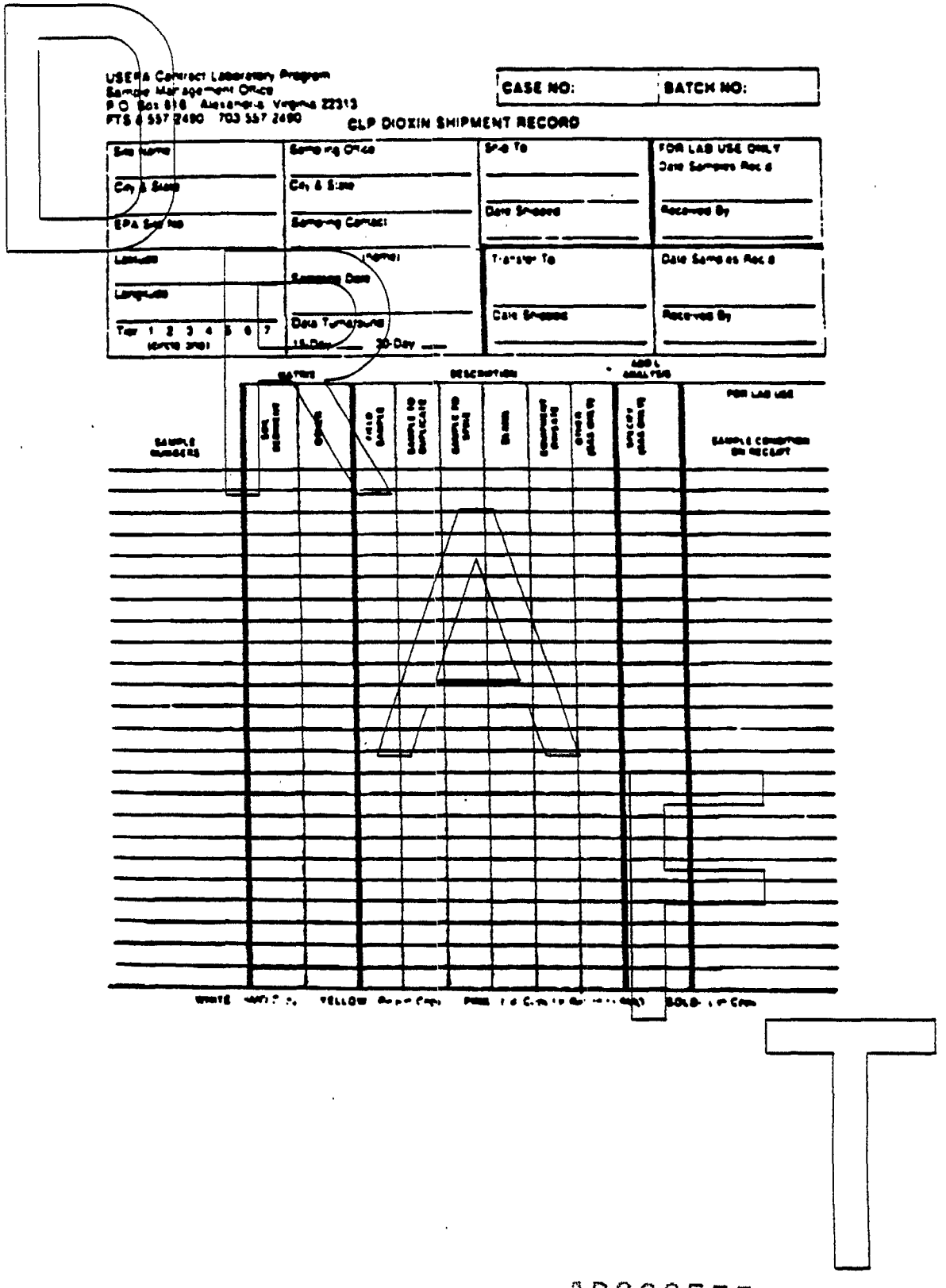
SPECIAL ANALYTICAL SERVICE
PACKING LIST

Sampling Office:	Sampling Date(s):	Ship To:	For Lab Use Only
Sampling Contact: (name)	Date Shipped:		Date Samples Rec'd:
(phone)	Site Name/Code:	Attn:	Received By:

Sample Numbers	Sample Description i.e., Analysis, Matrix, Concentration	Sample Condition on Receipt at Lab
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		
10.		
11.		
12.		
13.		
14.		
15.		
16.		
17.		
18.		
19.		
20.		For Lab Use Only

White - SMO Copy, Yellow - Region Copy, Pink - Lab Copy for return to SMO, Gold - Lab Copy

ATTACHMENT E-4



ATTACHMENT F

NUS CORPORATION
A Halliburton Company

SAMPLE LOG SHEET

☐ Monitoring Well Data
☐ Domestic Well Data
☐ Other _____

Page _____ of _____
Case # _____
By _____

Project Site Name _____ Project Site Number _____
NUS Source No. _____ Source Location _____

	Purge Data				
Total Well Depth:	Volume	pH	S.C.	Temp. (°C)	Color & Turbidity
Well Casing Size & Depth:					
Static Water Level:					
One Casing Volume:					
Start Purge (hrs.):					
End Purge (hrs.):					
Total Purge Time (min.):					
Total Amount Purged (gal.):					
Monitor Reading:					
Purge Method:					
Sample Method:					
Depth Sampled:					
Sample Date & Time:	Sample Data				
	pH	S.C.	Temp. (°C)	Color & Turbidity	
Sampled By:					
Signature(s):	Observations / Notes:				

Type of Sample
☐ Low Concentration
☐ High Concentration
☐ Grab
☐ Composite
☐ Grab - Composite

Analysis	Preservative		Organic	Inorganic
		Traffic Report #		
		Tag #		
		AB #		
		Date Shipped		
		Time Shipped		
		Lab		
		Volume		

AR300578

ATTACHMENT G
SAMPLE SHIPPING LOG

page___ of ___ EPA SAMPLE SHIPPING LOG FOR ALL SAMPLES SENT THROUGH THE CONTRACT LAB PROGRAM (12/85 version)

CASE#_________ SAS#_________ SITE NAME:______________________________

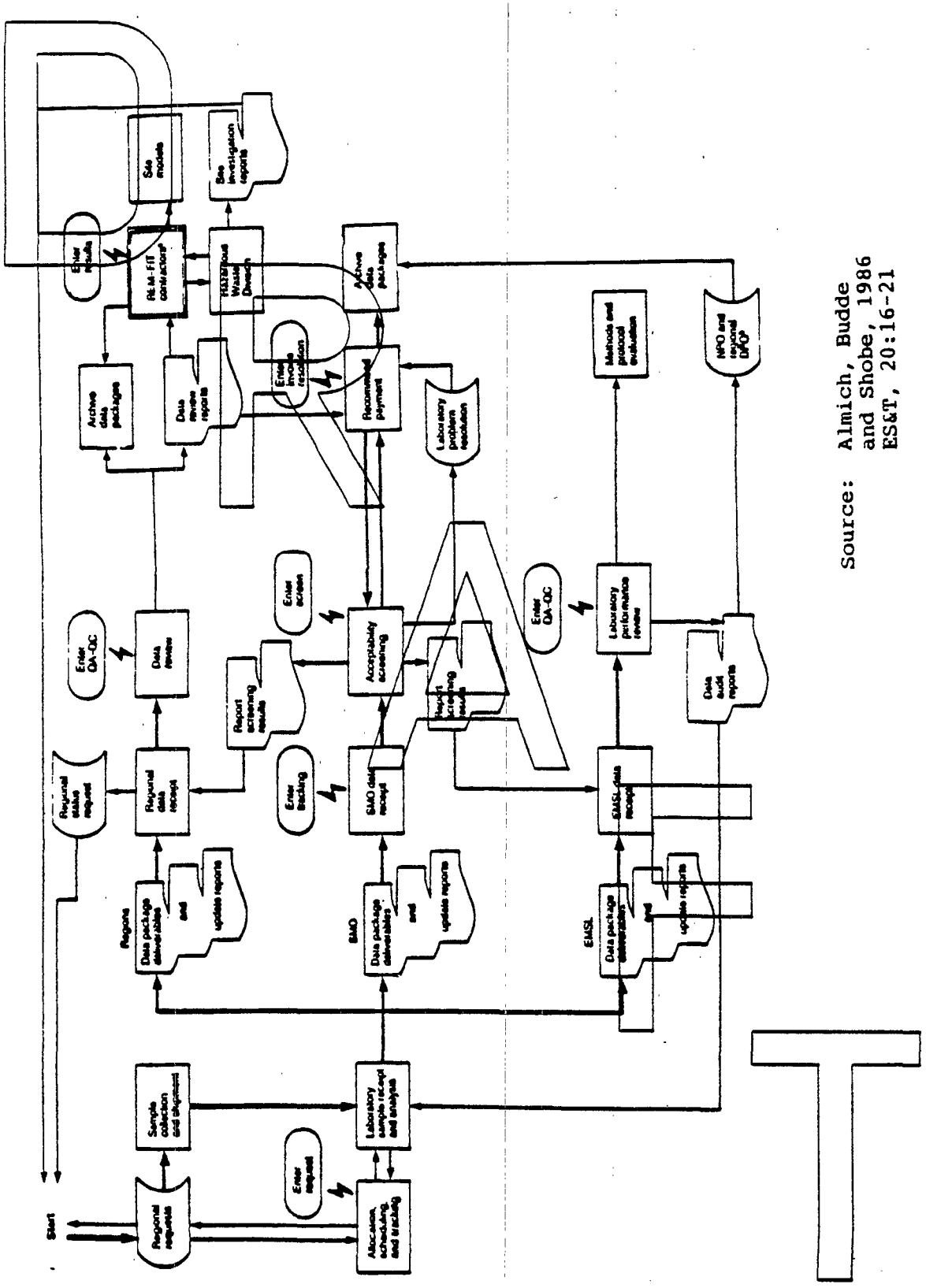
Site Leader:______________________ EPA Project Officer:______________________

Phone:

QC SAMPLE INFO AND/OR COMMENTS	CONC. (low/med/high)	SAMPLE PHASE (aq/sol)	TYPE OF REQUEST org,dioxin, inor, SAS	SAMPLE TRAFFIC REPORT NUMBER	ORGANICS OR INORGANICS LAB NAME	DATE SHIPPED	DATA RECEIVED XX out items not requested VOA	BNA	PEST	TCDD	METALS	CN	SAS REQUEST: (details required) LAB NAME	SAS REQUEST (itemize)	DATE SHIPPED	DATA REC'D

Subject	Number	Page
MANAGEMENT OF SAMPLING AND PREPARATION OF REQUIRED FORMS	SA-6.6	27 of 27
	Revision	Effective Date 01/01/88

ATTACHMENT H



Source: Almich, Budde and Shobe, 1986 ES&T, 20:16-21

NUS CORPORATION WASTE MANAGEMENT SERVICES GROUP	STANDARD OPERATING PROCEDURES	Number SF-1.1	Page 1 of 16
		Effective Date 08/10/88	Revision 1
		Applicability WMSG	
		Prepared Earth Sciences	
Subject ON-SITE WATER QUALITY TESTING		Approved A. K. Bomberger, P.E.	

TABLE OF CONTENTS

1.0 PURPOSE

This procedure describes the procedures and equipment required to measure the following parameters of an aqueous sample in the field:

- pH
- Specific Conductance
- Temperature
- Dissolved Oxygen (DO) Concentration
- Oxidation Reduction Potential
- Certain Dissolved Constituents Using Specific Ion Elements

2.0 SCOPE

This procedure is applicable for use in an on-site groundwater quality monitoring program to be conducted during a remedial investigation or site investigation program at a hazardous or non-hazardous site. The procedures and equipment described are applicable to nearly all aqueous samples, including potable well water, monitoring well water, surface water, leachate and drummed water, etc. and are not, in general, subject to solution interferences from color, turbidity and colloidal material, or suspended matter.

This procedure provides generic information for measuring the parameters listed above with instruments and techniques in common use. Since instruments from different manufacturers may vary, review of the manufacturer's literature pertaining to the use of a specific instrument is required before use.

3.0 GLOSSARY

3.1 pH MEASUREMENT

pH - The negative logarithm (base 10) of the hydrogen ion activity. The hydrogen ion activity is related to the hydrogen ion concentration, and, in relatively weak solution, the two are nearly equal. Thus, for all practical purposes, pH is a measure of the hydrogen ion concentration.

pH Paper - Paper that turns different colors depending on the pH of the solution to which it is exposed. Comparison with color standards supplied by the manufacturer will then give an indication of the solution pH.

3.2 SPECIFIC CONDUCTANCE MEASUREMENT

Ohm - Standard unit of electrical resistance (R). A siemen (or umho) is the standard unit of electrical conductance, the inverse of the ohm

Resistance - A measure of the solution's ability to oppose the passage of electrical current. For metals and solutions, resistance is defined by Ohm's law, $E = IR$, where E is the potential difference, I is the current, and R is the resistance.

Conductance - The conductance of a conductor 1 centimeter long and 1 square centimeter in cross-sectional area. Conductivity and specific conductance are used synonymously.

3.3 TEMPERATURE MEASUREMENT

None.

3.4 DISSOLVED OXYGEN MEASUREMENT

Galvanic Cell - An electrochemical cell in which chemical energy is spontaneously converted to electrical energy. The electrical energy produced is supplied to an external circuit.

Electrolytic Cell - An electrochemical cell in which electrical energy is supplied from an external source. This cell functions in much the same way as a galvanic cell, only in the opposite direction due to the external source of applied voltage.

3.5 OXIDATION-REDUCTION POTENTIAL MEASUREMENT

Oxidation - The process in which an atom or group of atoms loses electrons to achieve an increasing positive charge.

Reduction - The gaining of electrons by an atom or group of atoms and subsequent increase in negative charge.

Oxidation-Reduction Potential (ORP) - A measure of the activity ratio of oxidizing and reducing species as determined by the electromotive force developed by a noble metal electrode, immersed in water, as referenced against a standard hydrogen electrode.

3.6 SPECIFIC ION ELECTRODES MEASUREMENT

Specific Ion Electrode - An electrode which develops a potential difference across a membrane in response to the concentration differences for selected ions on either side of that membrane.

4.0 RESPONSIBILITIES

Site Manager - in consultation with the Project Geochemist, is responsible for determining which on-site water quality measurements can contribute to the RI, when these measurements shall be made, and the data quality objectives (DQOs) for these measurements. The Project Operations Plan (POP) shall contain details of type, frequency and locations of the desired measurements.

Project Geochemist - primarily responsible for determining the type, frequency and locations for on-site water quality measurements as presented in the POP and for interpreting the results, including determination of which measurements are unrepresentative.

Field Operations Leader - responsible for implementing the POP, and also for deciding under what field conditions a particular on-site measurement will be unrepresentative or unobtainable.

Field Samplers/Analysts - responsible for the actual analyses that take place, including calibration, quality control and recording of results, as well as for the care and maintenance of the equipment in the field.

5.0 GUIDELINES

5.1 MEASUREMENT OF pH

5.1.1 General

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment such as acid-base neutralization, water softening, and corrosion control, is pH dependent. Likewise, the pH of leachate can be correlated with other chemical analyses to determine the probable source of contamination. It is therefore important that reasonably accurate pH measurements be taken.

Measurements of pH can also be used to check the quality and corrosivity of soil and solid waste samples. However, these samples must be immersed in water prior to analysis, and specific techniques are not described.

Two methods are given for pH measurement: the pH meter and pH indicator paper. The indicator paper is used when only a rough estimate of the pH is required, and the pH meter when a more accurate measurement is needed. The response of a pH meter can be affected to a slight degree by high levels of colloidal or suspended solids, but the effect is usually small and generally of little significance. Consequently, specific methods to overcome this interference are not described. The response of pH paper is unaffected by solution interferences from color, turbidity, colloidal or suspended materials unless extremely high levels capable of coating or masking the paper are encountered. In such cases, use of a pH meter is recommended.

5.1.2 Principles of Equipment Operation

Use of pH papers for pH measurement relies on a chemical reaction caused by the acidity or basicity of the solution with the indicator compound on the paper. Depending on the indicator and the pH range of interest, a variety of different colors can be used. Typical indicators are weak acids or bases, or both. Process chemistry and molecular transformations leading to the color change are variable and complex.

Use of a pH meter relies on the same principle as other ion-specific electrodes. Measurement relies on establishment of a potential difference across a glass or other type of membrane in response to hydrogen ion concentration across that membrane. The membrane is conductive to ionic species and, in combination with a standard or reference electrode, a potential difference proportional to hydrogen ion concentration can be generated and measured.

5.1.3 Equipment

The following equipment is needed for taking pH measurements:

- Accumet 150 portable pH meter, or equivalent.
- Combination electrode with polymer body to fit the above meter (alternately a pH electrode and a reference electrode can be used if the pH meter is equipped with suitable electrode inputs.
- pH indicator paper, such as Hydrion or Alkacid, to cover the pH range 2 through 12.
- Buffer solutions of pH 4, 7 and 10, or other buffers which bracket the expected pH range.

5.1.4 Measurement Techniques for Field Determination of pH

1. pH Meter

The following procedure is used for measuring pH with a pH meter (Standardization is according to manufacturers instructions):

a. The instrument and batteries shall be checked and calibrated prior to initiation of the field effort.

b. The accuracy of the buffer solutions used for field and laboratory calibration shall be checked. Buffer solutions need to be changed often due to degradation upon exposure to the atmosphere.

c. Immerse the tip of the electrodes in water overnight. If this is not possible due to field conditions, immerse the electrode tip in water for at least an hour before use. The electrode tip may be immersed in a rubber or plastic sack containing buffer solution for field transport or storage. This is not applicable for all electrodes as some must be stored dry.

d. Make sure all electrolyte solutions within the electrode(s) are at their proper levels and that no air bubbles are present within the electrode(s).

e. Immerse the electrode(s) in a pH-7 buffer solution.

f. Adjust the temperature compensator to the proper temperature (on models with automatic temperature adjustment, immerse the temperature probe into the buffer solution). Alternately, the buffer solution may be immersed in the sample and allowed to reach temperature equilibrium before equipment calibration. It is best to maintain buffer solution at or near expected sample temperature before calibration.

g. Adjust the pH meter to read 7.0.

h. Remove the electrode(s) from the buffer and rinse well with demineralized water. Immerse the electrode(s) in pH-4 or 10 buffer solution (depending on the expected pH of the sample) and adjust the slope control to read the appropriate pH. For best results, the standardization and slope adjustments shall be repeated at least once.

i. Immerse the electrode(s) in the unknown solution, slowly stirring the probe until the pH stabilizes. Stabilization may take several seconds to minutes. If the pH continues to drift, the sample temperature may not be stable, a chemical reaction (e.g., degassing) may be taking place in the sample, or the meter or electrode may be malfunctioning. This must be clearly noted in the logbook.

j. Read and record the pH of the solution, after adjusting the temperature compensator to the sample temperature. pH shall be recorded to the nearest 0.1 pH unit. Also record the sample temperature.

k. Rinse the electrode(s) with deionized water.

l. Keep the electrode(s) immersed in deionized water when not in use.

The sample used for pH measurement shall never be saved for subsequent conductivity or chemical analysis. All pH electrodes leak small quantities of electrolytes (e.g., sodium or potassium chloride) into the solution. Precipitation of saturated electrolyte solution, especially at colder temperatures, or in cold water, may result in slow electrode response. Any visual observation of conditions which may interfere with pH measurement, such as oily materials, or turbidity, shall be noted.

2. pH Paper

Use of pH paper is very simple and requires no sample preparation, standardization, etc. pH paper is available in several ranges, including wide-range (indicating approximately pH 1 to 12), mid-range (approximately pH 0 to 6, 6 to 9, 8 to 14) and narrow-range (many available, with ranges as narrow as 1.5 pH units). The appropriate range of pH paper shall be selected. If the pH is unknown the investigation shall start with wide-range paper.

5.2 MEASUREMENT OF SPECIFIC CONDUCTANCE

5.2.1 General

Conductance provides a measure of dissolved ionic species in water and can be used to identify the direction and extent of migration of contaminants in groundwater or surface water. It can also be used as a measure of subsurface biodegradation or to indicate alternate sources of groundwater contamination.

Conductivity is a numerical expression of the ability of a water sample to carry an electric current. This value depends on the total concentration of the ionized substances dissolved in the water and the temperature at which the measurement is made. The mobility of each of the various dissolved ions, their valences, and their actual and relative concentrations affect conductivity.

It is important to obtain a specific conductance measurement soon after taking a sample, since temperature changes, precipitation reactions, and absorption of carbon dioxide from the air all affect the specific conductance.

5.2.2 Principles of Equipment Operation

An aqueous system containing ions will conduct an electric current. In a direct-current field, the positive ions migrate toward the negative electrode, while the negatively charged ions migrate toward the positive electrode. Most inorganic acids, bases and salts (such as hydrochloric acid, sodium carbonate, or sodium chloride, respectively) are relatively good conductors. Conversely, organic compounds such as sucrose or benzene, which do not disassociate in aqueous solution, conduct a current very poorly, if at all.

A conductance cell and a Wheatstone Bridge (for the measurement of potential difference) may be used for measurement of electrical resistance. The ratio of current applied to voltage across the cell may also be used as a measure of conductance. The core element of the apparatus is the conductivity cell containing the solution of interest. Depending on ionic strength of the aqueous solution to be tested, a potential difference is developed across the cell which can be converted directly or indirectly (depending on instrument type) to a measurement of specific conductance.

5.2.3 Equipment

The following equipment is needed for taking specific conductance measurements:

- YSI Model 33 portable conductivity, meter, or equivalent
- Probe for above meter

A variety of conductivity meters are available which may also be used to monitor salinity and temperatures. Probe types and cable lengths vary, so equipment may be obtained to meet the specific requirement of the sampling program.

5.2.4 Measurement Techniques for Specific Conductance

The steps involved in taking specific conductance measurements are listed below (standardization is according to manufacturers instructions):

- Check batteries and calibrate instrument before going into the field.
- Calibrate the instrument daily when used. Potassium chloride solutions with a specific conductance closest to the values expected in the field shall be used. Attachment A may be used for guidance.
- Rinse the cell with one or more portions of the sample to be tested or with deionized water.
- Immerse the electrode in the sample and measure the conductivity. Adjust the temperature setting to the sample temperature.
- Read and record the results in a field logbook or sample log sheet.

If the specific conductance measurements become erratic, or inspection shows that any platinum black has flaked off the electrode, replatinization of the electrode is necessary. See the manufacturer's instructions for details.

Note that specific conductance is occasionally reported at temperatures other than ambient.

5.3 MEASUREMENT OF TEMPERATURE

5.3.1 General

In combination with other parameters, temperature can be a useful indicator of the likelihood of biological action in a water sample. It can also be used to trace the flow direction of contaminated groundwater. Temperature measurements shall be taken in-situ, or as quickly as possible in the field. Collected water samples may rapidly equilibrate with the temperature of their surroundings.

5.3.2 Equipment

Temperature measurements may be taken with alcohol-toluene, mercury filled or dial-type thermometers. In addition, various meters such as specific conductance or dissolved oxygen meters, which have temperature measurement capabilities, may also be used. Using such instrumentation along with suitable probes and cables, in-situ measurements of temperature at great depths can be performed.

5.3.3 Measurement Techniques for Water Temperature

If a thermometer is used on a collected water sample:

- Immerse the thermometer in the sample until temperature equilibrium is obtained (1-3 minutes). To avoid the possibility of contamination, the thermometer shall not be inserted into samples which will undergo subsequent chemical analysis.
- Record values in a field logbook or sample log sheet.

If a temperature meter or probe is to be used, the instrument shall be calibrated according to manufacturer's recommendations with an approved thermometer before each measurement or group of closely spaced measurements.

5.4 MEASUREMENT OF DISSOLVED OXYGEN CONCENTRATION

5.4.1 General

Dissolved oxygen (DO) levels in natural water and wastewater depend on the physical, chemical and biochemical activities in the water body. Conversely, the growth of many aquatic organisms as well as the rate of corrosivity, are dependent on the dissolved oxygen concentration. Thus, analysis for dissolved oxygen is a key test in water pollution and waste treatment process control. If at all possible, DO measurements shall be taken in-situ, since concentration may show a large change in a short time if the sample is not adequately preserved.

The method monitoring discussed herein is limited to the use of dissolved oxygen meters only. Chemical methods of analysis (i.e., Winkler methods) are available, but require more equipment and greater sample manipulation. Furthermore, DO meters, using a membrane electrode, are suitable for highly polluted waters, because the probe is completely submersible, and are free from interference caused by color, turbidity, colloidal material or suspended matter.

5.4.2 Principles of Equipment Operation

Dissolved oxygen probes are normally electrochemical cells that have two solid metal electrodes of different nobility immersed in an electrolyte. The electrolyte is retained by an oxygen-permeable membrane. The metal of highest nobility (the cathode) is positioned at the membrane. When a suitable potential exists between the two metals, reduction of oxygen to hydroxide ion (OH) occurs at the cathode surface. An electrical current is developed that is directly proportional to the rate of arrival of oxygen molecules at the cathode.

Since the current produced in the probe is directly proportional to the rate of arrival of oxygen at the cathode, it is important that a fresh supply of sample always be in contact with the membrane. Otherwise, the oxygen in the aqueous layer along the membrane is quickly depleted and false low readings are obtained. It is therefore necessary to stir the sample (or the probe) constantly to maintain fresh solution near the membrane interface. Stirring, however, shall not be so vigorous that additional oxygen is introduced through the air-water interface at the sample surface. To avoid this possibility, some probes are equipped with stirrers to agitate the solution near the probe, but to leave the surface of the solution undisturbed.

Dissolved oxygen probes are relatively free of interferences. Interferences that can occur are reactions with oxidizing gases (such as chlorine) or with gases such as hydrogen sulfide which are not

easily depolarized from the indicating electrode. If the gaseous interference is suspected, it shall be noted in the field log book and checked if possible. Temperature variations can also cause interference because probes exhibit temperature sensitivity. Automatic temperature compensation is normally provided by the manufacturer.

5.4.3 Equipment

The following equipment is needed to measure dissolved oxygen concentration:

- YSI Model 56 dissolved oxygen monitor or equivalent.
- Dissolved oxygen/temperature probe for above monitor.
- Sufficient cable to allow the probe to contact the sample.

5.4.4 Measurement Techniques for Dissolved Oxygen Determination

Probes differ as to specifics of use. Follow the manufacturer's instructions to obtain an accurate reading. The following general steps shall be used to measure the dissolved oxygen concentration:

- The equipment shall be calibrated and have its batteries checked in the laboratory before going to the field.
- The probe shall be conditioned in a water sample for as long a period as practical before use in the field. Long periods of dry storage followed by short periods of use in the field may result in inaccurate readings.
- The instrument shall be calibrated in the field before each measurement or group of closely spaced measurements by placing the probe in a water sample of known dissolved oxygen concentration (i.e., determined by Winkler method) or in a freshly air-saturated water sample of known temperature. Dissolved oxygen values for air-saturated water can be determined by consulting a table listing oxygen solubilities as a function of temperature and salinity (see Attachment B).
- Immerse the probe in the sample. Be sure to provide for sufficient flow past the membrane, either by stirring the sample, or placing the probe in a flowing stream. Probes without stirrers placed in wells can be moved up and down.
- Record the dissolved oxygen content and temperature of the sample in a field logbook or sample log sheet.
- Recalibrate the probe when the membrane is replaced, or as needed. Follow the manufacturer's instructions.

Note that in-situ placement of the probe is preferable, since sample handling is not involved. This however, may not always be practical. Be sure to record whether the liquid was analyzed in-situ, or if a sample was taken.

Special care shall be taken during sample collection to avoid turbulence which can lead to increased oxygen solubilization and positive test interferences.

5.5 MEASUREMENT OF OXIDATION-REDUCTION POTENTIAL

5.5.1 General

The oxidation-reduction potential (ORP) provides a measure of the tendence of organic or inorganic compounds to exist in an oxidized state. The technique therefore provides evidence of the likelihood of anaerobic degradation of biodegradable organics or the ratio of activities of oxidized to reduced species in the sample.

5.5.2 Principles of Equipment Operation

When an inert metal electrode, such as platinum, is immersed in a solution, a potential is developed at that electrode depending on the ions present in the solution. If a reference electrode is placed in the same solution, an ORP electrode pair is established. This electrode pair allows the potential difference between the two electrodes to be measured and will be dependent on the concentration of the ions in solution. By this measurement, the ability to oxidize or reduce species in solution may be determined. Supplemental measurements, such as dissolved oxygen, may be correlated with ORP to provide a knowledge of the quality of the solution, water, or wastewater.

5.5.3 Equipment

The following equipment is needed for measuring the oxidation-reduction potential of a solution:

- Accumet 150 portable pH meter or equivalent, with a millivolt scale.
- Platinum electrode to fit above pH meter.
- Reference electrode such as a calomel, silver-silver chloride, or equivalent.

5.5.4 Measurement Techniques for Oxidation-Reduction Potential

The following procedure is used for measuring oxidation-reduction potential:

- The equipment shall be calibrated and have its batteries checked before going to the field.
- Check that the platinum probe is clean and that the platinum bond or tip is unoxidized. If dirty, polish with emery paper or, if necessary, clean the electrode using aqua regia, nitric acid, or chromic acid, in accordance with manufacturer's instructions.
- Thoroughly rinse the electrode with demineralized water.
- Verify the sensitivity of the electrodes by noting the change in millivolt reading when the pH of the test solution is altered. The ORP will increase when the pH of the test solution decreases and the ORP will decrease if the test solution pH is increased. Place the sample in a clean glass beaker and agitate the sample. Insert the electrodes and note the ORP drops sharply when the caustic is added, the electrodes are sensitive and operating properly. If the ORP increases sharply when the caustic is added, the polarity is reversed and must be corrected in accordance with the manufacturer's instructions. If the ORP does not respond as above when the caustic is added, the electrodes shall be cleaned and the above procedure repeated.
- After the assembly has been checked for sensitivity, wash the electrodes with three changes of water or by means of a flowing stream of water from a wash bottle. Place the sample in a clean glass beaker or sample cup and insert the electrodes. Set temperature

compensator throughout the measurement period. Read the millivolt potential of the solution, allowing sufficient time for the system to stabilize and reach temperature equilibrium. Measure successive portions of the sample until readings on two successive portions differ by no more an 10 mV. A system that is very slow to stabilize properly will not yield a meaningful ORP. Record all results in a field logbook, including ORP (to nearest 10 mV), sample temperature and pH at the time of measurement.

5.6 SPECIFIC ION ELECTRODE MEASUREMENTS

5.6.1 General

Use of specific ion electrodes can be beneficial in the field for determining the presence and concentration of dissolved inorganic species which may be associated with contaminant plumes or leachate. Thus, electrodes can be used for rapid screening of water quality and determination of water migration pathways.

This procedure provides generic information for specific ion electrodes commonly used in groundwater quality monitoring programs and describes the essential elements of a field investigation program. Analytical methods using some specific ion electrodes have not been approved by the USEPA. In addition, calibration procedures and solutions, interferences and conditions and requirements for use for various electrodes vary greatly. Consequently, review of manufacturer's literature is mandatory prior to use.

5.6.2 Principles of Equipment Operation

All specific ion electrode measurements involve the use of a reference electrode, a pH meter, and a specific ion electrode (SIE). When the SIE and the reference electrode are immersed in a solution of the ion to be measured, a potential difference is developed between the two electrodes. This potential can be measured by a pH meter and related to the concentration of the ion of interest through the use of standard solutions and calibration curves.

Several different types of SIEs are in use: glass, solid-state, liquid-liquid membrane, and gas-sensing. All of the electrodes function using an ion exchange process as the potential determining mechanism. Glass electrodes are used for pH measurement. The glass in the tip of the electrode actually acts as a semi-permeable membrane to allow solution. Solid-state electrodes replace the glass membrane with an ionically-conducting membrane, (but act in essentially the same manner) while liquid-liquid membrane electrodes have an organic liquid ion exchanger contained in the pores of a hydrophobic membrane. Maintenance of the conducting interface, in combination with a reference electrode, allows completion of the electrical circuit and subsequent measurement of the potential difference. Gas-sensing electrodes have a membrane that permits the passage of gas only, thus allowing for the measurement of gas concentration. Regardless of the mechanism involved in the electrode, most SIEs are easy to use under field conditions. The sensitivity and applicable concentration range for various membranes and electrodes will vary.

5.6.3 Equipment

The following equipment is required for performing quantitative analyses using a specific ion electrode:

- A pH meter with a millivolt scale, or equivalent.
- The specific ion electrode for the parameter to be measured. A partial list of ions which can be measured includes cyanide, sulfide, ammonia, lead, fluoride and chloride.

- A suitable reference electrode to go with the above SIE.

Specific electrodes for other ions have also been developed, but are not widel used for field investigation efforts at this time. Note that of the specific electrodes referenced abc , only fluoride and ammonia have analytical methods approved by the USEPA.

5.6.4 Measurement Techniques for Inorganic Ions Using Specific Ion Electrodes

Different types of electrodes are used in slightly different ways and are applica for different concentration ranges. Following the manufacturer's instructions, the general steps ven below are usually followed:

- Immerse the electrode in water for a suitable period of time prior to sample nalysis.
- Standardize the electrode according to the manufacturer's instruc ns, including necessary chemical additions for ionic strength adjustment, etc. Sta dard solutions normally differ by factors of ten in concentration. Constant stirring is nee d for accurate readings.
- Immerse the electrode in the sample. Allow the reading to stabilize and r ord the results in a site logbook. Stir the sample at the same rate as the standards. Air bbles near the membrane shall be avoided, since this may cause interference in millivolt re lings.

(NOTE: Each SIE has substances which interfere with proper measurement. These m be elimi using pretreatment methods as detailed by the manufacturer. It is important to kno f interferences are present so that suspect readings may be noted as such.)

- If the pH meter does not read out directly, plot millivolts versus conce ration for the standards and then determine sample concentration.

6.0 REFERENCES

American Public Health Association, 1980. Standard Methods for the Examinatic of Water and Wastewater, 15th Edition, APHA, Washington, D.C.

USEPA, 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020

U.S. Geological Survey, 1984. National Handbook of Recommended Methods r Water Data Acquisition, Chapter 5: Chemical and Physical Quality of Water and Sediment. I . Dept. of the Interior, Reston, VA.

Ebasco Services Incorporated; REM III Field Technical Guideline FT-7.10. February 3, 1 6.

7.0 RECORDS

Attachment A - Specific Conductance of KC1 Solutions at 25 degrees Centigrade

Attachment B - Variation of Dissolved Oxygen Concentration in Water as a a Functio f Temperature and Salinity.

ATTACHMENT A

SPECIFIC CONDUCTANCE OF M KCl AT VARIOUS TEMPERATURES[1]

Temperature (°C)	Specific Conductance (umhos/cm)
15	1,147
16	1,173
17	1,199
18	1,225
19	1,251
20	1,278
21	1,305
22	1,332
23	1,359
24	1,368
25	1,413
26	1,441
27	1,468
28	1,496
29	1,524
30	1,552

[1] Data derived from the International Critical Tables 1-3-8.

ATTACHMENT B

VARIATION OF DISSOLVED OXYGEN CONCENTRATION IN WATER AS A FUNCTION OF TEMPERATURE AND SALINITY

Temperature C	Dissolved Oxygen mg/l					
	Chloride Concentration in Water					Difference/100 mg/l ride
	0	5,000	10,000	15,000	20,000	
0	14.6	13.8	13.0	12.1	11.3	0.017
1	14.2	13.4	12.6	11.8	11.0	0.016
2	13.8	13.1	12.3	11.5	10.8	0.015
3	13.5	12.7	12.0	11.2	10.5	0.015
4	13.1	12.4	11.7	11.0	10.3	0.014
5	12.8	12.1	11.4	10.7	10.0	0.014
6	12.5	11.8	11.1	10.5	9.8	0.014
7	12.2	11.5	10.9	10.2	9.6	0.013
8	11.9	11.2	10.6	10.0	9.4	0.013
9	11.6	11.0	10.4	9.8	9.2	0.012
10	11.3	10.7	10.1	9.6	9.0	0.012
11	11.1	10.5	9.9	9.4	8.8	0.011
12	10.8	10.3	9.7	9.2	8.6	0.011
13	10.6	10.1	9.5	9.0	8.5	0.011
14	10.4	9.9	9.3	8.8	8.3	0.010
15	10.2	9.7	9.1	8.6	8.1	0.010
16	10.0	9.5	9.0	8.5	8.0	0.010
17	9.7	9.3	8.8	8.3	7.8	0.010
18	9.5	9.1	8.6	8.2	7.7	0.009
19	9.4	8.9	8.5	8.0	7.6	0.009
20	9.2	8.7	8.3	7.9	7.4	0.009
21	9.0	8.6	8.1	7.7	7.3	0.009
22	8.8	8.4	8.0	7.6	7.1	0.008
23	8.7	8.3	7.9	7.4	7.0	0.008
24	8.5	8.1	7.7	7.3	6.9	0.008

ATTACHMENT B

VARIATION OF DISSOLVED OXYGEN CONCENTRATION IN WATER AS A FUNCTION OF TEMPERATURE AND SALINITY

Temperature C	Dissolved Oxygen mg/l					
	Chloride Concentration in Water					Difference/100 mg chloride
	0	5,000	10,000	15,000	20,000	
25	8.4	8.0	7.6	7.2	6.7	0.008
26	8.2	7.8	7.4	7.0	6.6	0.008
27	8.1	7.7	7.3	6.9	6.5	0.008
28	7.9	7.5	7.1	6.8	6.4	0.008
29	7.8	7.4	7.0	6.6	6.3	0.008
30	7.6	7.3	6.9	6.5	6.1	0.008
31	7.5					
32	7.4					
33	7.3					
34	7.2					
35	7.1					
36	7.0					
37	6.9					
38	6.8					
39	6.7					
40	6.6					
41	6.5					
42	6.4					
43	6.3					
44	6.2					
45	6.1					
46	6.0					
47	5.9					
48	5.8					
49	5.7					
50	5.6					

Note: In a chloride solution, conductivity can be roughly related to chloride concenration (and therefore used to correct measured D.O. concentraiton) using Attachment A.

NUS CORPORATION WASTE MANAGEMENT SERVICES GROUP	STANDARD OPERATING PROCEDURES	Number SF-1.2	Page 1 of 10
		Effective Date 08/10/88	Revision 1
		Applicability WMSG	
		Prepared Earth Sciences	
Subject SAMPLE PRESERVATION		Approved A. K. Bomberger, P.E.	

TABLE OF CONTENTS

1.0 PURPOSE

This procedure describes the appropriate containers to be used for samples depending on the analyses to be performed, and the steps necessary to preserve the samples when shipped offsite for chemical analysis.

2.0 SCOPE

Different types of chemicals react differently with sample containers made of various materials. For example, trace metals adsorb more strongly to glass than to plastic, while many organic chemicals may dissolve various types of plastic containers. It is therefore critical to select the correct container in order to maintain the quality of the sample prior to analysis.

Many water and soil samples are unstable, and therefore require preservation when the time interval between field collection and laboratory analysis is long enough to produce changes in either the concentration or the physical condition of the constituent(s) requiring analysis. While complete and irreversible preservation of samples is not possible, preservation does retard the chemical and biological changes that inevitably take place after the sample is collected.

Preservation techniques are usually limited to pH control, chemical addition(s) and refrigeration/ freezing. Their purpose is to (1) retard biological activity, (2) retard hydrolysis of chemical compounds/complexes, (3) reduce constituent volatility, and (4) reduce adsorption effects.

3.0 GLOSSARY

HCl - Hydrochloric Acid
H_2SO_4 - Sulfuric Acid
HNO_3 - Nitric Acid
NaOH - Sodium Hydroxide

Normality (N) - Concentration of a solution expressed as equivalent per liter, an equivalent being the amount of a substance containing one gram-atom of replaceable hydrogen or its equivalent. Thus, a one molar solution of HCl, containing one gram-atom of H, is "one-normal," while a one molar solution of H_2SO_4 containing two gram-atoms of H, is "two-normal."

4.0 RESPONSIBILITIES

Field Operations Leader - retains overall responsibility for the proper storage and preservation of samples. During the actual collection of samples, the sampling technician(s) will be directly responsible for the bottling, preservation, labeling, and custody of the samples they collect until released to another party for storage or transport to the analytical laboratory.

5.0 PROCEDURES

5.1 SAMPLE CONTAINERS

For most samples and analytical parameters either glass or plastic containers are satisfactory. In general, if the analyte(s) to be determined is organic in nature, the container shall be made of glass. If the analyte(s) is inorganic, then the container shall be plastic. Since container specification will depend on the analyte and sample matrix types (as indicated in Attachment A) duplicate samples shall be taken when both organic and inorganic analyses are required. Containers shall be kept in

the dark (to minimize biological or photooxidation/photolysis breakdown of constituent) until they reach the analytical laboratory. The sample container shall allow approximately 5-10 percent air space ("ullage") to allow for expansion/vaporization if the sample is heated during transport (1 liter of water at 4°C expands by 15 ml if heated to 130°F/55°C), however, head space for volatile organic analyses shall be omitted.

For CLP laboratories, containers will be obtained through the CLP Sample Management Office. For Responsible party actions or non-CLP laboratories, the laboratory shall provide containers that have been cleaned according to U.S. EPA procedures. Sufficient lead time shall be allowed. Shipping containers for samples, consisting of sturdy ice chests, are provided by the laboratory of the remedial investigation contractor.

Once opened, the container must be used at once for storage of a particular sample. Unused but opened containers are to be considered contaminated and must be discarded; because of the potential for introduction of contamination, they cannot be reclosed and saved for later use. Likewise, any unused containers which appear contaminated upon receipt, or which are found to have loose caps or missing Teflon liner (if required for the container) shall be discarded.

General sample container and sample volume requirements are listed in Attachment A. Specific container requirements are listed in Attachment B.

5.2 PRESERVATION TECHNIQUES

The preservation techniques to be used for various analytes are listed in Attachments A and B. Reagents required for sample preservation will either be added to the sample containers by the laboratory prior to their shipment to the Field or added in the Field. In general, aqueous samples of low concentration organics (or soil samples of low or medium concentration organics) are cooled to 4°C. Medium concentration aqueous samples and high hazard organics sample are not preserved. Low concentration aqueous samples for metals are acidified with HNO_3, while medium concentration and high hazard aqueous metal samples are not preserved. Low or medium concentration soil samples for metals are cooled to 4°C while high hazard samples are not preserved.

The following subsections describe the procedures for preparing and adding chemical preservatives. Attachments A and B indicate the specific analytes which require these preservatives.

5.2.1 Addition of Acid (H_2SO_4, HCl, or HNO_3) or Base

Addition of the following acids or bases may be specified for sample preservation; these reagents shall be analytical reagent (AR) grade and shall be diluted to the required concentration with double-distilled, deionized water in the laboratory, before Field sampling commences:

Acid Base	Concentration	Normality	Amount for Acidification*
HCl	1:1 dilution of concentrated HCl	6N	5-10 ml
H_2SO_4	1:1 dilution of concentrated H_2SO_4	18N	2-5 ml
HNO_3	Undiluted concentrated HNO_3	16N	2-5 ml
NaOH	400 grams solid NaOH in 870 ml water	10N	2 ml**

* Amount of acid to add (at the specified strength) per liter of water to reduce the sample pH to less than 2, assuming that the water is initially at pH 7, and is poorly buffered and does not contain particulate matter.

** To raise pH of 1 liter of water to 12.

The approximate volumes needed to acidify one liter of neutral water to a pH of less than 2 (or raise the pH to 12) are shown in the last column of the above table. These volumes are only approximate; if the water is more alkaline, contains inorganic or organic buffers, or contains suspended particles, more acid may be required. The final pH must be checked using narrow-range pH paper.

Sample acidification or base addition shall proceed as follows:

- Check initial pH of sample with wide range (0-14) pH paper.
- Fill sample bottle to within 5-10 ml of final desired volume and add about 1/2 of estimated acid or base required, stir gently and check pH with medium range pH paper (pH 0-6 or pH 7.5-14, respectively).
- Add acid or base a few drops at a time while stirring gently. Check for final pH using narrow range (0-2.5 or 11-13, respectively) pH paper; when desired pH is reached, cap sample bottle and seal.

  Never dip pH paper into the sample; apply a drop of sample to the pH paper using the stirring rod.

5.2.2 Cyanide Preservation

Pre-sample preservation is required if oxidizing agents such as chlorine are suspected to be present. To test for oxidizing agents, place a drop of the sample on KI-starch paper; a blue color indicates the need for treatment. Add ascorbic acid to the sample, a few crystals at a time, until a drop of sample produces no color on the KI-starch paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume. Add NaOH solution to raise pH to greater than 12 as described in 5.2.1. If oxidizing agents are not suspected, add NaOH as directed.

5.2.3 Sulfide Preservation

Samples for sulfide analysis must be preserved by addition of 4 drops (0.2 ml) of 2N zinc acetate solution per 100 ml sample. The sample pH is then raised to 9 using NaOH. The 2N zinc acetate solution is made by dissolving 220 g of zinc acetate in 870 ml of distilled water to make 1 liter of solution.

5.2.4 Preservation of Organic Samples Containing Residual Chlorine

Some organic samples containing residual chlorine must be treated to remove this chlorine upon collection (See Attachment A). Test the samples for residual chlorine using EPA methods 330.4 or 330.5 (Field Test Kits are available for this purpose). If residual chlorine is present, add 0.008% sodium thiosulfate (80 mg per liter of sample).

5.2.5 Field Filtration

When the objective is to determine concentration of dissolved inorganic constituents in a water system, the sample must be filtered through a non-metallic 0.45 micron membrane filter immediately after collection. A filtration system is recommended if large quantities of samples must be filtered in the field. The filtration system shall consist of a Büchner funnel inserted into a single-hole rubber stopper, sized to form a seal when inserted into the top of a vacuum filter flask equipped with a single side arm. Heavy-wall Tygon tubing shall be attached to the single side arm of the vacuum filter flask and the suction port of a vacuum pump. The stem of the Büchner funnel shall extend below the level of the side arm of the vacuum filter flask to prevent any solvent from entering the tubing leading to the vacuum pump. Before filtration, the filter paper, which shall be of a size to lay flat on the funnel plate, shall be wetted with the solvent in order to "seal" it to the funnel. Slowly pour the solvent into the funnel and monitor the amount of solvent entering the vacuum filter flask. When the rate of solvent entering the flask is reduced to intermittent dripping and the added aliquot of solvent in the funnel has passed through the filter, the used filter paper shall be replaced with new filter paper. If the solvent contains a high percentage of suspended solids, a coarser-sized nonmetallic membrane filter may be used prior to usage of the 0.45 micron membrane filter. This "prefiltering" step may be necessary to expedite the filtration procedure. Discard the first 20 to 50 ml of filtrate from each sample to rinse the filter and filtration apparatus to minimize the risk of altering the composition of the samples by the filtering operation. For analysis of dissolved metals, the filtrate is collected in a suitable bottle (see Section 5.1) and is immediately acidified to pH 2.0 or less with nitric acid whose purity is consistent with the measurement to be made. Inorganic anionic constituents may be determined using a portion of the filtrate that has not been acidified.

Samples used for determining temperature, dissolved oxygen, Eh, and pH should not be filtered. Do not use vacuum filtering prior to determining carbonate and bicarbonate concentration because it removes dissolved carbon dioxide and exposes the sample to the atmosphere. Pressure filtration can be done using water pressure from the well. If gas pressure is required, use an inert gas such as argon or nitrogen.

Do not filter samples for analysis of volatile organic compounds. If samples are to be filtered for analyzing other dissolved organic constituents, use a glass-fiber or metal-membrane filter and collect the samples in a suitable container (see Section 5.1). Because most organic analyses require extraction of the entire sample, do not discard any of it. After filtering, the membrane containing the suspended fraction can be sealed in a glass container and analyzed separately as soon as practicable. Total recoverable inorganic constituents may be determined using a second unfiltered sample collected at the same time as the sample for dissolved constituents.

6.0 REFERENCES

American Public Health Association, 1981. Standard Methods for the Examination of Water and Wastewater. 15th Edition. APHA, Washington, D.C.

USEPA, 1984. "Guidelines Establishing Test Procedures for the Analysis of Pollutants under Clean Water Act." Federal Register, Volume 49 (209), October 26, 1984, p. 43234.

USEPA, 1979. Methods for Chemical Analysis of Water and Wastes. EPA-600/4-79-020. USEPA-EMSL, Cincinnati, Ohio.

Ebasco Services Incorporated; REM III Field Technical Guideline No. FT-7.06. March 4, 1986.

7.0 ATTACHMENTS

Attachment A - General Sample Container and Preservation Requirements CERCLA/RCRA Samples
Attachment B - Required Containers, Preservation Techniques, and Holding Times (3 sheets)

	SAMPLE TYPE & CONCENTRATION	CONTAINER[1]	SAMPLE SIZE	PRESERVATION[2]	HOLDING TIME[2]
WATER					
Organics (GC & GC/MS)	VOA	borosilicate glass	2 x 40 ml	Cool to 4°C	7 days
	Extractables				
	Low	amber glass	2 x 2 l or 4 x 1 l	Cool to 4°C	5 days to extraction 40 days after extraction
	Medium	wide-mouth glass	4 x 32 oz	None	Same as above
Inorganics	Metals				
	Low	high density (h.d.) polyethylene	1 l	HNO_3 to pH <2	6 months (Hg-30 days)
	Medium	wide-mouth glass	16 oz	None	6 months
	Cyanide				
	Low	h.d. polyethylene	1 l	NaOH to pH >12	14 days
	Medium	wide-mouth glass	16 oz	None	
Organic/Inorganic	High Hazard	8 oz wide-mouth glass	6 oz	None	14 days
COD	--	h.d. polyethylene	0.5 l	H_2SO_4 to pH <2	28 days
TOC	--	h.d. polyethylene	0.5 l	HCl to pH <2	28 days
Oil & Grease	--	glass	1.0 l	H_2SO_4 to pH <2	28 days
Phenols	--	h.d. polyethylene	1.0 l	H_2SO_4 to pH <2	28 days
General Chemistry	--	h.d. polyethylene	1.0 l	None	---
SOIL					
Organics (GC & GC/MS)	VOA	2 x 120 ml (4 oz) wide-mouth glass	240 ml	Cool to 4°C	10 days
	Extractables				
	Low/Medium	8 oz or 2 x 4 oz (120 ml) wide-mouth glass	6 oz	Cool to 4°C	10 days to extraction 40 days after extraction
Inorganics	Low/Medium	8 oz or 2 x 4 oz (120 ml) wide-mouth glass	6 oz	Cool to 4°C	NA
Organic/Inorganic	High Hazard	8 oz (120 ml) wide-mouth glass	6 oz	None	NA
Dioxin	All	4 oz (120 ml) wide-mouth glass	4 oz	None	NA
EP Toxicity	All	250 ml h.d. polyethylene	200 grams	None	NA
Air					
Volatile Organics	Low Medium	Charcoal Tube 7 cm long, 6 mm OD, 4 mm ID	100 l air	Cool to 4°C	NA

1. All glass containers should have Teflon cap liners or septa.
2. See Attachment B.

SAMPLE CONTAINER AND PRESERVATION REQUIRMENTS CERCLA/RCRA SAMPLES

ATTACHMENT B
REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter No./Name	Container[1]	Preservation[2,3]	Maximum Holding Time[4]
INORGANIC TESTS:			
Acidity	P,G	Cool, 4°C	14 days
Alkalinity	P,G	Cool, 4°C	14 days
Ammonia	P,G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Biochemical Oxygen Demand	P,G	Cool, 4°C	48 hours
Bromide	P,G	None required	28 days
Biochemical Oxygen Demand, Carbonaceous	P,G	Cool, 4°C	48 hours
Chemical Oxygen Demand	P,G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Chloride	P,G	None required	28 days
Chlorine, Total Residual	P,G	None required	Analyze immediately
Color	P,G	Cool, 4°C	48 hours
Cyanide, Total and Amenable to Chlorination	P,G	Cool, 4°C, NaOH to pH 12, 0.6g ascorbic acid[5]	14 days[6]
Fluoride	P	None required	28 days
Hardness	P,G	HNO_3 to pH 2, H_2SO_4 to pH 2	6 months
Hydrogen Ion (pH)	P,G	None required	Analyze immediately
Kjeldahl and Organic Nitrogen	P,G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Nitrate	P,G	Cool, 4°C	48 hours
Nitrate-Nitrite	P,G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Nitrite	P,G	Cool, 4°C	48 hours
Oil and Grease	G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Organic Carbon	P,G	Cool, 4°C, HCl or H_2SO_4 to pH 2	28 days
Orthophosphate	P,G	Filter immediately, Cool, 4°C	48 hours
Oxygen, Dissolved-Probe	G Bottle and top	None required	Analyze immediately
Oxygen, Dissolved-Winkler	G Bottle and top	Fix on site and store in dark	8 hours
Phenols	G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Phosphorus (elemental)	G	Cool, 4°C	48 hours
Phosphorus, Total	P,G	Cool, 4°C, H_2SO_4 to pH 2	28 days
Residue, Total	P,G	Cool, 4°C	7 days
Residue, Filterable	P,G	Cool, 4°C	48 hours
Residue, Nonfilterable (TSS)	P,G	Cool, 4°C	7 days
Residue, Settleable	P,G	Cool, 4°C	48 hours
Residue, Volatile	P,G	Cool, 4°C	7 days
Silica	P	Cool, 4°C	28 days
Specific Conductance	P,G	Cool, 4°C	28 days
Sulfate	P,G	Cool, 4°C	28 days
Sulfide	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH 9	7 days
Sulfite	P,G	None required	Analyze immediately
Surfactants	P,G	Cool, 4°C	48 hours
Temperature	P,G	None required	Analyze immediately
Turbidity	P,G	Cool, 4°C	48 hours
METALS:[7]			
Chromium VI	P,G	Cool, 4°C	24 hours
Mercury	P,G	HNO_3 to pH 2	28 days
Metals, except Chromium VI and Mercury	P,G	HNO_3 to pH 2	6 months

ATTACHMENT B
REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES
PAGE 2

Parameter No./Name	Container[1]	Preservation[2,3]	Maximum Holding Time[4]
ORGANIC TESTS:[6]			
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	14 days
Purgeable Aromatic Hydrocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], HCl to pH 2[9]	14 days
Acrolein and Acrylonitrile	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], adjust pH to 4-5[10]	14 days
Phenols[11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction[13]
Benzidines[11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction[13]
Phthalate Esters[11]	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitrosamines[11,14]	G, Teflon-lined cap	Cool, 4°C, store in dark, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction
PCBs[11] Acrylonitrile	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitroaromatics and Isophorone[11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], store in dark	7 days until extraction, 40 days after extraction
Polynuclear Aromatic Hydrocarbons[11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5], store in dark	7 days until extraction, 40 days after extraction
Haloethers[11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction
Chlorinated Hydrocarbons[11]	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
TCDD[11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	7 days until extraction, 40 days after extraction
PESTICIDES TESTS:			
Pesticides[11]	G, Teflon-lined cap	Cool, 4°C, pH 5-9[15]	7 days until extraction, 40 days after extraction
RADIOLOGICAL TESTS:			
1-3 Alpha, beta and radium	P, G	HNO_3 to pH 2	6 months

TABLE 1 Notes

(1) Polyethylene (P) or Glass (G).

(2) Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

(3) When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172).

(4) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has received a variance from the Regional Administrator.

(5) Should only be used in the presence of residual chlorine.

ATTACHMENT B
REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

(6) Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

(7) Samples should be filtered immediately on-site before adding preservative for dissolved metals.

(8) Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

(9) Sample receiving no pH adjustment must be analyzed within seven days of sampling.

(10) The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

(11) When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding time should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.0008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re: the requirement for chlorination and holding time of sampling) and footnote 12, 13 (re: the analysis of benzidine).

(12) If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0±0.2 to prevent rearrangement to benzidine.

(13) Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

(14) For the analysis of diphenylnitrosamine add 0.0008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

(15) The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.0008% $Na_2S_2O_3$.

NUS CORPORATION WASTE MANAGEMENT SERVICES GROUP	STANDARD OPERATING PROCEDURES	Number SF-1.4	Page 1 of 17
		Effective Date 01/01/88	Revision 0
		Applicability WMSG	
		Prepared Earth Sciences	
Subject: ONSITE COMPATIBILITY TESTING OF HAZARDOUS MATERIALS		Approved A. K. Bomberger, P.E.	

TABLE OF CONTENTS

1.0 PURPOSE

This procedure describes techniques and equipment/material requirements for rapid categorization of wastes into compatibility groups. This categorization is useful for minimizing disposal costs and risks to personnel which may occur during mixing of incompatible hazardous materials.

2.0 SCOPE

Techniques and general considerations for compatibility determination of generally uncharacterized wastes are presented in this procedure. The methods described herein allow identification of wastes by categories which, if mixed, would cause dangerous reactions to occur or which would lead to increases in disposal costs via contamination of less hazardous materials which could have been more cost-effectively disposed. A description of the major properties of each of the selected categories, including primary physical/chemical factors, determining compatibility characteristics, potential reactions and harmful by-products, and/or primary constituents affecting disposal costs, is provided.

In addition, techniques for compatibility testing for wastes which cannot otherwise be categorized are described. These techniques consist of empirical testing for binary mixtures of wastes to identify undesirable reactions upon mixing.

The methods herein described are applicable for discrete quantities of hazardous materials in drums, tanks and piles, and are particularly useful for drum staging operations or waste consolidation prior to removal and disposal. Field and on-site laboratory procedures are jointly described although many of the indicated field techniques are equally applicable for on-site laboratory use.

3.0 GLOSSARY

Bulking or Composting - The process of combining compatible hazardous wastes into a single vessel to achieve safety, convenience and cost-savings for transport and disposal.

Characterization - Classification of hazardous substances according to either reactions upon mixing or to required special methods of disposal.

Compatibility - The ability to mix hazardous materials without generating more hazardous conditions or increased difficulties and cost of disposal.

Consolidation Protocol - A step-by-step procedure by which wastes can be screened and placed in proper disposal categories.

Disposal Categories - Specific groupings of waste whose physical or chemical characteristics render them incompatible for mixing.

Screening - Rapid characterization, short of extensive chemical analysis, of hazardous materials to provide information for safe and cost-effective handling and disposal.

Electromotive Force (EMF) - The greatest potential difference that can be generated by a particular source of electric current.

4.0 RESPONSIBILITIES

Site Manager - In coordination with appropriate state and Federal agencies, is responsible for determining the necessity and scope of compatibility testing.

Field Operations Leader - Will insure that work is performed in accordance with Field Sampling and Analysis Plan (FSAP) and contract documents (if contractor personnel are used), and will provide overall supervision of on-site personnel.

Health and Safety Officer - Responsible for insuring compliance with the provision of the site Health and Safety Plan (HASP), including the wearing of appropriate personnel and respiratory protection equipment, establishment of safe working procedures, decontamination procedures, etc. The HSO has the authority to stop work work at the onset of dangerous working conditions.

Field Technicians - Unless contractor personnel are hired to conduct site sampling, sampling personnel will be responsible for assisting in sample collection, maintaining Chain-of-Custody records and other documentation, packaging and shipping samples and field screening and safety checks.

The field technicians may conduct compatibility testing under the direction of a site chemist or equivalent. The site chemist will direct the compatibility testing program and will retain responsibility for overall categorization.

Steps subsequent to compatibility testing, including drum handling, overpacking, consolidation of wastes, etc., are normally carried out by trained contractor personnel under the overall direction of the Field Operations Leader.

5.0 PROCEDURES

Waste sampling and subsequent compatibility testing are carried out to separate wastes into suitable categories for ultimate disposal. Although much of the information needed for categorization can be obtained from chemical analysis, such analyses are costly and time-consuming. Consequently, field personnel need a mechanism for rapid categorization of wastes to allow for rapid and cost-effective response and to provide useful information for subsequent RI/FS and contract document (e.g., drum removal) preparation.

Since categorization-related testing is usually done when little site-specific information is available, special care must be taken to protect the safety and health of on-site personnel. Several initial screening steps are necessary to minimize potential hazards, including screening for radioactivity, visual evidence of pressure buildup (bulging) or leakage in drums and the presence of wastes requiring special handling such as gas cylinders, explosive or shock-sensitive material or air reactive wastes.

Placement of wastes into suitable disposal categories will help to avoid chemical reactions and by-products which pose a threat to on-site personnel. Where wastes do not fall into specific categories defined within this guideline, compatibility testing for binary mixtures (i.e., empirical testing and observation of specific waste mixtures) is recommended to insure that no harmful reactions will occur.

The conditions which can result from the mixing of incompatible wastes include the following:

- Heat generation
- Fire
- Toxic gas and/or pressure generation
- Formation of shock-sensitive compounds
- Explosion
- Violent polymerization
- Solubilization of toxic substances
- Dispersal of toxic dusts, mists and particulates
- Formation of substances of greater toxicity

A comprehensive listing of incompatible chemical types and dangerous reactions resulting from mixture of incompatible chemicals is provided in Reference 1.

The scope of the on-site sampling and compatibility testing program will depend on the number of wastes on the site, the number of empty or partially full drums, the volume, marking and physical state of the containers and the eventual application of the test data relative to site clean-up. The sampling program should be designed to promote site clean-up without duplication of sampling which is often required before transport and disposal of wastes from the site.

5.1 WASTE CONSOLIDATION PROTOCOL

The primary physical and chemical characteristics which dictate mixing or disposal compatibility include water content, acidity, water solubility, reactivity, cyanide and sulfide content, halogenated organic content, combustibility, explosivity, oxidation-reduction potential and PCB content. Using this list of characteristics and the associated tests, waste materials can be placed into the following categories of incompatible wastes requiring special separate handling and treatment:

- Combustible and flammable materials
- Explosives
- Strong oxidizing agents
- Strong reducing agents
- Aqueous bases
- Aqueous acids
- Sulfide waste
- Cyanide waste
- Water-reactive materials
- High PCB content wastes
- High halogen content wastes
- Pathogenic and infectious wastes

Pathogenic and infectious wastes and strong reducing agents (because of slow oxidation by oxygen in the air) do not normally generate significant problems at hazardous wastes sites.

Mixing of materials from these basic disposal categories can result in the harmful reactions and by-products previously cited, or may result in contamination and require higher disposal costs for relatively uncontaminated materials. The latter situation would occur if wastes with high concentrations of PCBs were mixed with other wastes. With sufficiently high PCB concentrations, all of the mixed waste (rather than just the originally contaminated material) would have to go to expensive incineration disposal. Consequently, analyses should be conducted on wastes before compositing to determine and isolate the high PCB content materials.

Simple characterization methods are described herein for each of the waste disposal categories except for PCB determination, which requires sophisticated laboratory analysis. The halogen content screening procedure is designed to determine only gross halogen content (+/-1-2 percent). Tests for water content, solubility and reactivity are helpful in identifying organic, inorganic and water-soluble waste. An overall process diagram showing the sequence of tests necessary for waste categorization is given in Attachment A.

Subsequent to identification of incompatible waste and placement into waste disposal categories, wastes not otherwise categorized should be tested for compatibility. This can be done by visually observing reactions and taking temperature measurements in binary mixtures of materials. These will determine which materials can be composited for subsequent analysis and disposal.

5.2 FIELD APPLICABLE COMPATIBILITY TESTING METHODS

5.2.1 Water Miscibility

Equipment

- 13 x 42 mm culture tube or 23 x 85 clear glass vials with screw caps.
- Disposable glass transfer pipets.

Method

1. Place approximately 2 ml of distilled water in culture tube or vial, followed by addition of approximately 2 ml of sample.
2. Mix the sample and water for 1 minute.
3. Observe the number of phases present in the culture tube (vial) and whether the sample phase is heavier or lighter than water.
4. If only one phase is present, record the sample as water miscible in the notebook.
5. If there is more than one phase present, note whether the water phase is on the top or bottom. The following table shows the conclusion that may be drawn as to sample type.

Separation	Miscibility	Sample Type
Two phases, water on bottom	Immiscible	Light hydrocarbon
Two phases, water on top	Immiscible	Heavy hydrocarbon, probably chlorinated
Three phases, water in middle	Immiscible	Mixture of halogenated and nonhalogenated organic compounds

5.2.2 Flammability and Explosivity via Field Applicable WRA Ignition Test

Equipment

- Porcelain crucible or aluminum weighing dish
- Flame source

Method

1. Place 0.1 grams of waste in a porcelain crucible cover or aluminum weighing dish and carefully bring to the edge of a flame to determine flammability.
2. Heat gently over a low flame and finally ignite strongly. Note (a) the flammability and nature of the flame; (b) if the compound is a solid, whether the compound melted, and the manner of its melting; (c) the odor of gases or vapors evolved (caution); and (d) the residue left after ignition.
3. Carefully insert a piece of wide-range pH paper into the vapors. An intense acid reaction indicates the presence of halides. Note if the sample chars.

Violent ignition or slow burning with copious generation of fumes may be considered indicative of explosive materials.

5.2.3 Oxidation-Reduction Reactions

Equipment

- Disposable beakers
- 150 ml glass beakers
- 50 or 100 ml graduated cylinders
- Disposable glass Pasteur transfer pipets.
- Platinum Redox electrode electrode (Orion Models 96-78 or 97-78 or equivalent).
- Digital pH/mV meter (Orion Model 701A or equivalent)
- Parafilm
- Electrode filling solution

Reagents

- Test Solution A - prepare by dissolving 0.329 grams of ferrous ammonium sulfate in 500 ml deionized water. Add 2.8 ml concentrated (36N) sulfuric acid and dilute to 1,000 ml with deionized water.
- Test Solution B - prepare by dissolving 0.194 grams of potassium chromate, previously dried at 120°C for 2 hours, in 500 ml deionized water. Add 2.8 ml concentrated (36N) sulfuric acid and dilute to 1,000 ml with deionized water.
  - The electromotive force (EMF) values for the test solutions should be similar to those shown below. These values should be checked periodically during sample analysis.

Test Solution	Standard EMF
A	380* 340**
B	640* 600**

* Versus Silver-silver Chloride Reference Electrode

** Versus Calomel Reference Electrode

Method

A. Oxidation Reactions

1. Mark sample number near top of empty 150 ml beaker with permanent marker.
2. Record sample number in notebook.
3. Transfer approximately 50 ml of sample into beaker.
4. Add 40 ml of Test Solution A.
5. Seal the beaker with parafilm.
6. Shake vigorously for 15 seconds.
7. Let stand for 5 minutes.
8. Use a Pasteur transfer pipet to transfer the aqueous phase to a disposable beaker.
9. Place the electrode in the aqueous solution and turn the function switch on the meter to the millivolt mode.
10. Record the millivolt reading in notebook.

B. Reduction Reactions

1. Follow the same procedure outlined above in Section A, Oxidation Reactions, EXCEPT use test Solution B in Step 4.

Alternate methods for identification of oxidizing agents have also been developed.

Inorganic Oxidizer Determination

Equipment

- 13 x 42 mm culture tubes

Reagents

- A saturated solution of $MnCl_2\ 4H_2O$ in concentrated hydrochloric acid.

Method

1. Place 50-100 mg of solid sample or 1-2 drops of unknown liquid in culture tubes.
2. Add concentrated HCl until any effervescence stops.
3. Add 2 ml of saturated $MnCl_2\ 4H_2O$ solution.
4. Formation of a black or brown precipitate indicates the presence of an oxidizing agent (oxidation may be promoted by heating the sample).

For strong inorganic oxidizers, the methods can be modified as follows:

1. Place 50-100 mg of sample in test tube followed by 1 ml of concentrated sulfuric acid.
2. Production of a greenish-yellow chlorine dioxide gas, white fumes, or a violent reaction is indicative of strong oxidizing agents.

5.2.4 pH Determination

Equipment

- Broad and narrow-range pH paper
- 50 ml glass beakers
- Disposable glass transfer pipets

Method 1

1. Transfer enough sample to wide-range pH paper with transfer pipet to wet a significant fraction of the pH paper.
2. Compare the reaction color with the fixed indicator colors shown on container to estimate the pH of the sample and record estimated pH in field notebook. If a better estimate of pH is desired, repeat with narrow-range pH paper covering the approximate pH indicated on the wide-range paper.

Method 2

1. Measure pH using a pH electrode.

5.2.5 Sulfide

Note: Only samples with initial pH 7 or higher should be tested for sulfide.

Equipment

- 32 ml Wheaton vials with plastic caps
- Lead acetate test paper
- Disposable pasteur glass transfer pipets
- Dropping bottle of concentrated hydrochloric acid (HCl)

Method 1

1. Transfer a drop of sample to test paper with transfer pipet.
2. Record in notebook:

   Negative Sulfide - if no stain appears.
   Positive Sulfide - if brown or black stain appears.
   Uncertain Sulfide - if stain of other color appears. Describe stain.

   Note that sample was not pH adjusted.

3. If sample gave negative result, use Method 2 on another portion of the sample.

Method 2

1. Transfer approximately 5 ml sample into vial using transfer pipet.
2. Adjust pH of sample to 7 with concentrated HCl, then add 0.5 ml more HCl. Swirl solution to mix while adjusting pH and swirl again after final acid addition.
3. Quickly fold acetate paper strip over edge of vial and cap the vial. Swirl to wet paper.
4. Look for brown to black coloration on the test paper immediately and again after 15-30 minutes.
5. Record in notebook:

   Negative Sulfide - if no stain appears.
   Positive Sulfide - if brown or black stain appears.
   Uncertain Sulfide - if stain of other color appears. Describe stain.

5.2.6 Cyanide Determinations

Note: Only samples with initial pH 7 or higher should be tested for cyanide.

Equipment

- 32 ml Wheaton vials with plastic caps
- Cyantesmo Test Paper (Macherey-Nagel)
- Dropping bottle of concentrated sulfuric acid (H_2SO_4)
- Dropping bottle of concentrated hydrochloric acid (HCl)
- Hydrogen cyanide low range detector tubes and sampling pump

Method Using Cyanide Test Paper

1. Transfer approximately 5 ml sample into vial with pipet.
2. Add 2 drops of concentrated H_2SO_4.
3. Fold test paper strip over edge of vial so it is held in place by vial cap and extends into sample. Do this quickly so that any gas evolving is tested.
4. Cap vial and swirl to mix.
5. Look for blue stain immediately or after 15 minutes.
6. If no stain is visible after 15 minutes, check pH of sample in vial with pH paper. If pH is 6 or higher, add H_2SO_4 dropwise to bring pH between 4-6.
7. Insert new strip of test paper, following Steps 5-7 of this procedure.

8. Record in notebook:

   Negative Cyanide - if no stain appears in Step 5 or 7.
   Positive Cyanide - if blue stain appears in Step 5 or 7.
   Uncertain Cyanide - if stain of other color appears, describe stain.

9. Test positive and uncertain cyanide samples with detector tubes (see below).

Method Using Hydrogen Cyanide (HCN) Detector Tubes

1. Place new detector tube in sampling pump following manufacturer's instructions.
2. Transfer approximately 5 ml sample into vial with pipet.
3. Add HCl dropwise, with swirling between each addition, to bring pH to 5 or lower.
4. Place detector kit over acidified vial and take one stroke on the pump.
5. Record in notebook:

   Negative Cyanide - if no reading on scale.
   Positive Cyanide - if scale shows reading, include numerical reading.

Note: Ammonia, chlorine, hydrogen sulfide and sulfur dioxide may interfere with detector tube reading if present at high enough concentrations. To remove sulfide, pretreat samples with a few drops of cadmium nitrate solution prior to analysis. Repeat lead acetate paper test to insure that sulfide has been completely removed.

5.2.7 Chlorine (Halogens)

This test (called the Beilstein test) is an extremely rapid and sensitive test for the presence of halogens. However, some nonhalogenated organic compounds may yield a false positive test. Highly volatile, liquid halogenated compounds may evaporate completely before the test results are evident, thereby yielding a false negative result. In any case, the test should be repeated, and, if halogens are indicated or suspected, a confirmatory test, such as the WRA ignition test should be performed.

Equipment

- Fashion a loop 3 to 5 mm in diameter at the end of a 10- to 15-cm length of thin, uninsulated copper wire.

Method

1. Heat the wire to red heat in a Bunsen or Fisher burner flame until the flame is colorless. Allow the loop to cool without touching anything.
2. Dip the loop into the sample and immediately introduce the loop into the edge of the flame. A green color in the flame indicates the presence of halogens. Repeat the test at least once.

5.2.8 Field Compatibility Testing (Uncharacterized Wastes)

Equipment

- Heavy-walled test tubes calibrated at 10 and 20 ml
- Safety shields, face masks
- Liquid thermometer or digital thermometer with thermocouple
- Disposal pipets

Method

1. Place a 10 ml (10 gram if sample is solid) aliquot of the first test compound into a test tube held at an angle away from sampler.

2. Slowly add a 10 ml (10 g) aliquot of the second test compound to the test tube. The liquid should be trickled down the inside of the test tube and the addition stopped if an immediate reaction occurs.

3. Shake the test tube gently to mix the two chemicals.,

4. Observe and record any violent reaction such as sputtering, evolution of gases, or rapid change of temperature. If there is no reaction after 20 minutes, more comprehe testing should be performed at the discretion of the Field Operation Leader or site chemist.

Note that the two chemicals are considered hazardous and incompatible if there is any violent reaction in Step 4.

5.3 LABORATORY METHODS FOR COMPATIBILITY TESTING

Many of the methods previously cited for field use are equally applicable for use in the laboratory. However, some waste characterization methods require extensive equipment which is not normally available in the field or call for specialized analytical procedures. These methods have been designated as laboratory compatibility test methods and are described below. Most of these techniques can be performed in a well-equipped field (mobile) laboratory.

5.3.1 Specific Gravity

Equipment

- Disposable plastic beakers (50-250 ml)
- Top loading balance, accuracy to ± 0.01 grams

Method

1. Weigh a disposable plastic beaker or other disposable container to the nearest 0.01 gram on a top-loading balance.

2. Pour a carefully measured volume of sample into the tared container and weigh to nearest 0.01 gram.

3 Calculate the density of the sample in g/ml from the following equation.

$$D_s = \frac{\text{(net weight of sample in grams)}}{\text{(volume of sample in ml)}}$$

Specific Gravity = D_s/D_w (at ambient conditions)

where D_w is the density of water at the ambient temperature.

4. Report specific gravity to the nearest three significant figures if greater than 1.0 and to the nearest two figures if less than 1.0; for example, 1.02 or 0.95.

As a general rule, water-soluble organics have a specific gravity of less than 1.0, and water-soluble inorganics have a specific gravity greater than 1.0. Nonhalogenated organics have a specific gravity less than 1.0 and halogenated organics are greater than 1.0.

5.3.2 Flammability

Equipment

- 32 ml Wheaton vials
- Aluminum heat block with holes drilled to accept Wheaton vials and a dial thermometer
- Hot plate capable of maintaining temperature of heat block at 60°C
- Disposable glass transfer pipets
- Small propane torch used for soldering, etc.
- Dial thermometer with appropriate range

Method

1. Transfer approximately 5 ml of sample into vial with transfer pipet, and mark sample number on the top of the vial.
2. Insert vial into heat block so that sample number is visible.
3. Equilibrate 5 - 10 minutes.
4. Pass propane torch across top of vial 3 - 4 times.
5. Record in notebook if sample ignites (flames) or pops.

   Designate samples as follows:

   Flammable - sample pops and/or flames briefly or sustains flame.
   Non-Flammable - sample does not pop or flame.
   Explosive - sample undergoes violent ignition or burns slowly but with generation of large amounts of fumes.

5.3.3 Reactivity

Equipment

- 50 ml glass beakers
- 10 and 25 ml graduated cylinders
- Disposable glass Pasteur transfer pipets
- Distilled water at approximate temperature of samples.
- Foam plastic shaped to fit beakers. A thermocouple inserted in the bottom of the plastic holder is connected to a Digimite digital readout thermometer. Four beaker connected, two more can be accommodated.

Method

1. Transfer approximately 5 ml of sample into beaker with disposable pipet.
2. Insert beaker into holder and let equilibrate under a hood until temperature readout is stable.
3. Record temperature in notebook.
4. From a graduated cylinder, carefully pour approximately 5 ml distilled water down the side of the sample-containing beaker so it contacts the sample slowly. Have the hood door closed as much as possible for safety.
5. Observe and record any visible reaction such as:
   - Fuming or bubbling
   - Color change
   - Evolution of gas

   Record the temperature after 2 minutes or as soon as stable. Also note the relati.. solubility of the material as this may aid in further characterization.
6. If temperature has changed more than 2°C or any of Step 5 indications have occurred, classify sample as "Water Reactive" in notebook.
7. Place red sticker on reactive sample container and move it to reactive grouping.

5.3.4 Analysis of PCB Content

PCB analysis is performed using a gas chromatograph suitable for on-column injection and an electron capture or halogen-specific detector. The analytical methods are described in guideline LS-5, Gas Chromatographic Protocols for Screening of Organic Compounds.

5.3.5 Laboratory Analysis for Cyanide in Liquid Waste

Equipment

- Porcelain spot plate with 6-12 cavities
- Dropping pipets
- Glass stirring rods
- Chloramine-T solution (1.0 gram white Chloramine-T powder in 100 ml distilled water)
- Pyridine-barbituric acid reagent. To make, measure 15 grams barbituric acid, wet with H_2O, add 75 ml pyridine and mix. Add 15 ml conc. HCl, mix and cool.
- Hydrochloric acid - ~~add 10 ml~~ conc. HCl to 90 ml distilled water
- Anhydrous Sodium Carbonate (Na_2CO_3)
- Phenolphthalein indicator solution

Method

1. Dilute 1 ml of the sample solution to 10 ml with distilled water. Add approximately 100 mg Na_2CO_3 to the solution and swirl to dissolve.
2. Add one drop of phenolphthalein indicator then add 1:9 diluted HCl dropwise with constant swirling until the solution becomes colorless.
3. Place three drops of the sample and three drops of distilled water in separate cavities of a white spot plate.
4. To each cavity add one drop of Chloramine-T solution and ~~mix with a clean~~ stirring rod.
5. Add one drop of pyridine-barbituric acid solution to each cavity and again mix.
6. After one minute, the sample spot will turn pink to red if 0.5 mg/l or more of cyanides are present. The blank spot should be faint yellow.

5.3.6 Test for Organic Halogen in Liquid Wastes

Equipment

- 125 ml separatory funnels
- Assorted pipets and burets
- Electronic voltmeter and modified pH meter
- Glass and silver-silver chloride electrodes
- Sodium biphenyl reagent
- Reagent grade toluene
- 0.01N silver nitrate solution
- 0.01N sodium chloride solution

Method

1. Add 50 ml of toluene to a 125 ml separatory funnel.
2. Add 1-5 ml of sample (depending on estimated halogen content) to the toluene.
3. Extract twice with 20 ml of 3N HNO_3.
4. Transfer 5 ml of toluene solution (if halogen < 1 percent) or less (if halogen > 1 percent) to another 125 ml separatory funnel.
5. Add sodium biphenyl reagent in 10 ml increments and mix until a dark blue/green color remains.
6. Add 20 ml distilled water and mix until green color disappears (funnel should be mixed without capping because of potential exothermic reaction).
7. Drain aqueous layer and save.
8. Add 20 ml of 3N nitric acid and shake for 30 seconds. Repeat extraction and combine with previously drained aqueous layer.
9. Add 2 ml conc. HNO_3 to extracts.
10. Titrate with silver nitrate in increments, monitoring with pH meter (pH reading or mV can be used). The end point of the titration is the point of greatest change in instrument reading per unit volume of $AgNO_3$ addition.
11. Calculate the organic halogen content.

$$\frac{(V_T \times N_T \times \text{Eq. Wgt})}{V_s} \times \frac{(V_{TOL} + V_s)}{V_{TA}} = \text{concentration of halide as chloride (grams/liter)}$$

V_T = Volume 0.01 N $AgNO_3$ titrant (mls)
N_T = Normality of $AgNO_3$ titant
Eq. Wgt = 35.45 for Cl
V_{TOL} = Volume of toluene (Step 1) (mls)
V_S = Volume of waste sample (Step 2) (mls)
V_{TA} = Volume of toluene aliquot reduced (Step 4) (mls)

6.0 REFERENCES

H. K. Hatayama, J. J. Chen, E. R. deVera, R. D. Stevens and D. L. Storm, 1980. A Method for Determining the Compatibiity of Hazardous Wastes. EPA 600/2-80-076, ORD, USEPA Cincinnati, Ohio.

USEPA, 1984. Draft Guidance Document for Surface Tank and Drum Sites. USEPA Contract No. 68-01-6939.

Hina, E., A. B. Garlauskas and T. D. Cantor, 1983. Techniques for Identification and Neutralization of Unknown Hazardous Materials. Proc. 4th National Conference on Management of Uncontrolled Hazardous Waste Sites, Washington, DC, October 31 - November 2, 1983. HMCRI, Silver Springs, Maryland.

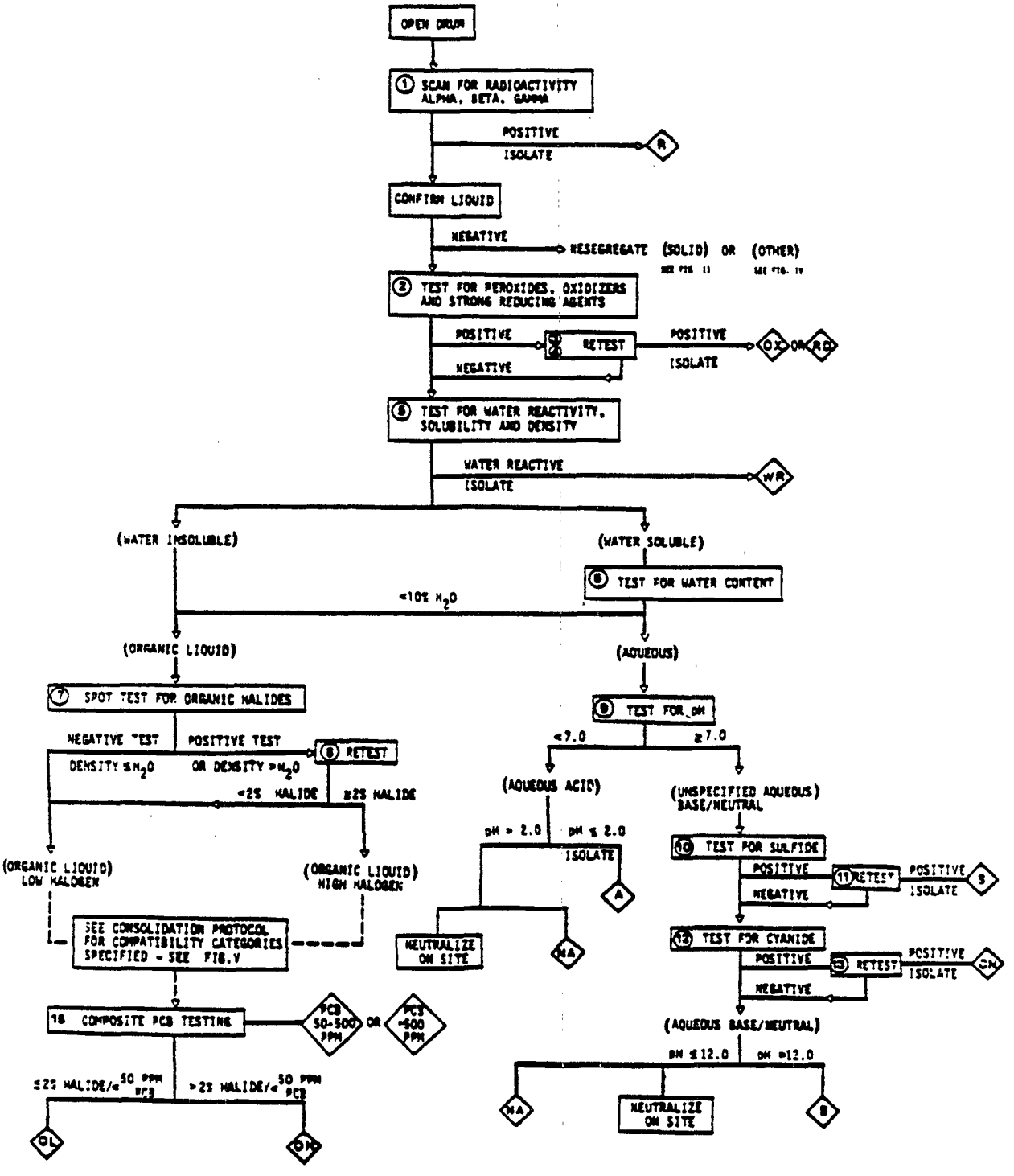
Chemical Manufacturers Association, 1982. A Hazardous Waste Site Management Plan.

Ebasco Services Incorporated; REM III Field Technical Guideline No. FT-7.13; April 9, 1986.

7.0 RECORDS

Attachment A - Waste Characterization Protocol

ATTACHMENT A
WASTE CHARACTERIZATION PROTOCOL



AR300623

NUS CORPORATION

ENVIRONMENTAL MANAGEMENT GROUP

STANDARD OPERATING PROCEDURES

Number	Page
SF-2.3	1 of 4
Effective Date: 05/04/90	Revision: 1
Applicability: EMG	
Prepared: Earth Sciences	
Approved: D. Senovich	

Subject: DECONTAMINATION OF CHEMICAL SAMPLING AND FIELD ANALYTICAL EQUIPMENT

TABLE OF CONTENTS

1.0 PURPOSE

The purpose of these procedures is to provide a general methodology, protocol, and reference information on the proper decontamination procedures to be used on chemical sampling and field analytical equipment.

2.0 SCOPE

This procedure addresses chemical sampling and field analytical equipment only, and should be consulted when equipment decontamination procedures are being developed as part of project-specific plans.

3.0 GLOSSARY

None.

4.0 RESPONSIBILITIES

Site Manager - responsible for ensuring that project-specific plans and the implementation of field investigations are in compliance with these guidelines.

Field Operations Leader - responsible for ensuring that decontamination procedures for all chemical sampling and field analytical equipment are programmed prior to the actual field effort and that personnel required to accomplish the task have been briefed and trained to execute the task.

5.0 PROCEDURES

In order to assure that chemical analysis results are reflective of the actual concentrations present at sampling locations, chemical sampling and field analysis equipment must be properly decontaminated prior to the field effort, during the sampling program (i.e., between sample points) and at the conclusion of the sampling program. This will minimize the potential for cross-contamination between sample points and the transfer of contamination offsite.

This procedure incorporates only those aspects of decontamination not addressed in other procedures. Specifically it incorporates those items involved in decontamination of chemical sampling and field analytical equipment.

5.1 ACCESS FOR SAMPLING

5.1.1 Bailers and Bailing Line

The potential for cross-contamination between sampling points via the use of common bailer, or its attached line, is high unless strict procedures for decontamination are followed. It is preferable, for the aforementioned reason, to dedicate an individual bailer and its line to each sample point, although this does not eliminate the need for decontamination of dedicated bailers. For non-dedicated sampling equipment, the following conditions and/or decontamination procedures should be followed.

Before the initial sampling and after each succeeding sampling point, the bailer must be decontaminated. The following steps should be followed if sampling for organic contaminants:

- Potable water rinse
- Alconox or Liquinox detergent wash
- Scrubbing of the line and bailer with a scrub brush may be required if the sample point if heavily contaminated with heavy or extremely viscous compounds
- Potable water rinse
- Rinse with 10 percent nitric acid solution*
- Deionized water rinse
- Acetone or methanol rinse
- Hexane rinse**
- Distilled/Deionized water rinse
- Air dry

If sampling for organics only, the nitric acid, acetone, methanol, and hexane rinses may be omitted. Contract-specific requirements may permit alternative procedures.

Braided nylon or polypropylene lines may be used with a bailer, however, the same line must not come in contact with the sample medium, otherwise, the line must be discarded in an approved receptacle and replaced. Prior to use, the bailer should be wrapped in aluminum foil or polyethylene sheeting.

5.1.2 Sampling Pumps

Most sampling pumps are normally low volume (less than 2 gpm) pumps. These include peristaltic, diaphragm, air-lift, pitcher and bladder pumps, to name a few. If these pumps are used for sampling from more than one sampling point, they must be decontaminated.

The procedures to be used for decontamination of sampling pumps compare to those used for a bailer except the 10 percent nitric acid solution is omitted. Each of the liquid factions is to be pumped through the system. The amount of pumping is dependent upon the size of the pump and the length of the intake and discharge hoses. Certain types of pumps are unacceptable for sampling purposes.

An additional problem is introduced when the pump relies on absorption of water via an inlet or outlet hose. For organic sampling, this hose should be Teflon. Other types of hoses leach organics into the water being sampled (especially the phthalate esters) or adsorb organics from the sampled water. For all other sampling, the hose should be Viton, polyethylene, or polyvinyl chloride (in order of preference). Whenever possible, dedicated hoses should be used.

---

* Due to the leaching ability of nitric acid, on stainless steel, this step is to be omitted if a stainless steel sampling device is being used and metals analysis is required with detection limits less than approximately 50 ppb; or the sampling equipment is dedicated.

** If sampling for pesticides, PCBs, or fuels.

5.1.3 Filtering Equipment

Part of the sampling plan may incorporate the filtering of groundwater samples, and subsequent preservation. This should occur as soon after sample retrieval as possible; preferably in the field as soon as the sample is obtained. To this end, three basic filtration systems are most commonly used - the in-line disposable Teflon filter, the inert gas over-pressure filtration system, and the vacuum filtration system.

For the in-line filter, decontamination is not required since the filter cartridge is disposable, however, the cartridge must be disposed of in an approved receptacle and the intake and discharge lines must still be decontaminated.

For the over-pressure and the vacuum filtration systems, the portions of the apparatus which come in contact with the sample must be decontaminated as outlined in the paragraphs describing the decontamination of bailers. (Note: Varieties of both of these systems come equipped from the manufacturer with Teflon-lined surfaces for those that would come into contact with the sample. These filtration systems are preferred when decontamination procedures must be employed.)

5.2 FIELD ANALYTICAL EQUIPMENT

5.2.1 Water Level Indicators

Water level indicators that come into contact with groundwater must be decontaminated using the following steps:

- Rinse with potable water
- Rinse with deionized water
- Acetone or methanol rinse
- Rinse with deionized water

Water level indicators that do not come in contact with the groundwater but may encounter incidental contact during installation or retrieval need only undergo the first and last steps stated above.

5.2.2 Probes

Probes, e.g., pH or specific ion electrodes, geophysical probes, or thermometers which would come in direct contact with the sample, will be decontaminated using the procedures specified above unless manufacturer's instructions indicate otherwise; in those cases, the methods of decontamination must be clearly described in the FSAP. Probes that contact a volume of groundwater not used for laboratory analyses can be rinsed with deionized water. For probes which make no direct contact, e.g., OVA equipment, the probe will be wiped with clean paper-towels or cloth wetted with alcohol.

6.0 REFERENCES

None.

7.0 RECORDS

None.

APPENDIX C

SAS REQUEST FORMS

AIW FRANK #1

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General Descrition of analytical services requested:

   Analysis of 34 groundwater samples for TCL Volatiles by the "Draft Low Concentration Water for Organic Compounds" CLP SOW. Only TCL Volatile compounds are requested. May include the analysis of 1 PEM/SDG as stated in the SOW.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   34 low/medium concentration groundwater samples from onsite monitoring wells, offsite monitoring wells, and residential wells (first round) plus 4 rinsate blanks and 8 trip blanks for a total of 46 units for TCL Volatiles by the "Draft Low Concentration Water for Organic Compounds" CLP SOW.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

   RI/FS - ARCS III

   SAS Approved By (signature):
   Date:

AR300629

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of .

6. **Number of days analysis and data required after laboratory receipt of samples:**

35 days from receipt of last sample. Samples must be analyzed within 10 days of laboratory receipt of the sample.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

Analysis of TCL Volatile compounds by the "Draft Low Concentration Water for Organic Compounds" CLP SOW.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

May include the analysis of 1 PEM/SDG as described in the SOW. Region III will arrange for PE to be shipped to laboratory upon award.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

10. **Other (use additional sheets or attach supplementary information, as needed):**

Laboratory must comply with purge file requirements. Contact SMO for details.

Previous sampling of onsite wells has shown total VOA concentrations as high as 3.5 mg/l. Field crew will identify possible medium concentration samples.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation - (412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

14. **Action Required if Limits are Exceeded:**

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

15. **Request Prepared By:**

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991; revised September 5, 1991.

16. **Request Reviewed By (CRL use only):**
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

AIW Frank = #2

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General Descrition of analytical services requested:**

   Analysis of 11 groundwater samples for COD, Total Organic Carbon (TOC), BOD_5, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), alkalinity, nitrite and nitrate, ammonia, chloride and sulfate by the methods listed in Item 7.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   11 low/medium concentration groundwater samples from onsite and offsite monitoring wells for the above analysis. Previous sampling of onsite wells has shown total VOA concentrations as high as 3.5 mg/l. Field crew will try to identify any medium concentration samples.

3. **Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):**

   RI/FS - ARCS III

SAS Approved By (signature):
Date:

AR300632

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of .

6. **Number of days analysis and data required after laboratory receipt of samples:**

35 days from receipt of last sample. Samples must be analyzed within the holding times established in the Federal Register for each analyte.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

COD	- EPA 410.2	Alkalinity	- EPA 310.1
TOC	- EPA 415.1	NO_3 and NO_2	- EPA 353.3
BOD_5	- SM 5210B	Ammonia	- EPA 350.2
TSS	- EPA 160.2	Chloride	- EPA 325.2
TDS	- EPA 160.1	Sulfate	- EPA 375.4

All methods are attached.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

Raw data, calculations, data sheets, blank results, duplicate results, signed and dated copy of chain-of-custody documentation, copies of air bill confirming sample receipt, and SAS Request Form.

10. **Other (use additional sheets or attach supplementary information, as needed):**

Laboratory must comply with purge file requirements. Contact SMO for details.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation
(412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)
COD	5 mg/l	± 20%
TOC	1 mg/l	± 20%
BOD_5	1 mg/l	± 20%
TSS	4 mg/l	± 20%
TDS	10 mg/l	± 20%
Alkalinity	1 mg/l	± 20%
NO_3 and NO_2	0.01 mg/l	± 20%
Ammonia	0.1 mg/l	± 20%
Chloride	2 mg/l	± 20%
Sulfate	1 mg/l	± 20%

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
Blank (except BOD_5, Alkalinity, TDS, TSS)	1/batch	Below method detection limits
Duplicate	1/batch	± 20%

14. Action Required if Limits are Exceeded:

Reanalyze sample once more and report both sets of data..

15. Request Prepared By:

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991, revised September 6, 1991.

16. Request Reviewed By (CRL use only):
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

CHEMICAL OXYGEN DEMAND

Method 410.2 (Titrimetric, Low Level)

STORET NO. 00335

1. Scope and Application
   - 1.1 The scope of this modification of the Chemical Oxygen Demand (COD) test is the same as for the high level test. It is applicable to the analysis of surface waters, domestic and industrial wastes with low demand characteristics.
   - 1.2 This method (low level) is applicable for samples having a COD in the range of 5–50 mg/l COD.
2. Summary of Method
   - 2.1 Organic and oxidizable inorganic substances in an aqueous sample are oxidized by potassium dichromate solution in 50 percent (by volume) sulfuric acid in solution. The excess dichromate is titrated with standard ferrous ammonium sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.
3. Sampling and Preservation
   - 3.1 Collect the samples in glass bottles, if possible. Use of plastic containers is permissible if it is known that no organic contaminants are present in the containers.
   - 3.2 Biologically active samples should be tested as soon as possible. Samples containing settleable material should be well mixed, preferably homogenized, to permit removal of representative aliquots.
   - 3.3 Samples should be preserved with sulfuric acid to a pH < 2 and maintained at 4°C until analysis.
4. Interferences
   - 4.1 Traces of organic material either from the glassware or atmosphere may cause a gross, positive error.
     - 4.1.1 Extreme care should be exercised to avoid inclusion of organic materials in the distilled water used for reagent preparation or sample dilution.
     - 4.1.2 Glassware used in the test should be conditioned by running blank procedures to eliminate traces of organic material.
   - 4.2 Volatile materials may be lost when the sample temperature rises during the sulfuric acid addition step.
   - 4.3 Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion flask to complex the chlorides, thereby effectively eliminating the interference on all but brine and estuarine samples.
5. Apparatus
   - 5.1 Reflux apparatus: Glassware should consist of a 500 ml Erlenmeyer flask or a 300 ml round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser

Issued 1971
Editorial revision 1974 and 1978

by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6. Reagents

6.1 Distilled water: Special precautions should be taken to insure that distilled water used in this test be low in organic matter.

6.2 Standard potassium dichromate solution (0.025 N): Dissolve 12.259 g $K_2Cr_2O_7$, primary standard grade, previously dried at 103°C for two hours, in distilled water and dilute to 1000 ml. Mix this solution thoroughly then dilute 100.0 ml to 1000 ml with distilled water.

6.3 Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5g silver sulfate, Ag_2SO_4, per 4.09kg bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)

6.4 Standard ferrous ammonium sulfate (0.025 N): Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 ml of conc. H_2SO_4 (6.8), cool and dilute to 1 liter. Dilute 100 ml of this solution to 1 liter with distilled water. This solution must be standardized daily against $K_2Cr_2O_7$ solution.

6.4.1 Standardization: To approximately 200 ml of distilled water add 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2) solution. Add 20 ml of H_2SO_4 (6.8) and cool. Titrate with ferrous ammonium sulfate (6.4) using 3 drops of ferroin indicator (6.6). The color change is sharp, going from blue-green to reddish-brown.

$$\text{Normality} = \frac{(\text{ml } K_2Cr_2O_7)(0.025)}{\text{ml } Fe(NH_4)_2(SO_4)_2}$$

6.5 Mercuric sulfate : Powdered $HgSO_4$.

6.6 Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1–10 (ortho)phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 ml of water. This indicator may be purchased already prepared.

6.7 Silver sulfate : Powdered Ag_2SO_4.

6.8 Sulfuric acid (sp. gr. 1.84) : Concentrated H_2SO_4.

7. Procedure

7.1 Place several boiling stones in the reflux flask, followed by 50.0 ml of sample or an aliquot diluted to 50.0 ml and 1 g of $HgSO_4$ (6.5). Add 5.0 ml conc. H_2SO_4 (6.8); swirl until the mercuric sulfate has dissolved. Place reflux flask in an ice bath and slowly add, with swirling, 25.0 ml of 0.025 N $K_2Cr_2O_7$ (6.2). Now add 70 ml of sulfuric acid-silver sulfate solution (6.3) to the cooled reflux flask, again using slow addition with swirling motion.

Caution: Care must be taken to assure that the contents of the flask are well mixed. If not, superheating may result, and the mixture may be blown out of the open end of the condenser.

7.1.1 If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

7.2 Apply heat to the flask and reflux for 2 hours. For some waste waters, the 2-hour reflux period is not necessary. The time required to give the maximum oxidation for a wastewater of constant or known composition may be determined and a shorter period of refluxing may be permissible.

7.3 Allow the flask to cool and wash down the condenser with about 25 ml of distilled water. If a round bottom flask has been used, transfer the mixture to a 500 ml Erlenmeyer flask, washing out the reflux flask 3 or 4 times with distilled water. Dilute the acid solution to about 300 ml with distilled water and allow the solution to cool to about room temperature. Add 8 to 10 drops of ferroin indicator (6.6) to the solution and titrate the excess dichromate with 0.025 N ferrous ammonium sulfate (6.4) solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.

7.4 Blank—Simultaneously run a blank determination following the details given in (7.1) and (7.2), but using low COD water in place of sample.

8. Calculation

8.1 Calculate the COD in the sample in mg/l as follows:

$$\text{COD, mg/l} = \frac{(A - B)N \times 8{,}000}{S}$$

where:

A = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the blank,
B = milliliters of $Fe(NH_4)_2(SO_4)_2$ solution required for titration of the sample,
N = normality of the $Fe(NH_4)_2(SO_4)_2$ solution, and
S = milliliters of sample used for the test.

9. Precision and Accuracy

9.1 Eighty-six analysts in fifty-eight laboratories analyzed a distilled water solution containing oxidizable organic material equivalent to 12.3 mg/l COD. The standard deviation was ±4.15 mg/l COD with an accuracy as percent relative error (bias) of 0.3%. (EPA Method Research Study 3.)

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

Approved for NPDES
Issued 1971
Editorial revision 1974

4. Sample Handling and Preservation

4.1 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples.
NOTE 1: A brief study performed in the EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

4.2 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4°C) and protected from sunlight and atmospheric oxygen.

4.3 In instances where analysis cannot be performed within two hours (2 hours) from time of sampling, the sample is acidified ($pH \leq 2$) with HCl or H_2SO_4.

5. Interferences

5.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

5.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

6. Apparatus

6.1 Apparatus for blending or homogenizing samples: Generally, a Waring-type blender is satisfactory.

6.2 Apparatus for total and dissolved organic carbon:

6.2.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

6.2.2 No specific analyzer is recommended as superior.

7. Reagents

7.1 Distilled water used in preparation of standards and for dilution of samples should be ultra pure to reduce the carbon concentration of the blank. Carbon dioxide-free, double distilled water is recommended. Ion exchanged waters are not recommended because of the possibilities of contamination with organic materials from the resins.

7.2 Potassium hydrogen phthalate, stock solution, 1000 mg carbon/liter: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 ml.
NOTE 2: Sodium oxalate and acetic acid are not recommended as stock solutions.

7.3 Potassium hydrogen phthalate, standard solutions: Prepare standard solutions from the stock solution by dilution with distilled water.

7.4 Carbonate-bicarbonate, stock solution, 1000 mg carbon/liter: Weigh 0.3500 g of sodium bicarbonate and 0.4418 g of sodium carbonate and transfer both to the same 100 ml volumetric flask. Dissolve with distilled water.

7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

5. Bibliography

THERIAULT, E.J., P.D. MCNAMEE & C.T. BUTTERFIELD. 1931. Selection of dilution water for use in oxygen demand tests. *Pub. Health Rep.* 46:1084.

LEA, W.L. & M.S. NICHOLS. 1937. Influence of phosphorus and nitrogen on biochemical oxygen demand. *Sewage Works J.* 9:34.

RUCHHOFT, C.C. 1941. Report on the cooperative study of dilution waters made for the Standard Methods Committee of the Federation of Sewage Works Associations. *Sewage Works J.* 13:669.

MOHLMAN, F.W., E. HURWITZ, G.R. BARNETT & H.K. RAMER. 1950. Experience with modified methods for BOD. *Sewage Ind. Wastes* 22:31.

5210 B. 5-Day BOD Test

1. General Discussion

a. Principle: The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 d. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined immediately after the dilution is made, all oxygen uptake, including that occurring during the first 15 min, is included in the BOD measurement.

b. Sampling and storage: Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20°C before analysis.

1) Grab samples—If analysis is begun within 2 h of collection, cold storage is unnecessary. If analysis is not started within 2 h of sample collection, keep sample at or below 4°C from the time of collection. Begin analysis within 6 h of collection; when this is not possible because the sampling site is distant from the laboratory, store at or below 4°C and report length and temperature of storage with the results. In no case start analysis more than 24 h after grab sample collection. When samples are to be used for regulatory purposes make every effort to deliver samples for analysis within 6 h of collection.

2) Composite samples—Keep samples at or below 4°C during compositing. Limit compositing period to 24 h. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the results.

2. Apparatus

a. Incubation bottles, 250- to 300-mL capacity. Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a water-seal. Obtain satisfactory water seals by inverting bottles in a water bath or by adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over flared mouth of bottle to reduce evaporation of the water seal during incubation.

b. Air incubator or water bath, thermostatically controlled at 20 ± 1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

3. Reagents

a. Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g NH_4Cl in about

about 500 mL distillec
1 L. The pH should be
adjustment. Discard re
following reagents) if
biological growth in t.

b. Magnesium sulfa
22.5 g $MgSO_4 \cdot 7H_2O$ i
dilute to 1 L.

c. Calcium chloride
27.5 g $CaCl_2$ in distill
to 1 L.

d. Ferric chloride so
g $FeCl_3 \cdot 6H_2O$ in distil
to 1 L.

e. Acid and alkali so
tralization of caustic c
ples.

1) Acid—Slowly an
28 mL conc sulfuric ac
Dilute to 1 L.

2) Alkali—Dissolve
droxide in distilled wa

f. Sodium sulfite solu
g Na_2SO_3 in 1000 mL
solution is not stable;

g. Nitrification inh
(trichloro methyl) pyri

h. Glucose-glutamic
reagent-grade glucose
glutamic acid at 103°C
mg glucose and 150 m
distilled water and dilu
fresh immediately befo

i. Ammonium chlor
solve 1.15 g NH_4Cl in
tilled water, adjust pH
solution, and dilute to
tains 0.3 mg N/mL.

4. Procedure

a. Preparation of di
desired volume of wate
and add 1 mL each o
$MgSO_4$, $CaCl_2$, and Fe
water. Seed dilution w

*Nitrification Inhibitor 2579-
Co., or equivalent.

H. Report on the cooperative
waters made for the Stand-
mmittee of the Federation of
Associations. *Sewage Works*

., HURWITZ, G.R. BARNETT
. 1950. Experience with mod-
r BOD. *Sewage Ind. Wastes*

ample collection. When
used for regulatory pur-
effort to deliver samples
1 6 h of collection.
samples—Keep samples
compositing. Limit
24 h. Use the same
ge of grab samples, start-
ent of holding time from
ng period. State storage
ns as part of the results.

ottles, 250- to 300-mL ca-
es with a detergent, rinse
rain before use. As a pre-
awing air into the dilu-
incubation, use a water-
factory water seals by
a water bath or by add-
flared mouth of special
e a paper or plastic cup
ared mouth of bottle to
1 of the water seal during

r or water bath, thermo-
d at 20 ± 1°C. Exclude
t possibility of photosyn-
of DO.

uffer solution: Dissolve
g K_2HPO_4, 33.4 g
.7 g NH_4Cl in about

about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Discard reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

b. Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 L.

c. Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

d. Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 L.

e. Acid and alkali solutions, 1N, for neutralization of caustic or acidic waste samples.

1) Acid—Slowly and while stirring, add 28 mL conc sulfuric acid to distilled water. Dilute to 1 L.

2) Alkali—Dissolve 40 g sodium hydroxide in distilled water. Dilute to 1 L.

f. Sodium sulfite solution: Dissolve 1.575 g Na_2SO_3 in 1000 mL distilled water. This solution is not stable; prepare daily.

g. Nitrification inhibitor, 2-chloro-6-(trichloro methyl) pyridine.*

h. Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 h. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

i. Ammonium chloride solution: Dissolve 1.15 g NH_4Cl in about 500 mL distilled water, adjust pH to 7.2 with NaOH solution, and dilute to 1 L. Solution contains 0.3 mg N/mL.

4. Procedure

a. Preparation of dilution water: Place desired volume of water in a suitable bottle and add 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions/L of water. Seed dilution water, if desired, as described in ¶ 4*d*. Test and store dilution water as described in ¶s 4*b* and *c* so that water of assured quality always is on hand.

Before use bring dilution water temperature to 20°C. Saturate with DO by shaking in a partially filled bottle or by aerating with organic-free filtered air. Alternatively, store in cotton-plugged bottles long enough for water to become saturated with DO. Protect water quality by using clean glassware, tubing, and bottles.

b. Dilution water check: Use this procedure as a rough check on quality of dilution water.

If the oxygen depletion of a candidate water exceeds 0.2 mg/L obtain a satisfactory water by improving purification or from another source. Alternatively, if nitrification inhibition is used, store the dilution water, seeded as prescribed below, in a darkened room at room temperature until the oxygen uptake is sufficiently reduced to meet the dilution-water check criteria. Check quality of stored dilution water on use, but do not add seed to dilution water stored for quality improvement. Storage is not recommended when BODs are to be determined without nitrification inhibition because nitrifying organisms may develop during storage. Check stored dilution water to determine whether sufficient ammonia remains after storage. If not, add ammonium chloride solution to provide a total of 0.45 mg ammonia/L as nitrogen. If dilution water has not been stored for quality improvement, add sufficient seeding material to produce a DO uptake of 0.05 to 0.1 mg/L in 5 d at 20°C. Incubate a BOD bottle full of dilution water for 5 d at 20°C. Determine initial and final DO as in ¶s 4*g* and *j*. The DO uptake in 5 d at 20°C should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L.

c. Glucose-glutamic acid check: Because the BOD test is a bioassay its results can be influenced greatly by the presence of toxicants or by use of a poor seeding ma-

*Nitrification Inhibitor 2579-24 (2.2% TCMP), Hach Co., or equivalent.

terial. Distilled waters frequently are contaminated with copper; some sewage seeds are relatively inactive. Low results always are obtained with such seeds and waters. Periodically check dilution water quality, seed effectiveness, and analytical technique by making BOD measurements on pure organic compounds and samples with known additions. In general, for BOD determinations not requiring an adapted seed, use a mixture of 150 mg glucose/L and 150 mg glutamic acid/L as a "standard" check solution. Glucose has an exceptionally high and variable oxidation rate but when it is used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes. Alternatively, if a particular wastewater contains an identifiable major constituent that contributes to the BOD, use this compound in place of the glucose-glutamic acid.

Determine the 5-d 20°C BOD of a 2% dilution of the glucose-glutamic acid standard check solution using the techniques outlined in ¶s 4*d-j*. Evaluate data as described in ¶ 6, Precision and Bias.

d. Seeding:

1) Seed source—It is necessary to have present a population of microorganisms capable of oxidizing the biodegradable organic matter in the sample. Domestic wastewater, unchlorinated or otherwise-undisinfected effluents from biological waste treatment plants, and surface waters receiving wastewater discharges contain satisfactory microbial populations. Some samples do not contain a sufficient microbial population (for example, some untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values). For such wastes seed the dilution water by adding a population of microorganisms. The preferred seed is effluent from a biological treatment system processing the waste. Where this is not available, use supernatant from domestic wastewater after settling at room temperature for at least 1 h but no longer than 36 h. When effluent from a biological treatment process is used, inhibition of nitrification is recommended.

Some samples may contain materials not degraded at normal rates by the microorganisms in settled domestic wastewater. Seed such samples with an adapted microbial population obtained from the undisinfected effluent of a biological process treating the waste. In the absence of such a facility, obtain seed from the receiving water below (preferably 3 to 8 km) the point of discharge. When such seed sources also are not available, develop an adapted seed in the laboratory by continuously aerating a sample of settled domestic wastewater and adding small daily increments of waste. Optionally use a soil suspension or activated sludge, or a commercial seed preparation to obtain the initial microbial population. Determine the existence of a satisfactory population by testing the performance of the seed in BOD tests on the sample. BOD values that increase with time of adaptation to a steady high value indicate successful seed adaptation.

2) Seed control—Determine BOD of the seeding material as for any other sample. This is the *seed control.* From the value of the seed control and a knowledge of the seeding material dilution (in the dilution water) determine seed DO uptake. Ideally, make dilutions of seed such that the largest quantity results in at least 50% DO depletion. A plot of DO depletion, in milligrams per liter, versus milliliters seed should present a straight line for which the slope indicates DO depletion per milliliter of seed. The DO-axis intercept is oxygen depletion caused by the dilution water and should be less than 0.1 mg/L (¶ 4*h*). To determine a sample DO uptake subtract seed DO uptake from total DO uptake. The DO uptake of seeded dilution water should be between 0.6 and 1.0 mg/L.

Techniques for adding seeding material to dilution water are described for two sample dilution methods (¶ 4*f*).

e. Sample pretre

1) Samples cont
or acidity— Neutr
to 7.5 with a sol
(H_2SO_4) or sodium
such strength that
does not dilute the
0.5%. The pH of
should not be affect
dilution.

2) Samples cont
compounds—If p
containing residua
ahead of chlorinati
ple has been chlori
chlorine residual is
tion water. If resid
dechlorinate sampl
water (¶ 4*f*). Do r
chlorinated sample
lution water. In son
dissipate within 1 t
light. This often
transport and han
which chlorine res
in a reasonably sho
residual by adding
termine required v
tion on a 100- t
neutralized sample
+ 1 acetic acid or
potassium iodide (
mL), and titrating
the starch-iodine
Add to neutralized
ume of Na_2SO_3 sol
above test, mix, a
check sample for r
Excess Na_2SO_3 ex
and reacts slowly
chloramine compo
ent in chlorinated

3) Samples cont
stances—Certain i
ample, plating was
Such samples ofte
and treatment.

4) Samples sup

n effluent from a biological
ss is used, inhibition of ni-
commended.
s may contain materials not
rmal rates by the micro-
ttled domestic wastewater.
les with an adapted micro-
obtained from the undisin-
of a biological process
ste. In the absence of such
n seed from the receiving
referably 3 to 8 km) the
ge. When such seed sources
ilable, develop an adapted
ratory by continuously aer-
of settled domestic waste-
ng small daily increments
ally use a soil suspension
or a commercial seed
n the initial microbial
termine the existence of a
ulation by testing the per-
seed in BOD tests on the
values that increase with
ion to a steady high value
ful seed adaptation.
ol—Determine BOD of the
l as for any other sample.
control. From the value of
l and a knowledge of the
l dilution (in the dilution
e seed DO uptake. Ideally,
f seed such that the largest
in at least 50% DO de-
of DO depletion, in milli-
versus milliters seed should
ht line for which the slope
depletion per milliliter of
xis intercept is oxygen de-
by the dilution water and
han 0.1 mg/L (¶ 4*h*). To
mple DO uptake subtract
from total DO uptake. The
eded dilution water should
and 1.0 mg/L.
adding seeding material
described for two sam-
es (¶ 4*f*).

e. Sample pretreatment:

1) Samples containing caustic alkalinity or acidity— Neutralize samples to pH 6.5 to 7.5 with a solution of sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) of such strength that the quantity of reagent does not dilute the sample by more than 0.5%. The pH of seeded dilution water should not be affected by the lowest sample dilution.

2) Samples containing residual chlorine compounds—If possible, avoid samples containing residual chlorine by sampling ahead of chlorination processes. If the sample has been chlorinated but no detectable chlorine residual is present, seed the dilution water. If residual chlorine is present, dechlorinate sample and seed the dilution water (¶ 4*f*). Do not test chlorinated/dechlorinated samples without seeding the dilution water. In some samples chlorine will dissipate within 1 to 2 h of standing in the light. This often occurs during sample transport and handling. For samples in which chlorine residual does not dissipate in a reasonably short time, destroy chlorine residual by adding Na_2SO_3 solution. Determine required volume of Na_2SO_3 solution on a 100- to 1000-mL portion of neutralized sample by adding 10 mL of 1 + 1 acetic acid or 1 + 50 H_2SO_4, 10 mL potassium iodide (KI) solution (10 g/100 mL), and titrating with Na_2SO_3 solution to the starch-iodine end point for residual. Add to neutralized sample the relative volume of Na_2SO_3 solution determined by the above test, mix, and after 10 to 20 min check sample for residual chlorine. (NOTE: Excess Na_2SO_3 exerts an oxygen demand and reacts slowly with certain organic chloramine compounds that may be present in chlorinated samples).

3) Samples containing other toxic substances—Certain industrial wastes, for example, plating wastes, contain toxic metals. Such samples often require special study and treatment.

4) Samples supersaturated with DO—Samples containing more than 9 mg DO/L at 20°C may be encountered in cold waters or in water where photosynthesis occurs. To prevent loss of oxygen during incubation of such samples, reduce DO to saturation at 20°C by bringing sample to about 20°C in partially filled bottle while agitating by vigorous shaking or by aerating with clean, filtered compressed air.

5) Sample temperature adjustment—Bring samples to 20 ± 1°C before making dilutions.

6) Nitrification inhibition—If nitrification inhibition is desired add 3 mg 2-chloro-6-(trichloro methyl) pyridine (TCMP) to each 300-mL bottle before capping or add sufficient amounts to the dilution water to make a final concentration of 10 mg/L. (NOTE: Pure TCMP may dissolve slowly and can float on top of the sample. Some commercial formulations dissolve more readily but are not 100% TCMP; adjust dosage accordingly.) Samples that may require nitrification inhibition include, but are not limited to, biologically treated effluents, samples seeded with biologically treated effluents, and river waters. Note the use of nitrogen inhibition in reporting results.

f. Dilution technique: Dilutions that result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after 5 d incubation produce the most reliable results. Make several dilutions of prepared sample to obtain DO uptake in this range. Experience with a particular sample will permit use of a smaller number of dilutions. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilutions. In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

Prepare dilutions either in graduated cylinders and then transfer to BOD bottles or

prepare directly in BOD bottles. Either dilution method can be combined with any DO measurement technique. The number of bottles to be prepared for each dilution depends on the DO technique and the number of replicates desired.

When using graduated cylinders to prepare dilutions, and when seeding is necessary, add seed either directly to dilution water or to individual cylinders before dilution. Seeding of individual cylinders avoids a declining ratio of seed to sample as increasing dilutions are made. When dilutions are prepared directly in BOD bottles and when seeding is necessary, add seed directly to dilution water or directly to the BOD bottles.

1) Dilutions prepared in graduated cylinders—If the azide modification of the titrimetric iodometric method (Section 4500-O.C) is used, carefully siphon dilution water, seeded if necessary, into a 1- to 2-L-capacity graduated cylinder. Fill cylinder half full without entraining air. Add desired quantity of carefully mixed sample and dilute to appropriate level with dilution water. Mix well with a plunger-type mixing rod; avoid entraining air. Siphon mixed dilution into two BOD bottles. Determine initial DO on one of these bottles. Stopper the second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, siphon dilution mixture into one BOD bottle. Determine initial DO on this bottle and replace any displaced contents with sample dilution to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C.

2) Dilutions prepared directly in BOD bottles—Using a wide-tip volumetric pipet, add the desired sample volume to individual BOD bottles of known capacity. Add appropriate amounts of seed material to the individual BOD bottles or to the dilution water. Fill bottles with enough dilution water, seeded if necessary, so that insertion of stopper will displace all air, leaving no bubbles. For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle. When using titrimetric iodometric methods for DO measurement, prepare two bottles at each dilution. Determine initial DO on one bottle. Stopper second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, prepare only one BOD bottle for each dilution. Determine initial DO on this bottle and replace any displaced contents with dilution water to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C. Rinse DO electrode between determinations to prevent cross-contamination of samples.

g. Determination of initial DO: If the sample contains materials that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If rapid initial DO uptake is insignificant, the time period between preparing dilution and measuring initial DO is not critical.

Use the azide modification of the iodometric method (Section 4500-O.C) or the membrane electrode method (Section 4500-O.G) to determine initial DO on all sample dilutions, dilution water blanks, and where appropriate, seed controls.

h. Dilution water blank: Use a dilution water blank as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. Together with each batch of samples incubate a bottle of unseeded dilution water. Determine initial and final DO as in ¶s 4*g* and *j*. The DO uptake should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L.

i. Incubation: Incubate at 20°C ± 1°C BOD bottles containing desired dilutions, seed controls, dilution water blanks, and glucose-glutamic acid checks. Water-seal bottles as described in ¶ 4*f*.

j. Determination of final DO: After 5 d

incubation determir
tions, blanks, and c

5. Calculation

When dilution w

$$BOD_5, mg/$$

When dilution wate

$$BOD_5, mg/L = \frac{(D$$

where:

D_1 = DO of dilute preparation,
D_2 = DO of dilut bation at 20°
P = decimal volu used,
B_1 = DO of seed mg/L (¶ 4*d*)
B_2 = DO of seed mg/L (¶ 4*d*
f = ratio of seed in seed cont sample)/(%

If seed material is
ple or to seed contr

$$f = \text{(volume of s}$$
ume of seed

Report results as
is inhibited.

If more than one
the criteria of a res
mg/L and a DO
mg/L and there is
at higher sample cc
istence of an obviou
sults in the accepta

In these calculat
rections for DO u
water blank during
rection is unneces
meets the blank cr
If the dilution wat

utions greater than 1:100
dilution in a graduated
making final dilution in the
ng titrimetric iodometric
measurement, prepare two
dilution. Determine initial
le. Stopper second bottle
l, and incubate for 5 d at
brane electrode method is
asurement, prepare only
for each dilution. Deter-
on this bottle and replace
ntents with dilution water
topper tightly, water-seal,
5 d at 20°C. Rinse DO
n determinations to pre-
nination of samples.
on of initial DO: If the
erials that react rap-
nine initial DO im-
g BOD bottle with
f rapid initial DO uptake
he time period between
n and measuring initial
l.
modification of the iodo-
ection 4500-O.C) or the
de method (Section 4500-
e initial DO on all sample
water blanks, and where
controls.
er blank: Use a dilution
rough check on quality
on water and cleanliness
tles. Together with each
incubate a bottle of un-
water. Determine initial
in ¶s 4*g* and *j*. The DO
not be more than 0.2
ably not more than 0.1

ncubate at 20°C ± 1°C
aining desired dilutions,
ution water blanks, and
acid checks. Water-seal
in ¶ 4*f*.
final DO: After 5 d

incubation determine DO in sample dilutions, blanks, and checks as in ¶ 4*g*.

5. Calculation

When dilution water is not seeded:

$$BOD_5, mg/L = \frac{D_1 - D_2}{P}$$

When dilution water is seeded:

$$BOD_5, mg/L = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

where:

D_1 = DO of diluted sample immediately after preparation, mg/L,
D_2 = DO of diluted sample after 5 d incubation at 20°C, mg/L,
P = decimal volumetric fraction of sample used,
B_1 = DO of seed control before incubation, mg/L (¶ 4*d*),
B_2 = DO of seed control after incubation mg/L (¶ 4*d*), and
f = ratio of seed in diluted sample to seed in seed control = (% seed in diluted sample)/(% seed in seed control).

If seed material is added directly to sample or to seed control bottles:

f = (volume of seed in diluted sample)/(volume of seed in seed control)

Report results as $CBOD_5$ if nitrification is inhibited.

If more than one sample dilution meets the criteria of a residual DO of at least 1 mg/L and a DO depletion of at least 2 mg/L and there is no evidence of toxicity at higher sample concentrations or the existence of an obvious anomaly, average results in the acceptable range.

In these calculations, do not make corrections for DO uptake by the dilution water blank during incubation. This correction is unnecessary if dilution water meets the blank criteria stipulated above. If the dilution water does not meet these criteria, proper corrections are difficult and results become questionable.

6. Precision and Bias

There is no measurement for establishing bias of the BOD procedure. The glucose-glutamic acid check prescribed in ¶ 4*c* is intended to be a reference point for evaluation of dilution water quality, seed effectiveness, and analytical technique. Single-laboratory tests using a 300-mg/L mixed glucose-glutamic acid solution provided the following results:[1]

Number of months:	14
Number of triplicates:	421
Average monthly recovery:	204 mg/L
Average monthly standard deviation:	10.4 mg/L

In a series of interlaboratory studies,[2] each involving 2 to 112 laboratories (and as many analysts and seed sources), 5-d BOD measurements were made on synthetic water samples containing a 1:1 mixture of glucose and glutamic acid in the total concentration range of 3.3 to 231 mg/L. The regression equations for mean value, $\overline{X}$, and standard deviation, S, from these studies were:

$\overline{X}$ = 0.658 (added level, mg/L) + 0.280 mg/L
S = 0.100 (added level, mg/L) + 0.547 mg/L

For the 300-mg/L mixed primary standard, the average 5-d BOD would be 198 mg/L with a standard deviation of 30.5 mg/L.

a. Control limits: Because of many factors affecting BOD tests in multilaboratory studies and the resulting extreme variability in test results, one standard deviation, as determined by interlaboratory tests, is recommended as a control limit for individual laboratories. Alternatively, for each laboratory, establish its control limits by performing a minimum of 25 glucose-glutamic acid checks (¶ 4*c*) over a period of several weeks or months and calculating

the mean and standard deviation. Use the mean ± 3 standard deviations as the control limit for future glucose-glutamic acid checks. Compare calculated control limits to the single-laboratory tests presented above and to interlaboratory results. If control limits are outside the range of 198 ± 30.5, re-evaluate the control limits and investigate source of the problem. If measured BOD for a glucose-glutamic acid check is outside the accepted control limit range, reject tests made with that seed and dilution water.

b. Working range and detection limit: The working range is equal to the difference between the maximum initial DO (7 to 9 mg L) and minimum DO residual of 1 mg/L multiplied by the dilution factor. A lower detection limit of 2 mg/L is established by the requirement for a minimum DO depletion of 2 mg/L.

7. References

1. KENNEY, W. & J. RESNICK. 1987. Personal communication with J. C. Young. Water Pollution Control Plant, Davenport, Iowa.
2. U.S. ENVIRONMENTAL PROTECTION AGENCY, OFFICE OF RESEARCH AND DEVELOPMENT. 1986. Method-by-Method Statistics from Water Pollution (WP) Laboratory Performance Evaluation Studies. Quality Assurance Branch, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

8. Bibliography

SAWYER, C.N. & L. BRADNEY. 1946. Modernization of the BOD test for determining the efficiency of the sewage treatment process. *Sewage Works J.* 18:1113.

RUCHHOFT, C.C., O.R. PLACAK, J. KACHMAR & C.E. CALBERT. 1948. Variations in BOD velocity constant of sewage dilutions. *Ind. Eng. Chem.* 40:1209.

ABBOTT, W. [illegible]e bacteriostatic effects of meth[illegible] the BOD test. *Water Sewage [illegible]*24.

SAWYER, C.N., P. CALLEJAS, M. MOORE & A.Q.Y. TOM. 1950. Primary standards for BOD work. *Sewage Ind. Wastes* 22:26.

YOUNG, J.C., G.N. MCDERMOTT & D. JENKINS. 1981. Alterations in the BOD procedure for the 15th edition of Standard Methods for the Examination of Water and Wastewater. *J. Water Pollut. Control Fed.* 53:1253.

atile organic compou
to the extent that th
with the oxidant. Am
in the waste or libe
containing organic m
in the absence of sig
of free chloride ions.

1. Selection of Meth

The open reflux m
for a wide range of
sample size is preferr
methods (C and D)
in the use of metall
require homogenizati
taining suspended so
ducible results. Ampu
with premeasured re
commercially. Follo
nished by the manufa

Determine COD va
L by using procedur
D.4. Use procedure
mine, with lesser acc
from 5 to 50 mg O_2/

2. Interferences and

Volatile straight-ch
pounds are not oxidize
extent. This failure o
volatile organics are
space and do not com
oxidizing liquid. Stra
compounds are oxidi
when silver sulfate (A
catalyst. However,
chloride, bromide, an
precipitates that are ox
The difficulties caused
the halides can be
though not completely
mercuric sulfate (Hg
fluxing procedure. Alt
specified for 50 mL sam
may be used where sa
centration is known t

5220 CHEMICAL OXYGEN DEMAND (COD)*

5220 A. Introduction

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variety of samples, and ease of manipulation. Oxidation of most organic compounds is 95 to 100% of the theoretical value. Pyridine and related compounds resist oxidation and vol-

*Approved by Standard Methods Committee, 1985.

(Total suspended Solids)

RESIDUE, NON-FILTERABLE

Method 160.2 (Gravimetric, Dried at 103–105°C)

STORET NO. 00530

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 4 mg/1 to 20,000 mg/1.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
   - 2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
   - 4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   - 4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
   - 5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
   - 6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.
     NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
   - 6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

Approved for NPDES
Issued 1971

NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

6.3 Suction flask.

6.4 Drying oven, 103–105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103–105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 ml of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm^2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five ml increments for timing are suggested. Continue to record the time and volume increments until fitration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

NOTE: Total volume of wash water used should equal approximately 2 ml per cm^2. For a 4.7 cm filter the total volume is 30 ml.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

RESIDUE, FILTERABLE (Total Dissolved Solids)

Method 160.1 (Gravimetric, Dried at 180°C)

STORET NO. 70300

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 10 mg/1 to 20,000 mg/1.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
   - 2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.
4. Sample Handling and Preservation
   - 4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
   - 5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
   - 5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
6. Apparatus
   - 6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.
   - 6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
   - 6.3 Suction flask, 500 ml.
   - 6.4 Gooch crucibles, 25 ml (if 2.1 cm filter is used).
   - 6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).
   - 6.6 Steam bath.
   - 6.7 Drying oven, 180°C ±2°C.
   - 6.8 Desiccator.

Approved for NPDES
Issued 1971

6.9 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ±50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ±2°C for one hour. Cool in desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter, rinse with three 10 ml portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180 ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8. Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in ml

9. Precision and Accuracy

9.1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

ALKALINITY

Method 310.1 (Titrimetric, pH 4.5)

STORET NO. 00410

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.
   - 1.3 Automated titrimetric analysis is equivalent.
2. Summary of Method
   - 2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.
3. Comments
   - 3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
   - 3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
   - 3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:
     Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).
   - 3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.
4. Apparatus
   - 4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2° C.
   - 4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
   - 4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.
   - 4.4 Burets, Pyrex 50, 25 and 10 ml.
5. Reagents
   - 5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HCl to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution with about 60 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:
A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 ml of 0.1000 N standard acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 ml 0.05 N Na_2CO_3 solution as above.

6. Procedure

6.1 Sample size

6.1.1 Use a sufficiently large volume of titrant (> 20 ml in a 50 ml buret) to obtain good precision while keeping volume low enough to permit sharp end point.

6.1.2 For < 1000 mg $CaCO_3$/l use 0.02 N titrant

6.1.3 For > 1000 mg $CaCO_3$/l use 0.1 N titrant

6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration

6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask

6.2.2 Measure pH of sample

6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.

6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

6.3.1 For alkalinity of < 20 mg/l titrate 100–200 ml as above (6.2) using a 10 ml microburet and 0.02 N acid solution (5.3).

6.3.2 Stop titration at pH in range of 4.3–4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7. Calculations

7.1 Potentiometric titration to pH 4.5

$$\text{Alkalinity, mg/l } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml of sample}}$$

where:

A = ml standard acid

N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg/l } CaCO_3 = \frac{(2B - C) \times N \times 50{,}000}{\text{ml of sample}}$$

where:

B = ml titrant to first recorded pH

C = total ml titrant to reach pH 0.3 units lower

N = normality of acid

8. Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Accuracy as Bias, mg/l, $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg $CaCO_3$/1, the standard deviation was ±3.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", p 113, D-1067, Method B, (1976).

NITROGEN, NITRATE-NITRITE

Method 353.3 (Spectrophotometric, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application
   1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/1 nitrate-nitrite nitrogen. The range may be extended with sample dilution.
2. Summary of Method
   2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.
3. Sample Handling and Preservation
   3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4°C. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H_2SO_4 per liter) and refrigeration.
   Caution: Samples for reduction column must not be preserved with mercuric chloride.
4. Interferences
   4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45*u* membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.
   4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
   4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.
   4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

Approved for NPDES and SDWA
Issued 1974

5. Apparatus

5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I.D. tubing is joined to a 25 cm length of 3.5 mm I.D. tubing.

5.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).

6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:

6.2.1 Wash the cadmium with dilute HCl (6.10) and rinse with distilled water. The color of the cadmium should be silver.

6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper-cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/l NO_3–N standard and 75 ml of ammonium chloride – EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.

6.4 Ammonium chloride – EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to 1 liter.

6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride-EDTA solution (6.4) to 500 ml with distilled water.

6.6 Color reagent: Dissolve 10 g sulfanilamide and 1 g N(1-naphthyl)–ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to 1 liter with distilled water.

6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 liter.

6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to 1 liter.

6.9 Ammonium hydroxide, conc.

6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCl to 100 ml with distilled water.

6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4 \cdot 5H_2O$ in 500 ml of distilled water and dilute to 1 liter.

6.12 Stock nitrate solution: Dissolve 7.218 g KNO_3 in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg NO_3–N.

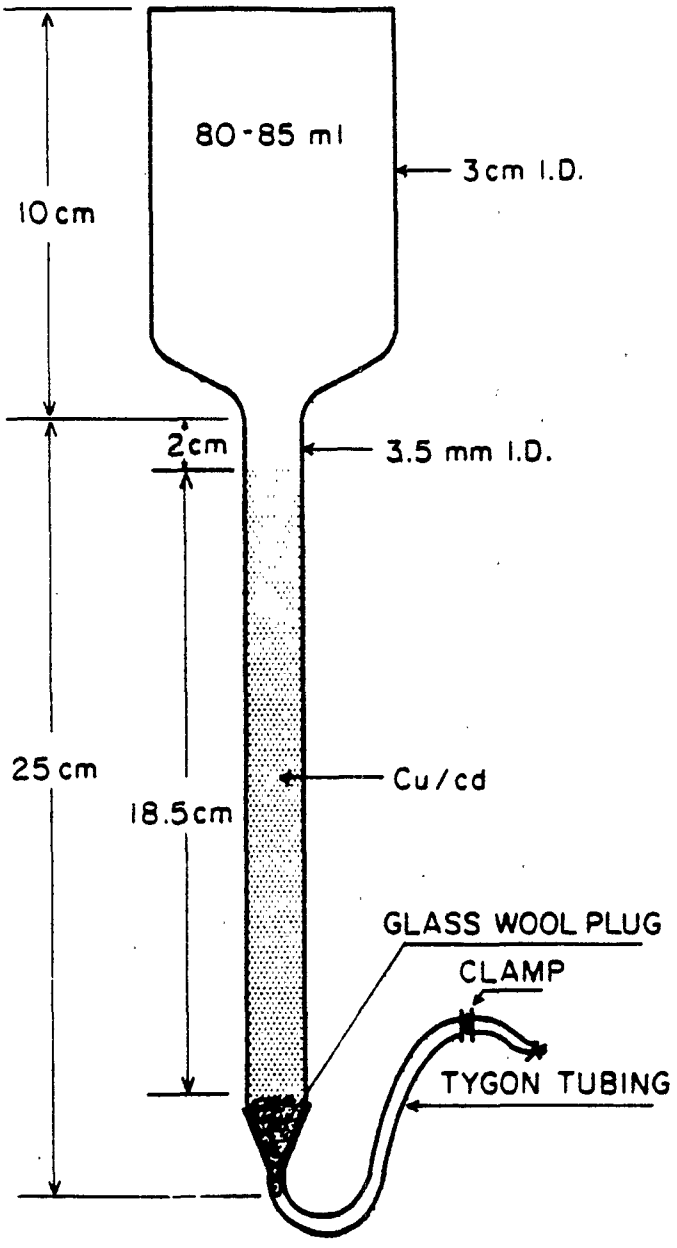


FIGURE 1. REDUCTION COLUMN

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_3–N.

6.14 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg NO_2–N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg NO_2–N.

6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 ml volumetric flasks:

Conc., mg-NO_3–N/l	ml of Standard Solution/100.0 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45*u* membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4–0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45*u* membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non-polar solvent (Freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HCl or conc. NH_4OH. This is done to insure a sample pH of 8.5 after step 7.4.

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride-EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7–10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. **NOTE:** If the concentration of sample exceeds 1.0 mg NO_3–N/1, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against NO_3–N mg/l. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$mgNO_2 + NO_3 - N/l = \frac{A \times 25}{ml\ sample\ used}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg $NO_3 + NO_2$-N/l, the standard deviations were ±0.005, ±0.004, ±0.005 and ±0.01, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg $NO_3 + NO_2$–N/l, the recoveries were 100%, 102% and 100%, respectively.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 423, Method 419C (1975).
2. Henrikson, A., and Selmer-Olsen, "Automatic Methods for Determining Nitrate and Nitrite in Water and Soil Extracts". Analyst, May 1970, Vol. 95, p 514–518.
3. Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water with Analog and Digital Data Record", "Advances in Automated Analysis", Technicon International Congress, 1969, Vol. 11, p 133–145.
4. Brewer, P. G., Riley, J. P., "The Automatic Determination of Nitrate in Sea Water", Deep Sea Research, 1965, Vol. 12, p 765–772.

NITROGEN, AMMONIA

Method 350.2 (Colorimetric; Titrimetric; Potentiometric – Distillation Procedure)

STORET NO. Total 00610
Dissolved 00608

1. Scope and Application
   1.1 This distillation method covers the determination of ammonia-nitrogen exclusive of total Kjeldahl nitrogen, in drinking, surface and saline waters, domestic and industrial wastes. It is the method of choice where economics and sample load do not warrant the use of automated equipment.
   1.2 The method covers the range from about 0.05 to 1.0 mg NH_3–N/1 for the colorimetric procedure, from 1.0 to 25 mg/1 for the titrimetric procedure, and from 0.05 to 1400 mg/1 for the electrode method.
   1.3 This method is described for macro glassware; however, micro distillation equipment may also be used.
2. Summary of Method
   2.1 The sample is buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The ammonia in the distillate can be determined colorimetrically by nesslerization, titrimetrically with standard sulfuric acid with the use of a mixed indicator, or potentiometrically by the ammonia electrode. The choice between the first two procedures depends on the concentration of the ammonia.
3. Sample Handling and Preservation
   3.1 Samples may be preserved with 2 ml of conc. H_2SO_4 per liter and stored at 4°C.
4. Interferences
   4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of Nessler reagent, so direct nesslerization (i.e., without distillation), has been discarded as an official method.
   4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out. Volatile alkaline compounds, such as certain ketones, aldehydes, and alcohols, may cause an off-color upon nesslerization in the distillation method. Some of these, such as formaldehyde, may be eliminated by boiling off at a low pH (approximately 2 to 3) prior to distillation and nesslerization.
   4.3 Residual chlorine must also be removed by pretreatment of the sample with sodium thiosulfate before distillation.

Approved for NPDES
Issued 1971
Editorial revision 1974

5. Apparatus

5.1 An all-glass distilling apparatus with an 800–1000 ml flask.

5.2 Spectrophotometer or filter photometer for use at 425 nm and providing a light path of 1 cm or more.

5.3 Nessler tubes: Matched Nessler tubes (APHA Standard) about 300 mm long, 17 mm inside diameter, and marked at 225 mm ±1.5 mm inside measurement from bottom.

5.4 Erlenmeyer flasks: The distillate is collected in 500 ml glass-stoppered flasks. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks.

6. Reagents

6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

NOTE 1: All solutions must be made with ammonia-free water.

6.2 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3–N. Dissolve 3.819 g NH_4Cl in distilled water and bring to volume in a 1 liter volumetric flask.

6.3 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg. Dilute 10.0 ml of stock solution (6.2) to 1 liter in a volumetric flask.

6.4 Boric acid solution (20 g/1): Dissolve 20 g H_3BO_3 in distilled water and dilute to 1 liter.

6.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethyl alcohol with 1 volume of 0.2% methylene blue in 95% ethyl alcohol. This solution should be prepared fresh every 30 days.

NOTE 2: Specially denatured ethyl alcohol conforming to Formula 3A or 30 of the U.S. Bureau of Internal Revenue may be substituted for 95% ethanol.

6.6 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g of potassium iodide in a small amount of water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of water. Dilute the mixture to 1 liter. If this reagent is stored in a Pyrex bottle out of direct sunlight, it will remain stable for a period of up to 1 year.

NOTE 3: This reagent should give the characteristic color with ammonia within 10 minutes after addition, and should not produce a precipitate with small amounts of ammonia (0.04 mg in a 50 ml volume).

6.7 Borate buffer: Add 88 ml of 0.1 N NaOH solution to 500 ml of 0.025 M sodium tetraborate solution (5.0 g anhydrous $Na_2B_4O_7$ or 9.5 g $Na_2B_4O_7 \cdot 10H_2O$ per liter) and dilute to 1 liter.

6.8 Sulfuric acid, standard solution: (0.02 N, 1 ml = 0.28 mg NH_3–N). Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to 1 liter with CO_2-free distilled water. Dilute 200 ml of this solution to 1 liter with CO_2-free distilled water.

NOTE 4: An alternate and perhaps preferable method is to standardize the approximately 0.1 N H_2SO_4 solution against a 0.100 N Na_2CO_3 solution. By proper dilution the 0.02 N acid can then be prepared.

6.8.1 Standardize the approximately 0.02 N acid against 0.0200 N Na_2CO_3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1000 ml with CO_2-free distilled water.

6.9 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in ammonia-free water and dilute to 1 liter.

6.10 Dechlorinating reagents: A number of dechlorinating reagents may be used to remove residual chlorine prior to distillation. These include:

a. Sodium thiosulfate (1/70 N): Dissolve 3.5 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water and dilute to 1 liter. One ml of this solution will remove 1 mg/l of residual chlorine in 500 ml of sample.

b. Sodium arsenite (1/70 N): Dissolve 1.0 g $NaAsO_2$ in distilled water and dilute to 1 liter.

7. Procedure

7.1 Preparation of equipment: Add 500 ml of distilled water to an 800 ml Kjeldahl flask. The addition of boiling chips which have been previously treated with dilute NaOH will prevent bumping. Steam out the distillation apparatus until the distillate shows no trace of ammonia with Nessler reagent.

7.2 Sample preparation: Remove the residual chlorine in the sample by adding dechlorinating agent equivalent to the chlorine residual. To 400 ml of sample add 1 N NaOH (6.9), until the pH is 9.5, checking the pH during addition with a pH meter or by use of a short range pH paper.

7.3 Distillation: Transfer the sample, the pH of which has been adjusted to 9.5, to an 800 ml Kjeldahl flask and add 25 ml of the borate buffer (6.7). Distill 300 ml at the rate of 6–10 ml/min. into 50 ml of 2% boric acid (6.4) contained in a 500 ml Erlenmeyer flask.

NOTE 5: The condenser tip or an extension of the condenser tip must extend below the level of the boric acid solution.

Dilute the distillate to 500 ml with distilled water and nesslerize an aliquot to obtain an approximate value of the ammonia-nitrogen concentration. For concentrations above 1 mg/l the ammonia should be determined titrimetrically. For concentrations below this value it is determined colorimetrically. The electrode method may also be used.

7.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate titrimetrically, colorimetrically or potentiometrically as described below.

7.4.1 Titrimetric determination: Add 3 drops of the mixed indicator to the distillate and titrate the ammonia with the 0.02 N H_2SO_4, matching the end point against a blank containing the same volume of distilled water and H_3BO_3 solution.

7.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3–N	mg NH_3–N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.01
2.0	0.02
3.0	0.03
4.0	0.04
5.0	0.05
8.0	0.08
10.0	0.10

Dilute each tube to 50 ml with distilled water, add 2.0 ml of Nessler reagent (6.6) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained plot absorbance vs. mg NH_3–N for the standard curve. Determine the ammonia in the distillate by nesslerizing 50 ml or an aliquot diluted to 50 ml and reading the absorbance at 425 nm as described above for the standards. Ammonia-nitrogen content is read from the standard curve.

7.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia: Selective Ion Electrode Method (Method 350.3) in this manual.

7.5 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree with undistilled standards the operator should find the cause of the apparent error before proceeding.

8. Calculations

8.1 Titrimetric

$$\text{mg/l } NH_3 - N = \frac{A \times 0.28 \times 1{,}000}{S}$$

where:

A = ml 0.02 N H_2SO_4 used.

S = ml sample.

8.2 Spectrophotometric

$$\text{mg/l } NH_3 - N = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:

A = mg NH_3–N read from standard curve.

B = ml total distillate collected, including boric acid and dilution.

C = ml distillate taken for nesslerization.

D = ml of original sample taken.

8.3 Potentiometric

$$mg/l\ NH_3 - N = \frac{500}{D} \times A$$

where:

A = mg NH_3–N/l from electrode method standard curve.

D = ml of original sample taken.

9. Precision and Accuracy

9.1 Twenty-four analysts in sixteen laboratories analyzed natural water samples containing exact increments of an ammonium salt, with the following results:

Increment as Nitrogen, Ammonia mg N/liter	Precision as Standard Deviation mgN/liter	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.21	0.122	-5.54	-0.01
0.26	0.070	-18.12	-0.05
1.71	0.244	+0.46	+0.01
1.92	0.279	-2.01	-0.04

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 410, Method 418A and 418B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1426–74, Method A, p 237 (1976).

CHLORIDE

Method 325.2 (Colorimetric, Automated Ferricyanide AAII)

STORET NO. 00940

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industral wastes. The applicable range is 1 to 200 mg Cl/1. This range may be extended by sample dilution. Approximately 30 samples per hour can be analyzed.
2. Summary of Method
   2.1 Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in concentration proportional to the original chloride concentration.
3. Sample Handling and Preservation
   3.1 No special requirements.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler.
      5.1.2 Continuous filter (optional).
      5.1.3 Analytical cartridge.
      5.1.4 Proportioning pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nm filters.
      5.1.6 Recorder.
      5.1.7 Digital printer (optional).
6. Reagents
   6.1 Mercuric thiocyanate solution: Dissolve 4.17 gm of $Hg(SCN)_2$ in 500 ml of methanol. Dilute to 1 liter with methanol, mix and filter through filter paper.
   6.2 Ferric nitrate solution, 20.2%: Dissolve 202 gm of $Fe(NO_3)_3 \cdot 9\ H_2O$ in 500 ml of distilled water. Add 31.5 ml conc nitric acid, mix and dilute to 1 liter with distilled water.
   6.3 Color reagent: Add 150 ml of mercuric thiocyanate solution (6.1) to 150 ml of ferric nitrate solution (6.2), mix, and dilute to 1 liter with distilled water.
   6.4 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 ml = 0.5 mg Cl.
      6.4.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 ml with distilled water. The following dilutions are suggested:

Approved for NPDES
Issued 1978

ml of Stock Solution	Conc., mg/l
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0

7. Procedure
   - 7.1 Where particulate matter is present, the sample must be filtered prior to the determination. This can be accomplished by having the Technicon continuous filter as an integral part of the system. The sample may be centrifuged in place of filtration.
   - 7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.
   - 7.3 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.
   - 7.4 When a stable baseline has been obtained, start the sampler.
8. Calculation
   - 8.1 Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve.
9. Precision and Accuracy
   - 9.1 Precision and accuracy data are not available at this time.

Bibliography

1. J. E. O'Brien, "Automatic Analysis of Chlorides in Sewage", Waste Engr., 33, 670–672 (Dec. 1962).
2. Technicon AutoAnalyzer II, Industrial Method No. 99–70W, Technicon Industrial Systems, Tarrytown, N. Y., 10591 (Sept. 1973).

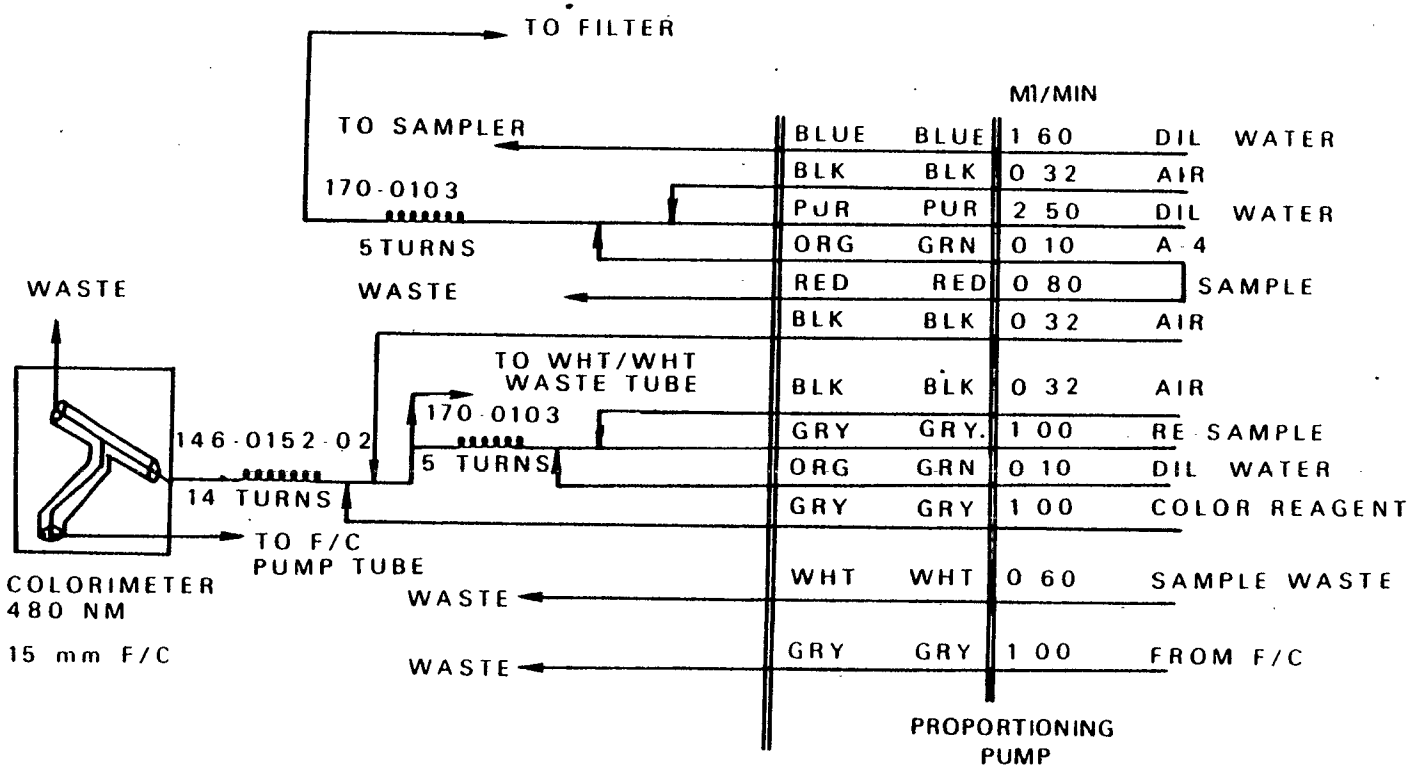


FIGURE 1
CHLORIDE MANIFOLD AA 11

SULFATE

Method 375.4 (Turbidimetric)

STORET NO. Total 00945

1. Scope and Application
   - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/1.
   - 1.3 The minimum detectable limit is approximately 1 mg/1 sulfate.
2. Summary of Method
   - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
   - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
   - 2.3 Silica in concentrations over 500 mg/1 will interfere.
3. Comments
   - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
   - 3.2 Preserve by refrigeration at 4°C.
4. Apparatus
   - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
   - 4.2 Photometer: one of the following which are given in order of preference.
     - 4.2.1 Nephelometer
     - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
     - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
   - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
   - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
5. Reagents
   - 5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.
   - 5.2 Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh.
   - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.4 Standard sulfate solution (1.00 ml = 100 μg SO_4): Prepare by either 5.4.1 or 5.4.2.

5.4.1 Standard sulfate solution from H_2SO_4

5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 ml volumetric and dilute to the mark.

5.4.2 Standard sulfate solution from Na_2SO_4: Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6. Procedure

6.1 Formation of barium sulfate turbidity

6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.

6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

6.1.3 Mix in the stirring apparatus.

6.1.4 While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals (5.2) and begin timing immediately.

6.1.5 Stir exactly 1.0 minutes at constant speed.

6.2 Measurement of barium sulfate turbidity

6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

6.2.2 Measure turbidity at 30 second intervals for 4 minutes.

6.2.3 Record the maximum reading obtained in the 4 minute period.

6.3 Preparation of calibration curve.

6.3.1 Prepare calibration curve using standard sulfate solution (5.4).

6.3.2 Space standards at 5 mg/1 increments in the 0–40 mg/1 sulfate range.

6.3.3 Above 50 mg/1 the accuracy decreases and the suspensions lose stability.

6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.

6.4 Correction for sample color and turbidity.

6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).

7. Calculations

7.1 Read mg SO_4 from calibration curve

$$\text{mg } SO_4/1 = \frac{\text{mg } SO_4 \times 1{,}000}{\text{ml sample}}$$

8. Precision and Accuracy

8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as Bias, %	Accuracy as Bias mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

8.2 A synthetic unknown sample containing 259 mg/1 sulfate, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 0.250 mg/1 nitrite N, 1.1 mg/1 nitrate N, and 42.5 mg/1 total alkalinity (contributed by $NaHCO_3$) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516–68, Method B, p 430 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 496, Method 427C, (1975).

AIW FRANK #3

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal

Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General Descrition of analytical services requested:

   Analysis of 9 surface water samples for TCL Volatiles by the "Draft Low Concentration Water for Organic Compounds" CLP SOW. Only TCL Volatile compounds are requested. May include the analysis of 1 PEM/SDG as stated in the SOW.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   9 low/medium concentration surface water samples plus 2 rinsate blanks and 2 trip blanks for a total of 13 units for TCL Volatiles by the "Draft Low Concentration Water for Organic Compounds" CLP SOW.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

   RI/FS - ARCS III

SAS Approved By (signature):
Date:

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of .

6. **Number of days analysis and data required after laboratory receipt of samples:**

35 days from receipt of last sample. Samples must be analyzed within 10 days of laboratory receipt of the sample.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

Analysis of TCL Volatile compounds by the "Draft Low Concentration Water for Organic Compounds" CLP SOW.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

May include the analysis of 1 PEM/SDG as described in the SOW. Region III will arrange for PE to be shipped to the laboratory upon award.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

10. **Other (use additional sheets or attach supplementary information, as needed):**

Laboratory must comply with purge file requirements. Contact SMO for details.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation
(412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

14. Action Required if Limits are Exceeded:

As per the Draft CLP Low Concentration Water for Organic Compounds SOW.

15. Request Prepared By:

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991; revised September 5, 1991.

16. Request Reviewed By (CRL use only):
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

AIW FRANK # 4

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General Descrition of analytical services requested:

   Analysis of 9 surface water samples for Hardness, alkalinity, acidity, sulfate, Total Dissolved Solids (TDS), and Total Suspended Solids (TSS) by the methods listed in Item 7.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   9 low concentration surface water samples for the above analysis.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

   RI/FS - ARCS III

   SAS Approved By (signature):
   Date:

AR300675

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of

6. **Number of days analysis and data required after laboratory receipt of samples:**

35 days from receipt of last sample. Samples must be analyzed within the holding times established in the Federal Register for each analyte.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

Hardness	- EPA 130.2	Sulfate	- EPA 375.4
Alkalinity	- EPA 310.1	TDS	- EPA 160.1
Acidity	- EPA 305.1	TSS	- EPA 160.2

All methods are attached.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

Raw data, calculations, data sheets, blank results, duplicate results, signed and dated copy of chain-of-custody documentation, copies of air bill confirming sample receipt, and SAS Request Form.

10. **Other (use additional sheets or attach supplementary information, as needed):**

Laboratory must comply with purge file requirements. Contact SMO for details.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation
(412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)
Hardness	10 mg/l	± 20%
Alkalinity	1 mg/l	± 20%
Acidity	10 mg/l	± 20%
Sulfate	10 mg/l	± 20%
TDS	10 mg/l	± 20%
TSS	4 mg/l	± 20%

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
Blank (sulfate only)	1/batch	Below method detection limits
Duplicate	1/batch	± 20%

14. Action Required if Limits are Exceeded:

Reanalyze samples once more and report both sets of data.

15. Request Prepared By:

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991, revised September 6, 1991.

16. Request Reviewed By (CRL use only):
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

HARDNESS, Total (mg/1 as $CaCO_3$)
Method 130.2 (Titrimetric, EDTA)

STORET NO. 00900

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of hardness: however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25 mg $CaCO_3$.
   - 1.3 Automated titration may be used.
2. Summary of Method
   - 2.1 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction is detected by means of Eriochrome Black T indicator, which has a red color in the presence of calcium and magnesium and a blue color when the cations are sequestered.
3. Sample Handling and Preservation
   - 3.1 Cool to 4°C, HNO_3 to pH < 2.
4. Comments
   - 4.1 Excessive amounts of heavy metals can interfere. This is usually overcome by complexing the metals with cyanide.
     - 4.1.1 Routine addition of sodium cyanide solution (Caution: deadly poison) to prevent potential metallic interference is recommended.
5. Apparatus
   - 5.1 Standard laboratory titrimetric equipment.
6. Reagents
   - 6.1 Buffer solution
     - 6.1.1 If magnesium EDTA is available: Dissolve; 16.9 g NH_4Cl in 143 ml conc. NH_4OH in a 250 ml volumetric, add 1.25 g of magnesium salt of EDTA and dilute to the mark with distilled water. Then go to 6.1.3.
     - 6.1.2 If magnesium EDTA is unavailable: Dissolve 1.179 g disodium EDTA (analytical reagent grade) and 780 mg $MgSO_4 \cdot 7H_2O$ (or 644 mg $MgCl_2 \cdot 6H_2O$) in 50 ml distilled water. Add this solution to a 250 ml volumetric flask containing 16.9 g NH_4Cl and 143 ml conc. NH_4OH with mixing and dilute to the mark with distilled water.
     - 6.1.3 Store in a tightly stoppered plastic bottle; stable for approximately one month. Dispense with bulb operated pipet. Discard when 1 or 2 ml added to sample fails to produce a pH of 10.0 ±0.1 at end point of titration.

Approved for NPDES
Issued 1971
Editorial revision 1978 and 1982

6.1.4 Commercially available "odorless buffers" which are more stable, may be used.

6.2 Inhibitors: For most waters inhibitors are not necessary. If interfering ions are present use one of the following:

6.2.1 Inhibitor I: NaCN powder. (Caution: extremely poisonous). Flush solutions or sample containing this down drain using large quantities of water. Make sure no acids are present which might liberate HCN gas.

6.2.2 Inhibitor II: Dissolve 5.0 g $Na_2S \cdot 9\ H_2O$ or 3.7 g $Na_2S \cdot 5\ H_2O$ in 100 ml distilled water. Exclude air with tightly fitted rubber stopper. This gives sulfide precipitates which may obscure the end point if large quantities of heavy metals are present. Deteriorates rapidly through air oxidation.

6.2.3 Inhibitor III: Dissolve 4.5 g hydroxylamine hydrochloride in 100 ml of 95% ethanol or isopropanol.

6.3 Indicator: Use a commercially available indicator such as Calmagite indicator (Mallinckrodt) or one of the formulations described below (6.3.1–6.3.3)

6.3.1 Mix 0.5 g Eriochrome Black T with 4.5 g hydroxylamine hydrochloride. Dissolve in 100 ml of 95% ethanol or isopropanol.

6.3.2 Dissolve 0.5 to 1.0 g Eriochrome Black T in an appropriate solvent such as triethanolamine or 2-methoxyethanol. Stable approximately one week.

6.3.3 Mix together 0.5 g Eriochrome Black T and 100 g NaCl.

6.4 Standard EDTA titrant, 0.02 N: Place 3.723 g analytical reagent grade disodium ethylenediamine tetraacetate dihydrate, $Na_2H_2C_{10}H_{12}O_8N_2 \cdot 2\ H_2O$ in a 1 liter volumetric flask and dilute to the mark with distilled water. Check with standard calcium solution (6.4.1) by titration (6.4.5). Store in polyethylene. Check periodically because of gradual deterioration.

6.4.1 Standard calcium solution 0.02 N: Place 1.000 g anhydrous calcium carbonate (primary standard low in metals) in a 500 ml flask. Add, a little at a time, 1 + 1 HCL (6.4.2) until all of the $CaCO_3$ has dissolved. Add 200 ml distilled water. Boil for a few minutes to expel CO_2. Cool. Add a few drops of methyl red indicator (6.4.3) and adjust to intermediate orange color by adding 3N NH_4OH (6.4.4) or 1 + 1 HCl (6.4.2) as required. Quantitatively transfer to a 1 liter volumetric flask and dilute to mark with distilled water.

6.4.2 Hydrochloric acid solution, 1 + 1.

6.4.3 Methyl red indicator: Dissolve 0.10 g methyl red in distilled water in a 100 ml volumetric flask and dilute to the mark.

6.4.4 Ammonium hydroxide solution, 3 N: Dilute 210 ml of conc. NH_4OH to 1 liter with distilled water.

6.4.5 Standardization titration procedure: Place 10.0 ml standard calcium solution (6.4.1) in vessel containing about 50 ml distilled water. Add 1 ml buffer solution (6.1). Add 1–2 drops indicator (6.3) or small scoop of dry indicator (6.3.3). Titrate slowly with continuous stirring until the last reddish tinge disappears, adding last

few drops at 3–5 second intervals. At end point the color is blue. Total titration duration should be 5 minutes from the time of buffer addition.

$$\text{N of EDTA} = \frac{0.2}{\text{ml of EDTA}}$$

6.5 Ammonium Hydroxide, 1N: Dilute 70 ml of conc. NH_4OH to 1 liter with distilled water.

7. Procedure

7.1 Pretreatment

7.1.1 For drinking waters, surface waters, saline waters, and dilutions thereof, no pretreatment steps are necessary. Proceed to 7.2.

7.1.2 For most wastewaters, and highly polluted waters, the sample must be digested as given in the Atomic Absorption Methods section of this manual, paragraphs 4.1.3 and 4.1.4. Following this digestion, proceed to 7.2.

7.2 Titration of sample-normal to high hardness:

7.2.1 Sample should require < 15 ml EDTA titrant (6.4) and titration should be completed within 5 minutes of buffer addition.

7.2.2 Place 25.0 ml sample in titration vessels, neutralize with 1N ammonium hydroxide (6.5) and dilute to about 50 ml.

7.2.3 Add 1 to 2 ml buffer solution (6.1).

7.2.4 If end point is not sharp (as determined by practice run) add inhibitor at this point (see 7.4).

7.2.5 Add 1 to 2 drops indicator solution (6.3.1 or 6.3.2) or small scoop of dried powder indicator formulation (6.3.3).

7.2.6 Titrate slowly with continuous stirring with standard EDTA titrant (6.4) until last reddish tint disappears. Solution is normally blue at end point.

7.3 Titration of sample–low hardness (less than 5 mg/l)

7.3.1 Use a larger sample (100 ml)

7.3.2 Use proportionately larger amounts of buffer, inhibitor and indicator

7.3.3 Use a microburet and run a blank using redistilled, distilled or deionized water.

7.4 To correct for interferences:

7.4.1 Some metal ions interfere by causing fading or indistinct end points. Inhibitors reduce this in accord with the scheme below for 25.0 ml samples diluted to 50 ml.

Maximum Concentrations of Interferences Permissible with Various Inhibitors[a]

Interfering Substance	Maximum Interference Concentration mg/l		
	Inhibitor I	Inhibitor II	Inhibitor III
Aluminum	20	20	20
Barium	b	b	b
Cadmium	b	20	b
Cobalt	over 20	0.3	0[c]
Copper	over 30	20	0.3
Iron	over 30	5	20
Lead	b	20	b
Manganese (Mn^{2+})	b	1	1
Nickel	over 20	0.3	0[c]
Strontium	b	b	b
Zinc	b	200	b
Polyphosphate		10	

a Based on 25-ml sample diluted to 50 ml.
b Titrates as hardness.
c Inhibitor fails if substance is present.

7.4.2 Inhibitor I: At step 7.2.4 add 250 mg NaCN. Add sufficient buffer to achieve pH 10.0 ± 0.1 to offset alkalinity resulting from hydrolysis of sodium cyanide.

7.4.3 Inhibitor II: At step 7.2.4 add 1 ml of inhibitor II (6.2.2)

7.4.4 Inhibitor III: At step 7.2.4 add 1 ml of inhibitor III (6.2.3).

8. Calculations:

$$\text{Hardness (EDTA) mg } CaCO^3/l = \frac{A \times N \times 50{,}000}{\text{ml sample}}$$

where:
A = ml EDTA titrant (6.4)
N = normality of EDTA titrant.

9. Precision and Accuracy

9.1 Forty-three analysts in nineteen laboratories analyzed six synthetic water samples containing exact increments of calcium and magnesium salts, with the following results:

Increment as Total Hardness mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Accuracy as Bias, mg/liter, $CaCO_3$
31	2.87	–0.87	–0.003
33	2.52	–0.73	–0.24
182	4.87	–0.19	–0.4
194	2.98	–1.04	–2.0
417	9.65	–3.35	–13.0
444	9.73	–3.23	–14.3

(FWPCA Method Study 1, Mineral and Physical Analyses)

9.2 In a single laboratory (EMSL), using surface water samples at an average concentration of 194 mg $CaCO_3$/1, the standard deviation was ±3.

9.3 A synthetic unknown sample containing 610 mg/1 total hardness as $CaCO_3$ contributed by 108 mg/1 Ca and 82 mg/1 Mg, and the following supplementary substances: 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 0.25 mg/1 nitrite N, 1.1 mg/1 nitrate N, 259 mg/1 sulfate, and 42.5 mg/1 total alkalinity (contributed by $NaHCO_3$) in distilled water was analyzed in 56 laboratories by the EDTA titrimetric method with a relative standard deviation of 2.9% and a relative error of 0.8%.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D 1126–67, p 161, Method B (1976).

ALKALINITY

Method 310.1 (Titrimetric, pH 4.5)

STORET NO. 00410

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of alkalinity; however, appropriate aliquots should be used to avoid a titration volume greater than 50 ml.
   - 1.3 Automated titrimetric analysis is equivalent.
2. Summary of Method
   - 2.1 An unaltered sample is titrated to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.
3. Comments
   - 3.1 The sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
   - 3.2 Substances, such as salts of weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.
   - 3.3 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9, using the procedure in:
     Annual Book of ASTM Standards, Part 31, "Water", p 115, D-1067, Method D, (1976).
   - 3.4 Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.
4. Apparatus
   - 4.1 pH meter or electrically operated titrator that uses a glass electrode and can be read to 0.05 pH units. Standardize and calibrate according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2° C.
   - 4.2 Use an appropriate sized vessel to keep the air space above the solution at a minimum. Use a rubber stopper fitted with holes for the glass electrode, reference electrode (or combination electrode) and buret.
   - 4.3 Magnetic stirrer, pipets, flasks and other standard laboratory equipment.
   - 4.4 Burets, Pyrex 50, 25 and 10 ml.
5. Reagents
   - 5.1 Sodium carbonate solution, approximately 0.05 N: Place 2.5 ±0.2 g (to nearest mg) Na_2CO_3 (dried at 250°C for 4 hours and cooled in desiccator) into a 1 liter volumetric flask and dilute to the mark.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.2 Standard acid (sulfuric or hydrochloric), 0.1 N: Dilute 3.0 ml conc H_2SO_4 or 8.3 ml conc HCl to 1 liter with distilled water. Standardize versus 40.0 ml of 0.05 N Na_2CO_3 solution with about 60 ml distilled water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using:

$$N = \frac{A \times B}{53.00 \times C}$$

where:
A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.3 Standard acid (sulfuric or hydrochloric), 0.02 N: Dilute 200.0 ml of 0.1000 N standard acid to 1 liter with distilled water. Standardize by potentiometric titration of 15.0 ml 0.05 N Na_2CO_3 solution as above.

6. Procedure

6.1 Sample size

6.1.1 Use a sufficiently large volume of titrant (> 20 ml in a 50 ml buret) to obtain good precision while keeping volume low enough to permit sharp end point.

6.1.2 For < 1000 mg $CaCO_3$/l use 0.02 N titrant

6.1.3 For > 1000 mg $CaCO_3$/l use 0.1 N titrant

6.1.4 A preliminary titration is helpful.

6.2 Potentiometric titration

6.2.1 Place sample in flask by pipetting with pipet tip near bottom of flask

6.2.2 Measure pH of sample

6.2.3 Add standard acid (5.2 or 5.3), being careful to stir thoroughly but gently to allow needle to obtain equilibrium.

6.2.4 Titrate to pH 4.5. Record volume of titrant.

6.3 Potentiometric titration of low alkalinity

6.3.1 For alkalinity of < 20 mg/l titrate 100–200 ml as above (6.2) using a 10 ml microburet and 0.02 N acid solution (5.3).

6.3.2 Stop titration at pH in range of 4.3–4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 pH units and record volume.

7. Calculations

7.1 Potentiometric titration to pH 4.5

$$\text{Alkalinity, mg/l } CaCO_3 = \frac{A \times N \times 50{,}000}{\text{ml of sample}}$$

where:

A = ml standard acid

N = normality standard acid

7.2 Potentiometric titration of low alkalinity:

$$\text{Total alkalinity, mg/l } CaCO_3 = \frac{(2B - C) \times N \times 50{,}000}{\text{ml of sample}}$$

where:

B = ml titrant to first recorded pH

C = total ml titrant to reach pH 0.3 units lower

N = normality of acid

8. Precision and Accuracy

8.1 Forty analysts in seventeen laboratories analyzed synthetic water samples containing increments of bicarbonate, with the following results:

Increment as Alkalinity mg/liter, $CaCO_3$	Precision as Standard Deviation mg/liter, $CaCO_3$	Accuracy as Bias, %	Accuracy as Bias, mg/l, $CaCO_3$
8	1.27	+10.61	+0.85
9	1.14	+22.29	+2.0
113	5.28	- 8.19	-9.3
119	5.36	- 7.42	-8.8

(FWPCA Method Study 1, Mineral and Physical Analyses)

8.2 In a single laboratory (EMSL) using surface water samples at an average concentration of 122 mg $CaCO_3$/1, the standard deviation was ±3.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 278, Method 403, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", p 113, D-1067, Method B, (1976).

ACIDITY

Method 305.1 (Titrimetric)

STORET NO. 70508

1. Scope and Application
   - 1.1 This method is applicable to surface waters, sewages and industrial wastes, particularly mine drainage and receiving streams, and other waters containing ferrous iron or other polyvalent cations in a reduced state.
   - 1.2 The method covers the range from approximately 10 mg/l acidity to approximately 1000 mg/l as $CaCO_3$, using a 50 ml sample.
2. Summary of Method
   - 2.1 The pH of the sample is determined and a measured amount of standard acid is added, as needed, to lower the pH to 4 or less. Hydrogen peroxide is added, the solution boiled for several minutes, cooled, and titrated electrometrically with standard alkali to pH 8.2.
3. Definitions
   - 3.1 This method measures the mineral acidity of a sample plus the acidity resulting from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.
4. Interferences
   - 4.1 Suspended matter present in the sample, or precipitates formed during the titration may cause a sluggish electrode response. This may be offset by allowing a 15–20 second pause between additions of titrant or by slow dropwise addition of titrant as the endpoint pH is approached.
5. Apparatus
   - 5.1 pH meter, suitable for electrometric titrations.
6. Reagents
   - 6.1 Hydrogen peroxide (H_2O_2, 30% solution).
   - 6.2 Standard sodium hydroxide, 0.02 N.
   - 6.3 Standard sulfuric acid, 0.02 N.
7. Procedure
   - 7.1 Pipet 50 ml of the sample into a 250 ml beaker.
   - 7.2 Measure the pH of the sample. If the pH is above 4.0, add standard sulfuric acid (6.3) in 5.0 ml increments to lower the pH to 4.0 or less. If the initial pH of the sample is less than 4.0, the incremental addition of sulfuric acid is not required.
   - 7.3 Add 5 drops of hydrogen peroxide (6.1).
   - 7.4 Heat the sample to boiling and continue boiling for 2 to 4 minutes. In some instances, the concentration of ferrous iron in a sample is such that an additional amount of hydrogen peroxide and a slightly longer boiling time may be required.

Approved for NPDES
Issued 1971
Technical revision 1974

7.5 Cool the sample to room temperature and titrate electrometrically with standard sodium hydroxide (6.2) to pH 8.2.

8. Calculations

8.1 Acidity, as mg/l $CaCO_3$ = $\frac{[(A \times B) - (C \times D)] \times 50{,}000}{\text{ml of sample}}$

where:

A = vol. of standard sodium hydroxide used in titration

B = normality of standard sodium hydroxide

C = volume of standard sulfuric acid used to reduce pH to 4 or less

D = normality of standard sulfuric acid

8.2 If it is desired to report acidity in millequivalents per liter, the reported values as $CaCO_3$ are divided by 50, as follows:

$$\text{Acidity as meq/l} = \frac{\text{mg/l } CaCO_3}{50}$$

9. Precision

9.1 On a round robin conducted by ASTM on 4 acid mine waters, including concentrations up to 2000 mg/1, the precision was found to be ±10 mg/1.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", p 116, D 1067, Method E(1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 277, Method 402(4d) (1975).

SULFATE

Method 375.4 (Turbidimetric)

STORET NO. Total 00945

1. Scope and Application
   - 1.1 This method is applicable to drinking and surface waters, domestic and industrial wastes.
   - 1.2 The method is suitable for all concentration ranges of sulfate; however, in order to obtain reliable readings, use a sample aliquot containing not more than 40 mg SO_4/1.
   - 1.3 The minimum detectable limit is approximately 1 mg/1 sulfate.
2. Summary of Method
   - 2.1 Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.
   - 2.2 Suspended matter and color interfere. Correct by running blanks from which the barium chloride has been omitted.
   - 2.3 Silica in concentrations over 500 mg/1 will interfere.
3. Comments
   - 3.1 Proprietary reagents, such as Hach Sulfaver or equivalent, are acceptable.
   - 3.2 Preserve by refrigeration at 4°C.
4. Apparatus
   - 4.1 Magnetic stirrer, variable speed so that it can be held constant just below splashing. Use identical shape and size magnetic stirring bars.
   - 4.2 Photometer: one of the following which are given in order of preference.
     - 4.2.1 Nephelometer
     - 4.2.2 Spectrophotometer for use at 420 nm with light path of 4 to 5 cm.
     - 4.2.3 Filter photometer with a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
   - 4.3 Stopwatch, if the magnetic stirrer is not equipped with an accurate timer.
   - 4.4 Measuring spoon, capacity 0.2 to 0.3 ml.
5. Reagents
   - 5.1 Conditioning reagent: Place 30 ml conc. HCl, 300 ml distilled water, 100 ml 95% ethanol or isopropanol and 75 g NaCl in solution in a container. Add 50 ml glycerol and mix.
   - 5.2 Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh.
   - 5.3 Sodium carbonate solution (approximately 0.05N): Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and cool in a desiccator. Weigh 2.5 ±0.2 g (to the nearest mg), transfer to a 1 liter volumetric flask and fill to the mark with distilled water.

Approved for NPDES
Issued 1971
Editorial revision 1978

5.4 Standard sulfate solution (1.00 ml = 100 *ug* SO_4): Prepare by either 5.4.1 or 5.4.2.

5.4.1 Standard sulfate solution from H_2SO_4

5.4.1.1 Standard sulfuric acid, 0.1N: dilute 3.0 ml conc. H_2SO_4 to 1 liter with distilled water. Standardize versus 40.00 ml of 0.05 N Na_2CO_3 solution (5.3) with about 60 ml distilled water by titrating potentiometrically to pH about 5. Lift electrodes and rinse into beaker. Boil gently for 3–5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to the pH inflection point. Calculate normality using

$$N = \frac{A \times B}{53.00 \times C}$$

where:

A = g Na_2CO_3 weighed into 1 liter
B = ml Na_2CO_3 solution
C = ml acid used to inflection point

5.4.1.2 Standard acid, 0.02 N: Dilute appropriate amount of standard acid, 0.1 N (5.4.1.1) to 1 liter (200.00 ml if 0.1000 N). Check by standardization versus 15 ml of 0.05 N Na_2CO_3 solution (5.3).

5.4.1.3 Place 10.41 ml standard sulfuric acid, 0.02 N (5.4.1.2) in a 100 mL volumetric and dilute to the mark.

5.4.2 Standard sulfate solution from Na_2SO_4: Dissolve 147.9 mg anhydrous Na_2SO_4 in distilled water in a 1 liter volumetric flask and dilute to the mark with distilled water.

6. Procedure

6.1 Formation of barium sulfate turbidity

6.1.1 Place 100 ml sample, or a suitable portion diluted to 100 ml, into a 250 Erlenmeyer flask.

6.1.2 Add exactly 5.0 ml conditioning reagent (5.1).

6.1.3 Mix in the stirring apparatus.

6.1.4 While the solution is being stirred, add a measuring spoonful of $BaCl_2$ crystals (5.2) and begin timing immediately.

6.1.5 Stir exactly 1.0 minutes at constant speed.

6.2 Measurement of barium sulfate turbidity

6.2.1 Immediately after the stirring period has ended, pour solution into absorbance cell.

6.2.2 Measure turbidity at 30 second intervals for 4 minutes.

6.2.3 Record the maximum reading obtained in the 4 minute period.

6.3 Preparation of calibration curve.

6.3.1 Prepare calibration curve using standard sulfate solution (5.4).

6.3.2 Space standards at 5 mg/1 increments in the 0–40 mg/1 sulfate range.

6.3.3 Above 50 mg/1 the accuracy decreases and the suspensions lose stability.

6.3.4 Check reliability of calibration curve by running a standard with every 3 or 4 samples.

6.4 Correction for sample color and turbidity.

6.4.1 Run a sample blank using the procedure 6.1 and 6.2 without the addition of barium chloride (6.1.4).

7. Calculations

7.1 Read mg SO_4 from calibration curve

$$\text{mg } SO_4/l = \frac{\text{mg } SO_4 \times 1{,}000}{\text{ml sample}}$$

8. Precision and Accuracy

8.1 Thirty-four analysts in 16 laboratories analyzed six synthetic water samples containing exact increments of inorganic sulfate with the following results:

Increment as Sulfate mg/liter	Precision as Standard Deviation mg/liter	Accuracy as Bias, %	Accuracy as Bias mg/liter
8.6	2.30	-3.72	-0.3
9.2	1.78	-8.26	-0.8
110	7.86	-3.01	-3.3
122	7.50	-3.37	-4.1
188	9.58	+0.04	+0.1
199	11.8	-1.70	-3.4

(FWPCA Method Study 1, Mineral and Physical Analyses).

8.2 A synthetic unknown sample containing 259 mg/1 sulfate, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/1 Na, 241 mg/1 chloride, 0.250 mg/1 nitrite N, 1.1 mg/1 nitrate N, and 42.5 mg/1 total alkalinity (contributed by $NaHCO_3$) was analyzed in 19 laboratories by the turbidimetric method, with a relative standard deviation of 9.1% and a relative error of 1.2%.

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D516–68, Method B, p 430 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 496, Method 427C, (1975).

RESIDUE, FILTERABLE (Total Dissolved Solids)

Method 160.1 (Gravimetric, Dried at 180°C)

STORET NO. 70300

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 10 mg/1 to 20,000 mg/1.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.
   - 2.2 If Residue, Non-Filterable is being determined, the filtrate from that method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Filterable residue is defined as those solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.
4. Sample Handling and Preservation
   - 4.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride and/or sulfate may be hygroscopic and will require prolonged drying, desiccation and rapid weighing.
   - 5.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
   - 5.3 Too much residue in the evaporating dish will crust over and entrap water that will not be driven off during drying. Total residue should be limited to about 200 mg.
6. Apparatus
   - 6.1 Glass fiber filter discs, 4.7 cm or 2.1 cm, without organic binder, Reeve Angel type 934-AH, Gelman type A/E, or equivalent.
   - 6.2 Filter holder, membrane filter funnel or Gooch crucible adapter.
   - 6.3 Suction flask, 500 ml.
   - 6.4 Gooch crucibles, 25 ml (if 2.1 cm filter is used).
   - 6.5 Evaporating dishes, porcelain, 100 ml volume. (Vycor or platinum dishes may be substituted).
   - 6.6 Steam bath.
   - 6.7 Drying oven, 180°C ±2°C.
   - 6.8 Desiccator.

Approved for NPDES
Issued 1971

6.9 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the disc on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Discard washings.

7.2 Preparation of evaporating dishes: If Volatile Residue is also to be measured heat the clean dish to 550 ±50°C for one hour in a muffle furnace. If only Filterable Residue is to be measured heat the clean dish to 180 ±2°C for one hour. Cool in desiccator and store until needed. Weigh immediately before use.

7.3 Assemble the filtering apparatus and begin suction. Shake the sample vigorously and rapidly transfer 100 ml to the funnel by means of a 100 ml graduated cylinder. If total filterable residue is low, a larger volume may be filtered.

7.4 Filter the sample through the glass fiber filter, rinse with three 10 ml portions of distilled water and continue to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible.

7.5 Transfer 100 ml (or a larger volume) of the filtrate to a weighed evaporating dish and evaporate to dryness on a steam bath.

7.6 Dry the evaporated sample for at least one hour at 180 ±2°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained or until weight loss is less than 0.5 mg.

8. Calculation

8.1 Calculate filterable residue as follows:

$$\text{Filterable residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of dried residue + dish in mg
B = weight of dish in mg
C = volume of sample used in ml

9. Precision and Accuracy

9.1 Precision and accuracy are not available at this time.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 92, Method 208B, (1975).

(Total Suspended Solids)

RESIDUE, NON-FILTERABLE

Method 160.2 (Gravimetric, Dried at 103–105°C)

STORET NO. 00530

1. Scope and Application
   - 1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   - 1.2 The practical range of the determination is 4 mg/l to 20,000 mg/l.
2. Summary of Method
   - 2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
   - 2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
   - 3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
   - 4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   - 4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   - 5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
   - 5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
   - 6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.
     NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
   - 6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

Approved for NPDES
Issued 1971

NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Buchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fritted disc.

6.3 Suction flask.

6.4 Drying oven, 103–105°C.

6.5 Desiccator.

6.6 Analytical balance, capable of weighing to 0.1 mg.

7. Procedure

7.1 Preparation of glass fiber filter disc: Place the glass fiber filter on the membrane filter apparatus or insert into bottom of a suitable Gooch crucible with wrinkled surface up. While vacuum is applied, wash the disc with three successive 20 ml volumes of distilled water. Remove all traces of water by continuing to apply vacuum after water has passed through. Remove filter from membrane filter apparatus or both crucible and filter if Gooch crucible is used, and dry in an oven at 103–105°C for one hour. Remove to desiccator and store until needed. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg). Weigh immediately before use. After weighing, handle the filter or crucible/filter with forceps or tongs only.

7.2 Selection of Sample Volume

For a 4.7 cm diameter filter, filter 100 ml of sample. If weight of captured residue is less than 1.0 mg, the sample volume must be increased to provide at least 1.0 mg of residue. If other filter diameters are used, start with a sample volume equal to 7 ml/cm^2 of filter area and collect at least a weight of residue proportional to the 1.0 mg stated above.

NOTE: If during filtration of this initial volume the filtration rate drops rapidly, or if filtration time exceeds 5 to 10 minutes, the following scheme is recommended: Use an unweighed glass fiber filter of choice affixed in the filter assembly. Add a known volume of sample to the filter funnel and record the time elapsed after selected volumes have passed through the filter. Twenty-five ml increments for timing are suggested. Continue to record the time and volume increments until fitration rate drops rapidly. Add additional sample if the filter funnel volume is inadequate to reach a reduced rate. Plot the observed time versus volume filtered. Select the proper filtration volume as that just short of the time a significant change in filtration rate occurred.

7.3 Assemble the filtering apparatus and begin suction. Wet the filter with a small volume of distilled water to seat it against the fritted support.

7.4 Shake the sample vigorously and quantitatively transfer the predetermined sample volume selected in 7.2 to the filter using a graduated cylinder. Remove all traces of water by continuing to apply vacuum after sample has passed through.

7.5 With suction on, wash the graduated cylinder, filter, non-filterable residue and filter funnel wall with three portions of distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

NOTE: Total volume of wash water used should equal approximately 2 ml per cm^2. For a 4.7 cm filter the total volume is 30 ml.

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B) \times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

AIW FRANK #5

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General Descrition of analytical services requested:

   Extraction of 3 sediment samples by the TCLP Extraction method with the extracts being analyzed for the organic TCLP Parameters by the 3/90 CLP Organic SOW and SW-846, Method 8150. Add pyridine and 3 methylphenol to the semivolatile method target list. See Attachment 2 for the full TCLP constituent list.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   3 low/medium concentration sediment samples from offsite locations and 2 rinsate blanks to be subjected to the TCLP extraction procedure and the extracts analyzed for the organic TCLP parameters. Analyze VOAs, BNAs, and Pesticides by the 3/90 CLP SOW and the herbicides by SW 846, Method 8150.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

   RI/FS - ARCS III

SAS Approved By (signature):
Date:

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of

6. **Number of days analysis and data required after laboratory receipt of samples:**

Completed data packages are due within 35 days from receipt of last sample.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

TCLP Extraction - Appendix II of 40 CFR 261.

TCLP Organic Parameters Analysis (VOAs, BNAs, Pesticides) by the 3/90 CLP Organic SOW.

TCLP Herbicide Analysis by SW 846, Method 8150.

Results are to be reported in ug/L.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

All raw data. Deliverables as per the CLP SOWs. In addition, copies of TCLP extraction log book, signed and dated copy of chain-of-custody documentation, copies of air bill confirming sample receipt, and SAS Request Form are also required. TCLP extraction must be indicated on all Form I's.

10. **Other (use additional sheets or attach supplementary information, as needed):**

Laboratory must comply with the CSF requirements as specified in the 3/90 SOW. Laboratory will be responsible for the disposal of all sample remnants and extracts.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation
(412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)
TCLP organic compounds	As per 3/90 CLP SOW and SW 846, Method 8150	As per 3/90 CLP SOW and SW 846, Method 8150

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
TCLP organic compounds	As per 3/90 CLP SOW and SW 846, Method 8150	As per 3/90 CLP SOW and SW 846, Method 8150

See Attachment 1 for additional requirements.

14. **Action Required if Limits are Exceeded:**

As per 3/90 CLP SOW.

15. **Request Prepared By:**

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991; revised September 5, 1991.

16. **Request Reviewed By (CRL use only):**
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

ATTACHMENT 1

13. QC Requirements: For TCLP Organics by OLM01.0 (3/90), follow QC requirements specified in the SOW with the following deviations.

13.A. All TCLP target compounds must be spiked. Report all recoveries but do not perform recovery correction. Chlordane and Toxaphene will require separate leachate aliquots for the matrix spike because of their multicomponent responses. Generation of sufficient leachate volume for spiking may require the lab to spike leachate aliquots from more than one sample. Matrix spike duplicates are not required except for herbicides if volume allows as stated below.

13.B. Pyridine and 3-Methylphenol must be added to the semivolatile analysis. Achieve the following criteria for Pyridine and 3-Methylphenol:

* Calibrate at 5 levels.
* Minimum relative response factor = 0.010
* Quantitate using the internal standard with the closest retention time (must be free of interferences) to the Pyridine and 3-Methylphenol peaks individually.
* Quantitate using the most abundant m/z that is free of interferences. Major ions for Pyridine are 79, 52, 51 and 50 (descending abundance). Major ions for 3-Methylphenol are 107, 108, 77, 79, 90. If coelution occurs among some or all of the Methylphenol isomers, the quantitation method and the final report (Form Is) must reflect the sum of the isomers (e.g., Total 2 and 3-Methylphenol or Total Cresol).

13.C. For analysis of 2,4-D, 2,4,5-T, 2,4,6-T and Silvex, follow QC specified in SW 846 method 8150.

* Perform a matrix spike (60-120% recovery) and, if volume allows, a matrix spike duplicate (<30 RPD).
* Perform a sample duplicate (<30 RPD).
* Perform a method blank (<MDL for all target compounds).
* If greater than %50 separation cannot be achieved for 2,4,5-T and 2,4,6-T, quantitate and report as total Trichlorophenol.

Attachment 2

alculated regulatory level (i.e., the hronic toxicity reference level ultiplied by the DAF) is below the ical quantitation limit, the quantitation limit is the final regulatory level. Note that the list of constituents in Table II.2 contains the 14 constituents currently regulated under the existing EPTC. As specified in today's rule, these constituents will continue to be regulated at their current levels.

TABLE II.2.—TOXICITY CHARACTERISTIC CONSTITUENTS AND REGULATORY LEVELS

EPA HW No.[1]	Constituent (mg/L)	CAS No.[2]	Chronic toxicity reference level (mg/L)	Regulatory level[3] (mg/L)
004	Arsenic	7440-38-2	0.05	5.0
005	Barium	7440-39-3	1.0	100.0
018	Benzene	71-43-2	0.005	0.5
006	Cadmium	7440-43-9	0.01	1.0
019	Carbon tetrachloride	56-23-5	0.005	0.5
020	Chlordane	57-74-9	0.0003	0.03
021	Chlorobenzene	108-90-7	1	100.0
022	Chloroform	67-66-3	0.06	6.0
007	Chromium	7440-47-3	0.05	5.0
023	o-Cresol	95-48-7	2	[4] 200.0
024	m-Cresol	108-39-4	2	[4] 200.0
025	p-Cresol	106-44-5	2	[4] 200.0
026	Cresol		2	[4] 200.0
016	2,4-D	94-75-7	0.1	10.0
027	1,4-Dichlorobenzene	106-46-7	0.075	7.5
028	1,2-Dichloroethane	107-06-2	0.005	0.5
029	1,1-Dichloroethylene	75-35-4	0.007	0.7
030	2,4-Dinitrotoluene	121-14-2	0.0005	[4] 0.13
012	Endrin	72-20-8	0.0002	0.02
031	Heptachlor (and its hydroxide)	76-44-8	0.00008	0.008
032	Hexachlorobenzene	118-74-1	0.0002	[4] 0.13
033	Hexachloro-1,3-butadiene	87-68-3	0.005	0.5
034	Hexachloroethane	67-72-1	0.03	3.0
008	Lead	7439-92-1	0.05	5.0
013	Lindane	58-89-9	0.004	0.4
009	Mercury	7439-97-6	0.002	0.2
014	Methoxychlor	72-43-5	0.1	10.0
035	Methyl ethyl ketone	78-93-3	2	200.0
036	Nitrobenzene	98-95-3	0.02	2.0
037	Pentachlorophenol	87-86-5	1	100.0
038	Pyridine	110-86-1	0.04	[4] 5.0
010	Selenium	7782-49-2	0.01	1.0
011	Silver	7440-22-4	0.05	5.0
039	Tetrachloroethylene	127-18-4	0.007	0.7
015	Toxaphene	8001-35-2	0.005	0.5
040	Trichloroethylene	79-01-6	0.005	0.5
041	2,4,5-Trichlorophenol	95-95-4	4	400.0
042	2,4,6-Trichlorophenol	88-06-2	0.02	2.0
017	2,4,5-TP (Silvex)	93-72-1	0.01	1.0
043	Vinyl chloride	75-01-4	0.002	0.2

[1] Hazardous waste number.
[2] Chemical abstracts service number.
[3] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.
[4] If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level for total cresol is 200 mg/l.

he regulatory levels reflect lifications to some chronic toxicity rence levels since the original posal. EPA has revised some of the imum Contaminant Levels, Risk-cific Doses, and Reference Doses to ct new data and better methods. In onse to comments received, EPA decided not to apportion reference s of noncarcinogens to account for iple routes of exposure, as was nally proposed (51 FR 21648). See on III.C for further discussion of nents on apportionment and the cy's reasons for not including rtionment of reference doses in the Today's rule also promulgates to replace the EP. The TCLP nts an improvement over the EP at it more accurately addresses leaching potential for use in evaluating wastes containing organic constituents, and also corrects several minor technical deficiencies in the original EP. The version of the TCLP promulgated today reflects additional improvements and modifications made to the TCLP since the original proposal. The TCLP promulgated today will also replace the earlier version of the TCLP promulgated as part of the land disposal restrictions program.

Today's rule incorporates a schedule for compliance that classifies the universe of potentially affected TC waste handlers into two groups: (1) All generators of greater than 100 kg/month and less than 1,000 kg/month of hazardous waste (small-quantity generators) must come into compliance with the subtitle C requirements for management of their TC waste within 1 year; and (2) all generators of 1,000 kg/month or more of hazardous waste are required to comply with all subtitle C requirements for TC wastes within 6 months. The phased schedule for compliance is further discussed in section V.

Wastes identified as hazardous under the Toxicity Characteristic will also become hazardous substances under section 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), as amended. Today's rule amends the list of reportable quantities (RQs) in 40 CFR part 302 by adding appropriate values for each of the new 25 TC toxicants. All of the newly-

AR300700

AIW FRANK #5a.

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General Descrition of analytical services requested:

   Extraction of 3 sediment samples by the TCLP Extraction method with the extracts being analyzed for the TCLP Metals by the 3/90 CLP Inorganic SOW. See Attachment 1 for the full list of TCLP metals .

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   3 low/medium concentration sediment samples from offsite locations and 2 rinsate blanks to be subjected to the TCLP extraction procedure and the extracts analyzed for TCLP metals. See Attachment 1 for the full list of TCLP metals.

3. Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):

   RI/FS - ARCS III

SAS Approved By (signature):
Date:

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of .

6. **Number of days analysis and data required after laboratory receipt of samples:**

Completed data packages are due within 35 days from receipt of last sample.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

TCLP Extraction - Appendix II of 40 CFR 261.

TCLP Metals Analysis - 3/90 CLP Inorganic SOW

TCLP results are to be reported in ug/L.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

All raw data. Deliverables as per the CLP SOWs. In addition, copies of TCLP extraction log book, signed and dated copy of chain-of-custody documentation, copies of air bill confirming sample receipt, and SAS Request Form are also required. TCLP extraction must be indicated on the Form I's.

10. **Other (use additional sheets or attach supplementary information, as needed):**

Laboratory must comply with CSF requirements as specified in the 3/90 SOW. Laboratory will be responsible for the disposal of all sample remnants and extracts.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation
(412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)
TCLP Metals	As per 3/90 CLP SOW	As per 3/90 CLP SOW

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
TCLP Metals	As per 3/90 CLP SOW	As per 3/90 CLP SOW

With the following deviation:

Spike one TCLP leachate with all of the TCLP regulated metals. Provide all recovery data but do not perform recovery corrections.

14. **Action Required if Limits are Exceeded:**

As per 3/90 CLP SOW.

15. **Request Prepared By:**

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991.

16. **Request Reviewed By (CRL use only):**
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

Attachment 1

calculated regulatory level (i.e., the chronic toxicity reference level multiplied by the DAF) is below the analytical quantitation limit, the quantitation limit is the final regulatory level. Note that the list of constituents in Table II.2 contains the 14 constituents currently regulated under the existing EPTC. As specified in today's rule, these constituents will continue to be regulated at their current levels.

TABLE II.2.—TOXICITY CHARACTERISTIC CONSTITUENTS AND REGULATORY LEVELS

EPA HW No [1]	Constituent (mg/L)	CAS No [2]	Chronic toxicity reference level (mg/L)	Regulatory level (mg/L)
D004	Arsenic	7440-38-2	0.05	5.0
D005	Barium	7440-39-3	1.0	100.0
D018	Benzene	71-43-2	0.005	0.5
D006	Cadmium	7440-43-9	0.01	1.0
D019	Carbon tetrachloride	56-23-5	0.005	0.5
D020	Chlordane	57-74-9	0.0003	0.03
D021	Chlorobenzene	108-90-7	1	100.0
D022	Chloroform	67-66-3	0.06	6.0
D007	Chromium	7440-47-3	0.05	5.0
D023	o-Cresol	95-48-7	2	[4] 200.0 *
D024	m-Cresol	108-39-4	2	[4] 200.0 *
D025	p-Cresol	106-44-5	2	[4] 200.0 *
D026	Cresol		2	[4] 200.0 *
D016	2,4-D	94-75-7	0.1	10.0
D027	1,4-Dichlorobenzene	106-46-7	0.075	7.5
D028	1,2-Dichloroethane	107-06-2	0.005	0.5
D029	1,1-Dichloroethylene	75-35-4	0.007	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.0005	[3] 0.13
D012	Endrin	72-20-8	0.0002	0.02
	Heptachlor (and its hydroxide)	76-44-8	0.00008	0.008
	Hexachlorobenzene	118-74-1	0.0002	[3] 0.13
	Hexachloro-1,3-butadiene	87-68-3	0.005	0.5
	Hexachloroethane	67-72-1	0.03	3.0
	Lead	7439-92-1	0.05	5.0
D013	Lindane	58-89-9	0.004	0.4
D009	Mercury	7439-97-6	0.002	0.2
D014	Methoxychlor	72-43-5	0.1	10.0
D035	Methyl ethyl ketone	78-93-3	2	200.0
D036	Nitrobenzene	98-95-3	0.02	2.0 *
D037	Pentachlorophenol	87-86-5	1	100.0 *
D038	Pyridine	110-86-1	0.04	[3] 5.0 *
D010	Selenium	7782-49-2	0.01	1.0
D011	Silver	7440-22-4	0.05	5.0
D039	Tetrachloroethylene	127-18-4	0.007	0.7
D015	Toxaphene	8001-35-2	0.005	0.5
D040	Trichloroethylene	79-01-6	0.005	0.5
D041	2,4,5-Trichlorophenol	95-95-4	4	400.0 *
D042	2,4,6-Trichlorophenol	88-06-2	0.02	2.0 *
D017	2,4,5-TP (Silvex)	93-72-1	0.01	1.0
D043	Vinyl chloride	75-01-4	0.002	0.2

[1] Hazardous waste number.
[2] Chemical abstracts service number.
[3] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.
[4] If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level for total cresol is 200 mg/l.

The regulatory levels reflect modifications to some chronic toxicity reference levels since the original proposal. EPA has revised some of the Maximum Contaminant Levels, Risk-Specific Doses, and Reference Doses to reflect new data and better methods. In response to comments received, EPA has decided not to apportion reference doses of noncarcinogens to account for multiple routes of exposure, as was originally proposed (51 FR 21648). See section III.C for further discussion of comments on apportionment and the agency's reasons for not including apportionment of reference doses in the final rule. Today's rule also promulgates the TCLP to replace the EP. The TCLP presents an improvement over the EP in that it more accurately addresses leaching potential for use in evaluating wastes containing organic constituents, and also corrects several minor technical deficiencies in the original EP. The version of the TCLP promulgated today reflects additional improvements and modifications made to the TCLP since the original proposal. The TCLP promulgated today will also replace the earlier version of the TCLP promulgated as part of the land disposal restrictions program.

Today's rule incorporates a schedule for compliance that classifies the universe of potentially affected TC waste handlers into two groups: (1) All generators of greater than 100 kg/month and less than 1,000 kg/month of hazardous waste (small-quantity generators) must come into compliance with the subtitle C requirements for management of their TC waste within 1 year; and (2) all generators of 1,000 kg/month or more of hazardous waste are required to comply with all subtitle C requirements for TC wastes within 6 months. The phased schedule for compliance is further discussed in section V.

Wastes identified as hazardous under the Toxicity Characteristic will also become hazardous substances under section 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA), as amended. Today's rule amends the list of reportable quantities (RQs) in 40 CFR part 302 by adding appropriate values for each of the new 25 TC toxicants. All of the newly-

AIW FRANK #6

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General Descrition of analytical services requested:**

   Analysis of 10 sediment samples for pH, Oxidation-Reduction Potential (Eh), and specific conductance, and 3 sediment samples for Cation Exchange Capacity (CEC) by the methods listed in Item 7. Sodium determination as per the 3/90 Inorganic CLP SOW.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   10 low concentration sediment samples for pH, Eh, and specific conductance, and 3 low concentration sediment samples for CEC.

3. **Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):**

   RI/FS - ARCS III

SAS Approved By (signature):
Date:

4. **Estimated date(s) of collection:**

   To be determined.

5. **Estimated date(s) and method of shipment:**

   To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of .

6. **Number of days analysis and data required after laboratory receipt of samples:**

   pH and Eh must be analyzed within 48 hours of VTSR and Conductance within 24 hours of VTSR for each sample. Written results within 35 days of the receipt of the last sample.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

   pH - SW 846, Method 9045.

   Specific Conductance - EPA 120.1, Methods for Chemical Analysis of Water and Wastewater. See Attachment 2.

   Eh - ASTM D-1498. A slurry will have to be created using deionized water if the moisture content of the sediment is not high enough to allow the specific conductance or the Eh to be measured. Stir for at least half an hour. Refer to SW9045 Section 7.2.

   CEC - SW 846 - 9081

   All methods are attached.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

   See Attachment 1.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

   See Attachment 2.

10. **Other (use additional sheets or attach supplementary information, as needed):**

    Laboratory must comply with purge file requirements. Contact SMO for details.

11. **Name of sampling/handling contact:**

    Jeff Orient - NUS Corporation
    (412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)
pH buffer check standard (1/10) should be within 0.05 pH units.		
CEC	1 meq/100 g	± 20%
Sodium	as per CLP SOW	as per CLP SOW

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
pH audit Material (EPA or commercially available)	1/10	95% CI (include true values with data)
Specific Conductance (EPA or commercially available)	1/10	95% CI (include true values with data)
Duplicate (Eh and pH)	1/10	± 10 mv/± 0.3 pH units
Eh and Spec. Cond. Blank (only if water has been added)	1/10	Blank should not register an Eh or Spec. Cond.
Sodium	as per CLP SOW	as per CLP SOW
pH meter calibration	daily	
CEC method blank	analyze 1 blank as per Section 8.2 of method 9081	≤ Method Det. Limit

14. Action Required if Limits are Exceeded:

Re-analyze samples once more and report both sets of data and all associated QC.

15. Request Prepared By:

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991; revised September 5, 1991.

16. Request Reviewed By (CRL use only):
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.

ATTACHMENT 1

Calibrate pH meter using 4.0, 7.0 and 10.0 buffers. Indicate expiration date for each buffer with lot number. Document dates of analysis and submit written worksheet of results.

ATTACHMENT 2

Raw data, calculations, data sheets, blank results, duplicate results, signed and dated chain-of-custody documentation, SAS packing list, copy of the air bill confirming sample receipt, and SAS request form. Narrative must include description of the process used to obtain the Eh and Specific conductance readings and the weights and volumes used.

Provide all certified reference materials (audits) sheets from manufacturer with true values and lot numbers.

Specific Conductance - Document instrument standardization and cell calibration. Also utilize cell constant in calculations. Provide all calculations.

METHOD 9045

SOIL pH

1.0 SCOPE AND APPLICATION

1.1 Method 9045 is an electrometric procedure which has been approved for measuring pH in calcareous and noncalcareous soils.

2.0 SUMMARY OF METHOD

2.1 The soil sample is mixed either with Type II water or with a calcium chloride solution (see Section 5.0), depending on whether the soil is considered calcareous or noncalcareous. The pH of the solution is then measured with a pH meter.

3.0 INTERFERENCES

3.1 Samples with very low or very high pH may give incorrect readings on the meter. For samples with a true pH of >10, the measured pH may be incorrectly low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions, with a true pH of <1, may give incorrectly high pH measurements.

3.2 Temperature fluctuations will cause measurement errors.

3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that will not rinse free, the electrode can either (1) be cleaned with an ultrasonic bath, or (2) be washed with detergent, rinsed several times with water, placed in 1:10 HCl so that the lower third of the electrode is submerged, and then thoroughly rinsed with water.

4.0 APPARATUS AND MATERIALS

4.1 pH Meter with means for temperature compensation.

4.2 Electrodes:

4.2.1 Calomel electrode.

4.2.2 Glass electrode.

4.2.3 A combination electrode can be employed instead of calomel or glass.

4.5 Beaker: 50-mL.

4.6 Volumetric flask: 2-Liter.

4.7 Volumetric flask: 1-Liter.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Primary standard buffer salts are available from the National Bureau of Standards (NBS) and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling, such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.3 Secondary standard buffers may be prepared from NBS salts or purchased as solutions from commercial vendors. These commercially available solutions, which have been validated by comparison with NBS standards, are recommended for routine use.

5.4 Stock calcium chloride solution ($CaCl_2$), 3.6 M: Dissolve 1059 g of $CaCl_2 \cdot 2H_2O$ in Type II water in a 2-liter volumetric flask. Cool the solution, dilute it to volume with Type II water, and mix it well. Dilute 20 mL of this solution to 1 liter with Type II water in a volumetric flask and standardize it by titrating a 25-mL aliquot of the diluted solution with standard 0.1 N $AgNO_3$, using 1 mL of 5% K_2CrO_4 as the indicator.

5.5 Calcium chloride ($CaCl_2$), 0.01 M: Dilute 50 mL of stock 3.6 M $CaCl_2$ to 18 liters with Type II water. If the pH of this solution is not between 5 and 6.5, adjust the pH by adding a little $Ca(OH)_2$ or HCl. As a check on the preparation of this solution, measure its electrical conductivity. The specific conductivity should be 2.32 $\pm$ 0.08 mmho per cm at 25°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration:

7.1.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Sample preparation and pH measurement of noncalcareous soils:

7.2.1 To 20 g of soil in a 50-mL beaker, add 20 mL of Type II water and stir the suspension several times during the next 30 min.

7.2.2 Let the soil suspension stand for about 1 hr to allow most of the suspended clay to settle out from the suspension.

7.2.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrodes into the sample solution in this manner. For combination electrodes, immerse just below the suspension.

7.2.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.2.5 Report the results as "soil pH measured in water."

7.3 Sample preparation and pH measurement of calcareous soils:

7.3.1 To 10 g of soil in a 50-mL beaker, add 20 mL of 0.01 M $CaCl_2$ (Step 5.5) solution and stir the suspension several times during the next 30 min.

7.3.2 Let the soil suspension stand for about 30 min to allow most of the suspended clay to settle out from the suspension.

7.3.3 Adjust the electrodes in the clamps of the electrode holder so that, upon lowering the electrodes into the beaker, the glass electrode will be immersed well into the partly settled suspension and the calomel electrode will be immersed just deep enough into the clear supernatant solution to establish a good electrical contact through the ground-glass joint or the fiber-capillary hole. Insert the electrode into the sample solution in this manner.

7.3.4 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected.

7.3.5 Report the results as "soil pH measured in 0.01 M $CaCl_2$".

8.0 QUALITY CONTROL

8.1 Duplicate samples and check standards should be analyzed routinely.

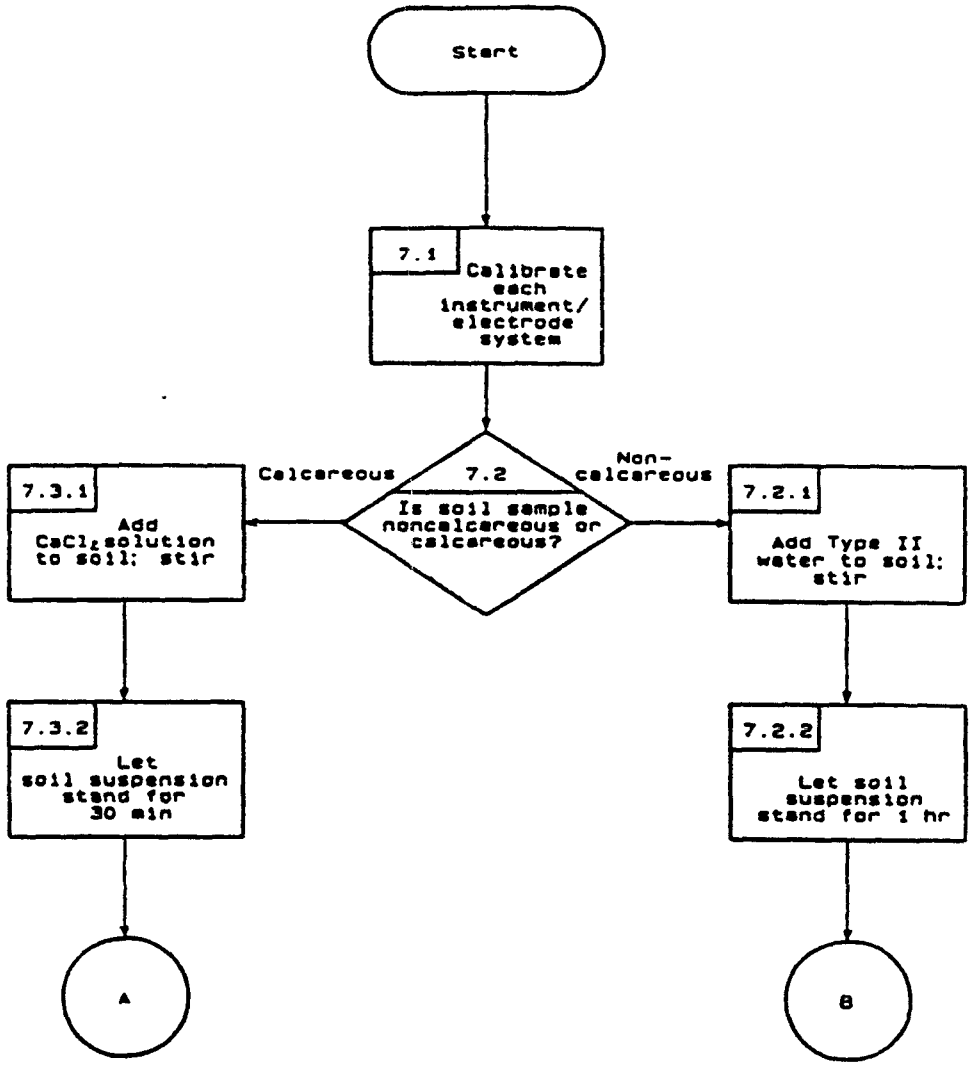
8.2 Electrodes must be thoroughly rinsed between samples.

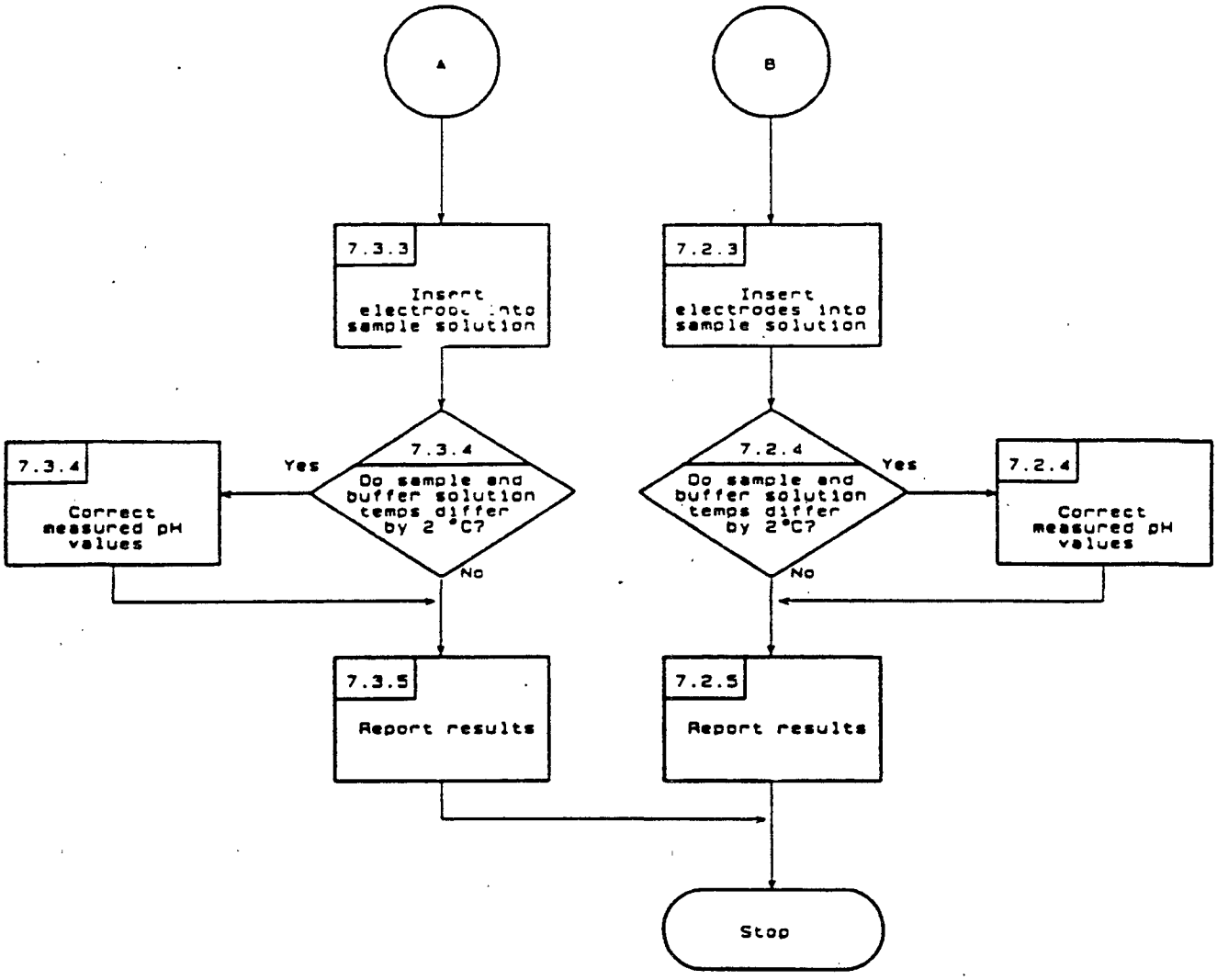
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 None required.


Start
7.1
Calibrate each instrument/ electrode system
7.2
Is soil sample noncalcareous or calcareous?
Calcareous
Non-calcareous
7.3.1
Add $CaCl_2$ solution to soil; stir
7.3.2
Let soil suspension stand for 30 min
A
7.2.1
Add Type II water to soil; stir
7.2.2
Let soil suspension stand for 1 hr
B


A
B
7.3.3
Insert electrode into sample solution
7.2.3
Insert electrodes into sample solution
7.3.4
Do sample and buffer solution temps differ by 2 °C?
Yes
No
7.3.4
Correct measured pH values
7.2.4
Do sample and buffer solution temps differ by 2°C?
Yes
No
7.2.4
Correct measured pH values
7.3.5
Report results
7.2.5
Report results
Stop

CONDUCTANCE

Method 120.1 (Specific Conductance, umhos at 25°C)

STORET NO. 00095

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline wates, domestic and industrial wastes and acid rain (atmospheric deposition).
2. Summary of Method
   2.1 The specific conductance of a sample is measured by use of a self-contained conductivity meter, Wheatstone bridge-type, or equivalent.
   2.2 Samples are preferable analyzed at 25°C. If not, temprature corrections aremade and results reported at 25°C.
3. Comments
   3.1 Instrument must be standardized with KCl solution before daily use.
   3.2 Conductivity cell must be kept clean.
   3.3 Field measurements with comparable instruments are reliable.
   3.4 Temperature variations and corrections represent the largest source of potential error.
4. Sample Handling and Preservation
   4.1 Analyses can be performed either in the field or laboratory.
   4.2 If analysis is not completed within 24 hours of sample collection, sample should be filtered through a 0.45 micron filter and stored at 4°C. Filter and apparatus must be washed with high quality distilled water and pre-rinsed with sample before use.
5. Apparatus
   5.1 Conductivity bridge, range 1 to 1000 μmho per centimeter.
   5.2 Conductivity cell, cell constant 1.0 or micro dipping type cell with 1.0 constant. YSI #3403 or equivalent.
   5.4 Thermometer
6. Reagents
   6.1 Standard potassium chloride solutions, 0.01 M: Dissolve 0.7456 gm of pre-dried (2 hour at 105°C) KCl in distilled water and dilute to 1 liter at 25°C.
7. Cell Calibration
   7.1 The analyst should use the standard potassium chloride solution (6.1) and the table below to check the accuracy of the cell constant and conductivity bridge.

Approved for NPDES
Issued 1971
Editorial revision, 1982

Conductivity 0.01 m KCl

°C	Micromhos/cm
21	1305
22	1332
23	1359
24	1386
25	1413
26	1441
27	1468
28	1496

8. Procedure
   - 8.1 Follow the direction of the manufacturer for the operation of the instrument.
   - 8.2 Allow samples to come to room temperature (23 to 27°C), if possible.
   - 8.3 Determine the temperature of samples within 0.5°C. If the temperature of the samples is not 25°C, make temperature correction in accordance with the instruction in Section 9 to convert reading to 25°.
9. Calculation
   - 9.1 These temperature corrections are based on the standard KCl solution.
     - 9.1.1 If the temperature of the sample is below 25°C, add 2% of the reading per degree.
     - 9.1.2 If the temperature is above 25°C, subtract 2% of the reading per degree.
   - 9.2 Report results as Specific Conductance, μmhos/cm at 25°.
10. Precision and Accuracy
    - 10.1 Forty-one analysts in 17 laboratories analyzed six synthetic water samples containing increments of inorganic salts, with the following results:

Increment as Specific Conductance	Precision as Standard Deviation	Accuracy as Bias, %	Accuracy as Bias, μmhos/cm
100	7.55	-2.02	-2.0
106	8.14	-0.76	-0.8
808	66.1	-3.63	-29.3
848	79.6	-4.54	-38.5
1640	106	-5.36	-87.9
1710	119	-5.08	-86.9

(FWPCA Method Study 1, Mineral and Physical Analyses.)

10.2 In a single laboratory (EMSL) using surface water samples with an average conductivity of 536 μmhos/cm at 25°C, the standard deviation was ±6.

Bibliography

1. The procedure to be used for this determination is found in:
   Annual Book of ASTM Standards Part 31, "Water," Standard D1125-64, p. 120 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 71, Method 205 (1975).
3. Instruction Manual for YSI Model 31 Conductivity Bridge.
4. Peden, M. E., and Skowron. "Ionic Stability of Precipitation Samples," Atmospheric Environment, Vol. 12, p. 2343-2344, 1978.

Designation: D 1498 – 76 (Reapproved 1981)ε¹

Standard Practice for OXIDATION-REDUCTION POTENTIAL OF WATER[1]

This standard is issued under the fixed designation D 1498; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε¹ NOTE—New Section 7.9 was editorially added in December 1982.

1. Scope

1.1 This practice covers the apparatus and procedure for the electrometric measurement of oxidation-reduction potential (ORP) in water. It does not deal with the manner in which the solutions are prepared, the theoretical interpretation of the oxidation-reduction potential, or the establishment of a standard oxidation-reduction potential for any given system. The practice described has been designed for the routine and process measurement of oxidation-reduction potential.

2. Applicable Documents

2.1 *ASTM Standards:*

D 1129 Definitions of Terms Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 3370 Practices for Sampling Water[2]

3. Summary of Practice

3.1 This is a practice designed to measure the ORP which is defined as the electromotive force between a noble metal electrode and a reference electrode when immersed in a solution. The practice describes the electronic equipment available to make the measurement and describes how to determine the sensitivity of the electrodes as well as the calibration of equipment to solutions having a known potential. The ORP electrodes are inert and measure the ratio of the activities of the oxidized to the reduced species in the process reactions.

4. Definitions

4.1 The term "oxidation-reduction potential" used in this method is defined in accordance with Definitions D 1129 as follows:

4.1.1 *oxidation-reduction potential*—the electromotive force developed by a noble metal electrode immersed in the water, referred to the standard hydrogen electrode.

4.1.2 The oxidation-reduction potential (ORP) of a process solution can be described as the millivolt signal, E_m, produced when a noble metal electrode and a reference electrode are placed in water. The millivolt signal produced can be represented as follows:

$$E_m = E^\circ + 2.3\frac{RT}{nF}\log A_{ox}/A_{red}$$

where:

E_m = ORP,

E° = constant that depends on the choice of reference electrodes.

F = Faraday constant,

R = gas constant,

T = absolute temperature, °C + 273.15,

n = number of electrons involved in process reaction, and

A_{ox} and A_{red} = activities of the reactants in the process.

4.2 For definitions of other items used in this method, refer to Definitions D 1129.

[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.09 on Saline and Brackish Water.

Current edition approved Sept. 24, 1976. Published November 1976. Originally published as D 1498 – 57 T. Last previous edition D 1498 – 59 (1970).

[2] *Annual Book of ASTM Standards*, Vol 11.01.

5. Interferences

5.1 The ORP electrodes reliably measured ORP in nearly all aqueous solutions and in general are not subject to solution interference from color, turbidity, colloidal matter, and suspended matter.

5.2 The ORP of an aqueous solution is sensitive to change in temperature of the solution, but temperature correction is rarely done due to its minimal effect and complex reactions. Temperature corrections are usually applied only when it is desired to relate the ORP to the activity of an ion in the solutions.

5.3 The ORP of an aqueous solution is sensitive to pH variations when the oxidation-reduction reaction involves either hydrogen or hydroxyl ions. The ORP generally tends to increase with an increase in hydrogen ions and to decrease with an increase in hydroxyl ions during such reactions.

5.4 Reproducible oxidation-reduction potentials cannot be obtained for chemical systems that are not reversible. The measurement of end point potential in oxidation-reduction titration is sometimes of this type.

5.5 If the metallic portion of the ORP electrode is sponge-like, materials absorbed from solutions may not be washed away, even by repeated rinsings. In such cases, the electrode may exhibit a memory effect, particularly if it is desired to detect a relatively low concentration of a particular species immediately after a measurement has been made in a relatively concentrated solution. A brightly polished metal electrode surface is required for accurate measurements.

5.6 The ORP resulting from interactions among several chemical systems present in mixed solutions may not be assignable to any single chemical.

6. Apparatus

6.1 *Meter*—Most laboratory pH meters can be used for measurements of ORP by substitution of an appropriate set of electrodes and meter scale. The characteristics of a variety of laboratory meters are shown in Table 1. The choice will depend on the accuracy desired in the determination.

6.1.1 Most process pH meters can be used for measurement of ORP by substitution of an appropriate set of electrodes and meter scale. These instruments are generally much more rugged than those which are used for very accurate measurements in the laboratory. Usually, these more rugged instruments produce results that are somewhat less accurate and precise than those obtained from laboratory instruments. The characteristics of three types of process ORP analyzers are presented in Table 2. Each of these analyzers is satisfactory for process ORP measurements. The choice of analyzer is generally based on how closely the characteristics of the analyzer match the requirements of the application. Typical factors which may be considered include, for example, the types of signals which the analyzer can produce to drive external devices, and the span ranges available.

6.1.2 For remote ORP measurements the potential generated can be transmitted to an external indicating meter. Special shielded cable is required to transmit the signal.

6.2 *Reference Electrode*—A calomel, silver-silver chloride, or other reference electrode of constant potential shall be used. If a saturated calomel electrode is used, some potassium chloride crystals shall be contained in the saturated potassium chloride solution. If the reference electrode is of the flowing junction type, the design of the electrode shall allow for each measurement a fresh liquid junction to be formed between the solution of potassium chloride and the standard or the test solution. The electrode design shall also allow traces of solution to be washed from the outer surfaces of the electrodes. To ensure the desired slow outward flow of the reference-electrode solution, the solution pressure inside the liquid junction should be somewhat in excess of that outside the junction. In nonpressurized applications this requirement can be met by maintaining the inside solution level higher than the outside solution level. If the reference electrode is of the nonflowing junction type, these outward flow and pressurization considerations shall not apply. The reference electrode and junction shall perform satisfactorily as required in the procedure for checking sensitivity described in Section 9.

6.3 *Oxidation-Reduction Electrode*—A noble metal is used in the construction of oxidation-reduction electrodes. The most common metals employed are: platinum, gold, and silver. It is

important to sel
by the test solu
electrode shall
metal comes in
The area of the
test solution shc

6.4 *Electrode*
electrode holde
for laboratory
styles of electro
ious process app
in an open tan
vessel, or a high

7. Reagents an

7.1 *Purity c*
chemicals shall
otherwise indic
agents shall con
Committee on
American Che
may be used,
that the reagent
permit its use w
the determinati

7.2 *Purity of*
cated, reference
mean reagent
tions D 1193, T

7.3 *Aqua Re*
trated nitric ac
volumes of cc
(HCl, sp gr 1.1
enough solutio
requirements.

7.4 *Buffer St*
buffer salts ava
of Standards sp
standard buffe
numbers and d

7.4.1 *Phthalc*
(pH_s = 4.00 a
potassium hydr
water and dilut

7.4.2 *Phosph*
(pH_s = 6.86 at
tassium dihydr
3.53 g of anhy
phate (Na_2HPO

7.5 *Chromic*
solve about 5
($K_2Cr_2O_7$) in 5

important to select a metal that is not attacked by the test solution. The construction of the electrode shall be such that only the noble metal comes in contact with the test solution. The area of the noble metal in contact with the test solution should be approximately 1 cm^2.

6.4 *Electrode Assembly*—A conventional electrode holder or support can be employed for laboratory measurements. Many different styles of electrode holders are suitable for various process applications such as measurements in an open tank, process pipe line, pressure vessel, or a high pressure sample line.

7. Reagents and Materials

7.1 *Purity of Reagents*—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.[3] 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 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specifications D 1193, Type II.

7.3 *Aqua Regia*—Mix 1 volume of concentrated nitric acid (HNO_3, sp gr 1.42) with 3 volumes of concentrated hydrochloric acid (HCl, sp gr 1.18). It is recommended that only enough solution be prepared for immediate requirements.

7.4 *Buffer Standard Salts*—Table 3 lists the buffer salts available from the National Bureau of Standards specifically for the preparation of standard buffer solutions. The NBS included numbers and drying procedures.

7.4.1 *Phthalate Reference Buffer Solution* (pH_s = 4.00 at 25°C)—Dissolve 10.12 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water and dilute to 1 L.

7.4.2 *Phosphate Reference Buffer Solution* (pH_s = 6.86 at 25°C)—Dissolve 3.39 g of potassium dihydrogen phosphate (KH_2PO_4) and 3.53 g of anhydrous disodium hydrogen phosphate (Na_2HPO_4) in water and dilute to 1 L.

7.5 *Chromic Acid Cleaning Solution*—Dissolve about 5 g of potassium dichromate ($K_2Cr_2O_7$) in 500 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84).

7.6 *Detergent*—Use any commercially available "low-suds" liquid or solid detergent.

7.7 *Nitric Acid* (1 + 1)—Mix equal volumes of concentrated nitric acid (HNO_3, sp gr 1.42) and water.

7.8 *Redox Standard Solution; Ferrous-Ferric Reference Solution*[4]—Dissolve 39.21 g of ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$), 48.22 g of ferric ammonium sulfate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) and 56.2 mL of sulfuric acid (H_2SO_4, sp gr 1.84) in water and dilute to 1 L. It is necessary to prepare the solution using reagent grade chemicals that have an assay confining them to be within 1 % of the nominal composition. The solution should be stored in a closed glass or plastic container.

7.8.1 The ferrous-ferric reference solution is a reasonably stable solution with a measurable oxidation - reduction potential. Table 4 presents the potential of the platinum electrode for various reference electrodes at 25°C in the standard ferrous-ferric solution.

7.9 *Redox Reference Quinhydrone Solutions*—Mix 1 L of pH 4 buffer solution, see 7.4.1, with 10 g of quinhydrone. Mix 1 L of pH 7 buffer solution, see 7.4.2, with 10 g of quinhydrone. Be sure that excess quinhydrone is used in each solution so that solid crystals are always present. These reference solutions are stable for only 8 h. Table 5 lists the nominal millivolt redox readings for the quinhydrone reference solutions at temperatures of 20°C, 25°C, and 30°C.

8. Sampling

8.1 Collect the samples in accordance with Practices D 3370.

9. Preparation

9.1 *Electrode Treatment*—Condition and maintain ORP electrodes as recommended by the manufacturer. If the assembly is in intermittent use, the immersible ends of the elec-

[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chem. Soc., Washington, D. C. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N. Y., and "The United States Pharmacopeia."

[4] "Standard Solution for Redox Potential Measurements," Analytical Chemistry, Vol 44, 1972, p. 1038.

trode should be kept in water between measurements. Cover the junctions and fill-holes of reference electrodes to reduce evaporation during prolonged storage.

9.2 *ORP Electrode Cleaning*—Remove traces of foreign matter. Immerse the oxidation-reduction electrode in warm aqua regia (70°C) and allow to stand for a period of about 1 min. This solution dissolves the noble metal as well as any foreign matter so that the electrode should not be allowed to stand in it longer than the time specified. The above treatment in aqua regia may also be used cautiously to recondition an electrode that has become unreliable in its operation. It is also possible to clean the electrode in HNO_3 (1 + 1). Warm the solution and electrode gradually to boiling. Maintain it just below the boiling point for about 5 min and then allow the solution and electrode to cool. Wash the electrode in water several times. It is desirable to clean the electrode daily. An alternative cleaning procedure is to immerse the electrode at room temperature in chromic acid cleaning mixture and then rinse first with dilute hydrochloric acid and then thoroughly with water. Preliminary cleaning with a detergent sometimes is desirable to remove oily residues. A mild abrasive can be used to remove some particulate matter. In these cleaning operations particular care must be exercised to protect the glass-metal seals from sudden changes of temperature, which might crack them.

10. Calibration and Standardization

10.1 Before using electronic type meters, turn them on and allow them to warm up thoroughly. Bring them to electrical balance by carefully following the manufacturer's instructions. Set the scale or range to the desired millivolt level expected in the test solution.

10.2 Verify the sensitivity of the electrodes by noting the change in millivolt reading when the pH of the test solution is altered. The ORP will increase when the pH of the test solution decreases and the ORP will decrease if the test solution pH is increased. Place the sample in a clean glass beaker and agitate the sample. Insert the electrodes and note the ORP or millivolt reading. Add a small amount of a dilute NaOH solution and note the value of the ORP. If the ORP drops sharply when the caustic is added, the electrodes are sensitive and operating properly. If the ORP increases sharply when the caustic is added, the polarity is reversed and must be corrected in accordance with the manufacturer's instructions. If the ORP does not respond as above when the caustic is added, the electrodes should be cleaned as described in 9.2 and the above procedure repeated.

10.3 *Checking Response Electrodes to the Standard Redox Solutions* (see 7.8 and 7.9)—Wash the metal and reference electrode and the sample cup or container with three changes of water or by means of a flowing stream from a wash bottle. Fill the sample container with fresh redox standard solution and immerse the electrodes. Turn the range switch to the proper range and engage the operating button. Adjust the asymmetry control to the millivolt potential of the standard redox solution. Without changing the setting of the asymmetry potential knob, repeat the above procedure until two successive instrument readings are constant. The readings should not differ from the millivolt value of the standard redox solution by more than 10 mV.

10.3.1 It usually suffices to check the sensitivity of the electrodes since the important feature is the change of potential as related to the concentration of the oxidant or reductant present. The actual numerical value of the potential will vary depending on the constituents present in the water.

10.4 *Indirect Calibration and Standardization:*

10.4.1 Employ this procedure when it is not convenient or practical to remove the electrodes from the flowing stream or container in which the ORP is being determined. Use of a laboratory ORP meter or an additional analyzer is required.

10.4.2 Verify the sensitivity of the laboratory ORP meter or additional process analyzer in accordance with 10.2.

10.4.3 Collect a grab sample that is representative of the material that is in contact with the electrodes of the analyzer that is to be standardized. If a submersion-style electrode chamber is in use, collect the sample from the discharge of the chamber. Immediately transport the sample to the laboratory ORP meter or additional process analyzer and measure the ORP. It is absolutely essential that the sample be representative of the solution in contact with

the electr
and that
tained ur
particular
remain cc
tion contr
ibrated u
ORP of t
scribed at
obtained
This proc
of the sol
more thai
tion.

10.4.4
also be ve
centration
grab sam
10.4.3. It
tions requ
this meth
For exam
tion can b
ORP elec
line chlor

11. Proce

11.1 Af
for sensit
scribed in
changes c
stream fro
a clean gl
the electr
throughou
millivolt p
ficient tim
successive
on two su
than 10 r
stabilize p
ORP.

11.2 *Cc*
of Flowing
ORP anal
electrode
surements
matic con
and electr

the electrodes of the analyzer being adjusted and that the integrity of the sample be maintained until its ORP has been measured. In particular, the temperature of the sample must remain constant. Then adjust the standardization control on the process analyzer being calibrated until the reading corresponds to the ORP of the sample. Repeat the procedure described above until two successive readings are obtained that differ by no more than 10 mV. This procedure cannot be employed if the ORP of the solution being tested is fluctuating by more than 10 mV at the time of standardization.

10.4.4 The sensitivity of the electrodes can also be verified by a determination of the concentration of the oxidants or reductants in a grab sample collected in accordance with 10.4.3. It is necessary to determine the conditions required in each individual system to use this method of verifying electrode sensitivity. For example, the chlorine residual determination can be used to verify the sensitivity of an ORP electrode system used to control an alkaline chlorination-cyanide destruction system.

11. Procedure

11.1 After the assembly has been checked for sensitivity (10.2) or standardized as described in 10.4, wash the electrodes with three changes of water or by means of a flowing stream from a wash bottle. Place the sample in a clean glass beaker or sample cup and insert the electrodes. Provide adequate agitation throughout the measurement period. Read the millivolt potential of the solution allowing sufficient time for the system to stabilize. Measure successive portions of the sample until readings on two successive portions differ by no more than 10 mV. A system that is very slow to stabilize probably will not yield a meaningful ORP.

11.2 *Continuous Determination of the ORP of Flowing Streams or Batch Systems*—Process ORP analyzers with their rugged electrodes and electrode chambers provide continuous measurements which are the basis for fully automatic control. Make selection of the electrodes and electrode chamber to suit the physical and chemical characteristics of the process material. Locate the submersion-style electrode chamber so that fresh solution representative of the process stream or batch continuously passes across the electrodes. Agitation may be employed in order to make the stream or batch more nearly homogeneous. The ORP value is usually displayed continuously and can be noted at any specific time. Frequently, the pH value is continuously recorded, yielding a permanent record.

12. Calculation

12.1 If the meter is calibrated in millivolts, read the oxidation-reduction potential directly from the meter scale. This ORP potential is related to the reference electrode used in the measurement.

12.2 Calculate the oxidation-reduction potential of the sample, in millivolts, referred to the hydrogen scale as follows:

$$E_h = E_{obs} + E_{ref}$$

where:

E_h = oxidation-reduction potential referred to the hydrogen scale, mV,

E_{obs} = observed oxidation-reduction potential of the noble metal-reference electrode employed, mV, and

E_{ref} = oxidation-reduction potential of the reference electrode as related to the hydrogen electrode, mV.

13. Report

13.1 Report the oxidation-reduction potential to the nearest 10 mV, interpolating the meter scale as required. When considered appropriate, the temperature at which the measurement was made, the electrode system employed, and the pH at the time of measurement, may also be reported.

14. Precision and Accuracy

14.1 Precision and accuracy of the measurement depends largely on the condition of the electrode system and on the degree to which the chemical system being measured fits the qualifications given in Sections 3 and 5. In the absence of substances that coat or poison the electrode, the precision is ± 10 mV.

Table 1 Laboratory ORP Meters

	Type I	Type II	Type III	Type IV
Range:				
Normal	0 – ±1400 mV	0 – ±1400 mV	0 – ±1400 mV	0 – ±1400 mV
Expanded		any 200 mV	any 140 mV	
Scale:				
Normal	10	10	10	0.1
Expanded		1	1	
Accuracy	±7	±1	±0.7	±0.1
Repeatability	±2	±0.5	±0.2	±0.2
Asymmetry potential compensator	yes	yes	yes	yes

Table 2 ORP Analyzers for Process Measurements

	Type I	Type II	Type III
Range	200, 500, or 1000 mV with lower limit between ±700 mV	0 to 1000 mV	100 to 200 mV
Stability	±2 mV/24 h	±0.06 mV/week	±0.1% of span
Output signal, full scale:			
Potentiometric	10,100 mV 1, 5 V	1, 10 V	...
Current	4 to 20, 10 to 50 mA	0 to 16, 0 to 20, 4 to 20, 5 to 25, 10 to 50 mA	4 to 20, 10 to 50 mA

Table 3 National Bureau of Standards (NBS) Materials for Reference Buffer Solutions

NBS Standard Sample Designation[a]	Buffer Salt	Drying Procedure
186-II-C	disodium hydrogen phosphate	2 h in over at 130° C
186-I-C	potassium dihydrogen phosphate	2 h in over at 130° C
185-e	potassium hydrogen phthalate	drying not necessary

[a] The buffer salts listed can be purchased from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

Table 4 Potential of the Platinum Electrode for Several Reference Electrodes at 25°C in Ferrous-Ferric Reference Solution

Reference Electrode	Potential EMF, mV
Hg, Hg_2Cl_2, satd KCl	+430
Ag, AgCl, 1.00 M KCl	+439
Ag, AgCl, 4.00 M KCl	+475
Ag, AgCl, satd KCl	+476
Pt, H_2 (p = 1), H (a = 1)	+675

Table 5 Nominal ORP of Reference Quinhydrone Solutions

	ORP = mV.					
Buffer solution, nominal pH		4			7	
Temperature, °C	20	25	30	20	25	30
Reference Electrode						
Silver-silver chloride	268	263	258	92	86	79
Calomel	223	218	213	47	41	34
Hydrogen	470	462	454	295	285	275

X1.1 *Meaning o*
measurement establ
reductants prevailin
waste water. The r
contrast, for examp
The ORP electrode
potential of a soluti
ability to oxidize or
may be determined

X1.2 *Use of ORF*

X1.2.1 ORP me
trial process control
unwanted materials
tion or reduction. F
solution is to be tre
tion-reduction profi
dicted with some ac
category are found
cyanide is oxidized t
to carbon dioxide ar
lent-chromium is re
ORP Measurements
in both instances if
trolled.

X1.2.2 In additi
which a specific mat
ments can be used t
if a correlation can b
ing ORP and the rea
ple is the use of ORP
of municipal waste b
the extent of odor pr
Also, sewage treatm
from unwanted oxid
might harm treatme
influent is monitored

X1.3 *Temperature*
ments

X1.3.1 The effe
Measurements can
the Nernst equation

$$E = E^\circ -$$

where
E = measured pote
E° = potential whe

APPENDIX

(Nonmandatory Information)

X1. OXIDATION REDUCTION POTENTIAL

X1.1 *Meaning of the Term ORP* —The ORP measurement establishes the ratio of oxidants and reductants prevailing within a solution of water or waste water. The measurement is nonspecific in contrast, for example, to the pH measurement. The ORP electrode pair senses the prevailing net potential of a solution. By this measurement, the ability to oxidize or reduce species in the solution may be determined.

X1.2 *Use of ORP Control of Waste Processes:*

X1.2.1 ORP measurements are used in industrial process control to monitor the treatment of unwanted materials which are amenable to oxidation or reduction. Frequently, only one species in solution is to be treated, in which case the oxidation-reduction profile of the process can be predicted with some accuracy. Two examples in this category are found in the plating industry: Waste cyanide is oxidized to cyanate and then (if required) to carbon dioxide and nitrogen, and waste hexavalent-chromium is reduced to the trivalent state. ORP Measurements are useful for process control in both instances if the pH is constant and controlled.

X1.2.2 In addition to control of processes in which a specific material is treated, ORP measurements can be used to control nonspecific processes if a correlation can be established between prevailing ORP and the reaction in the process. An example is the use of ORP measurements in odor control of municipal waste by chlorination. In some cases, the extent of odor production correlates with ORP. Also, sewage treatment plants may be protected from unwanted oxidizing or reducing agents which might harm treatment materials if the ORP of the influent is monitored.

X1.3 *Temperature Effects on ORP Measurements:*

X1.3.1 The effect of temperature on ORP Measurements can be understood by considering the Nernst equation:

$$E = E^\circ - 2.3 \frac{RT}{nF} \log Q$$

where

E = measured potential
E° = potential when all components involved in the reaction are at unit activity and 25° C,
R = gas constant,
T = absolute temperature, t° C + 273.15,
F = Faraday,
n = number of electrons involved in the reaction, and
Q = product of the activities of the oxidants divided by the product of the activities of the reductants, each activity raised to that power whose exponent is the coefficient of the substance in the applicable chemical reaction.

Changes in E° with temperature produce the same changes in E. Further, the slope of the curve that relates E and T depends directly on T. Finally, changes in activity with temperature will produce changes in E.

X1.3.2 Automatic temperature compensation is seldom attempted in ORP Measurements, due to the appearance of n in the prelogarithmic factor of the Nernst equation. The slope of the plot of E versus T thus depends not only on T, but on n as well, so that different amounts of compensation are required, depending on the value of n. If the process under study is well characterized and the value of n known, automatic temperature compensation is possible. However, if the value of n is unknown or variable (see X1.2.1), then compensation is not possible.

X1.4 *Polarity Check* —The polarity of the input of the analyzer may also be determined by connecting a battery of known polarity and observing the deflection of the meter. A resistive voltage divider may be connected between the battery and analyzer, if necessary, to prevent the meter from being driven off-scale due to application of an excessively high potential.

X1.5 Increase Precision of Measurement. If a precision of greater than 5 mV is desired, control the temperature of the assembly to within ± 1° C. Higher precision will require closer control of temperature. Electrodes, test solutions, and wash water must be allowed to stand for a sufficient time to obtain thermal equilibrium at the temperature of measurement, in order to reduce to a negligible value the effects of the thermal or electrical hysteresis of the reference electrode.

METHOD 9081

CATION-EXCHANGE CAPACITY OF SOILS (SODIUM ACETATE)

1.0 SCOPE AND APPLICATION

1.1 Method 9081 is applicable to most soils, including calcareous and noncalcareous soils. The method of cation-exchange capacity by summation (Chapman, 1965, p. 900; see Paragraph 10.1) should be employed for distinctly acid soils.

2.0 SUMMARY OF METHOD

2.1 The soil sample is mixed with an excess of sodium acetate solution, resulting in an exchange of the added sodium cations for the matrix cations. Subsequently, the sample is washed with isopropyl alcohol. An ammonium acetate solution is then added, which replaces the adsorbed sodium with ammonium. The concentration of displaced sodium is then determined by atomic absorption, emission spectroscopy, or an equivalent means.

3.0 INTERFERENCES

3.1 Interferences can occur during analysis of the extract for sodium content. Thoroughly investigate the chosen analytical method for potential interferences.

4.0 APPARATUS AND MATERIALS

4.1 Centrifuge tube and stopper: 50-mL, round-bottom, narrow neck.

4.2 Mechanical shaker.

4.3 Volumetric flask: 100-mL.

5.0 REAGENTS

5.1 Sodium acetate (NaOAc), 1.0 N: Dissolve 136 g of $NaC_2H_2O_2 \cdot 3H_2O$ in water and dilute it to 1,000 mL. The pH of this solution should be 8.2. If needed, add a few drops of acetic acid or NaOH solution to bring the reaction of the solution to pH 8.2.

5.2 Ammonium acetate (NH_4OAc), 1 N: Dilute 114 mL of glacial acetic acid (99.5%) with water to a volume of approximately 1 liter. Then add 138 mL of concentrated ammonium hydroxide (NH_4OH) and add water to obtain a volume of about 1,980 mL. Check the pH of the resulting solution, add more NH_4OH, as needed, to obtain a pH of 7, and dilute the solution to a volume of 2 liters with water.

Revision 0
Date September 1986

5.3 Isopropyl alcohol: 99%.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

7.0 PROCEDURE

7.1 Weigh 4 g of medium- or fine-textured soil or 6 g of coarse-textured soil and transfer the sample to a 50-mL, round-bottom, narrow-neck centrifuge tube. (A fine soil has >50% of the particles <0.074 mm, medium soil has >50% >0.425 mm, while a coarse soil has more than 50% of its particles >2 mm.

7.2 Add 33 mL of 1.0 N NaOAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

7.3 Decant the liquid, and repeat Paragraph 7.2 three more times.

7.4 Add 33 mL of 99% isopropyl alcohol, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear.

7.5 Repeat the procedure described in Paragraph 7.4 two more times.

7.6 Add 33 mL of NH_4OAc solution, stopper the tube, shake it in a mechanical shaker for 5 min, and centrifuge it until the supernatant liquid is clear. Decant the washing into a 100-mL volumetric flask.

7.7 Repeat the procedure described in Paragraph 7.6 two more times.

7.8 Dilute the combined washing to the 100-mL mark with ammonium acetate solution and determine the sodium concentration by atomic absorption, emission spectroscopy, or an equivalent method.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

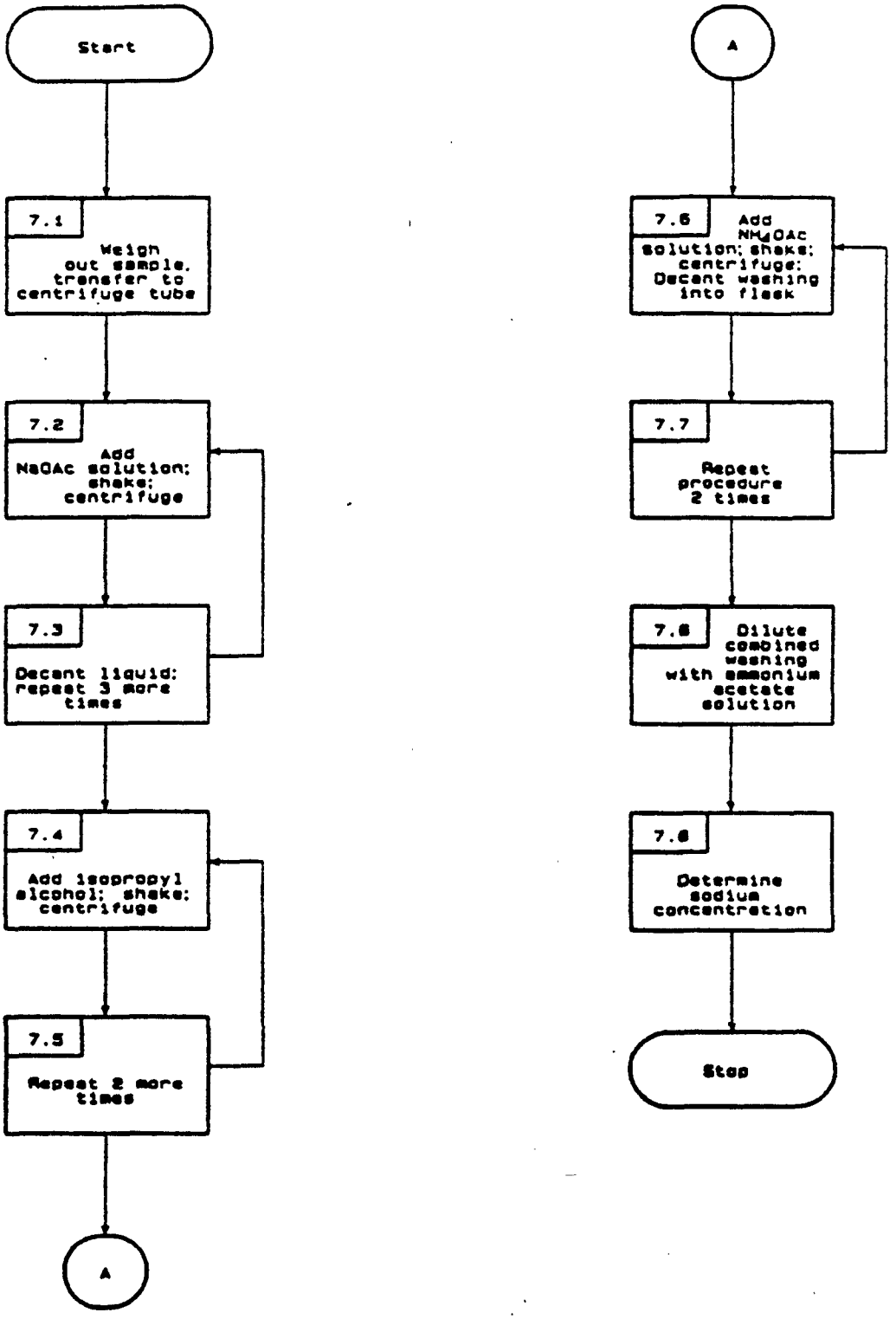
8.3 Materials of known cation-exchange capacity must be routinely analyzed.

9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

10.1 This method is based on Chapman, H.D., "Cation-exchange Capacity," pp. 891-900, in C.A. Black (ed.), Method of Soil Analysis, Part 2: Chemical and Microbiological Properties, Am. Soc. Agron., Madison, Wisconsin (1965).



Revision 0
Date September 1986

AIW FRANK #7

U.S. ENVIRONMENTAL PROTECTION AGENCY
CLP SAMPLE MANAGEMENT OFFICE
P.O. BOX 818 - ALEXANDRIA, VIRGINIA 22313
PHONE: 703/557-2490 - FTS/557-2490

SAS NUMBER

SPECIAL ANALYTICAL SERVICES
Client Request

Regional Transmittal Telephone Request

A. EPA Region/Client: EPA-REGION III-ARCS III

B. RSCC Representative: COLLEEN WALLING

C. Telephone Number: (301) 266-9180

D. Date of Request: _____

E. Site Name: AIW FRANK, CHESTER COUNTY, PA

Please provide below description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete information may result in a delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General Descrition of analytical services requested:**

   Analysis of 2 sediment samples for Grain Size Distribution, Bulk density, and soil moisture by the methods listed in Item 7.

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**

   2 low concentration sediment samples for the above analysis.

3. **Purpose of analysis (specify whether Superfund (enforcement or remedial action), RCRA, NPDES, etc.):**

   RI/FS - ARCS III

SAS Approved By (signature):
Date:

4. **Estimated date(s) of collection:**

To be determined.

5. **Estimated date(s) and method of shipment:**

To be determined.

Samples will be shipped overnight by overnight air carrier. This schedule is tentative and is dependant on the project remaining on schedule. Sampling may continue into the week of .

6. **Number of days analysis and data required after laboratory receipt of samples:**

Written results within 35 days of the receipt of the last sample.

7. **Analytical protocol required (attach copy if other than protocol currently used in this program):**

Grain size - Analysis by ASTM D-422-63 (Attachment 1) with required "Dry Preparation of Soil Samples..." ASTM D-421 (Attachment 2) and Sieve Accuracy Testing, Chapter 3 from "Procedures in Sediment Petrology (Attachment 3). Balance check using NBS Class "S" weights.

Bulk density - Chapter 13 of Methods of Soil Analysis - Agronomy No. 9 (Attachment 4).

Soil moisture - ASTM D2216-80 (Attachment 5).

All methods are attached.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Grain Size - see Attachment 6.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:**

See Attachment 7.

10. **Other (use additional sheets or attach supplementary information, as needed):**

See Attachment 6.

11. **Name of sampling/handling contact:**

Jeff Orient - NUS Corporation (412)-788-1080.

12. Data Requirements:

Parameter	Detection Limit	Precision Desired (+/-% or Concentration)

Grain size - must meet report requirements and data specifications as stated in ASTM D-422-63, Section 18, page 93.

13. QC Requirements:

Audits Required	Frequency of Audits	Limits (Percent or Concentration)
Sieve calibration	See Attachment 3	Table 1, pages 49-50 and 65-106
Balance calibration	One per batch	As per manufacturer's specifications (also record in deliverables)

14. Action Required if Limits are Exceeded:

If sieves do not meet sieve accuracy requirements, new sieves that meet the requirements must be used.

15. Request Prepared By:

Gregory L. Zimmerman - NUS Corporation - (412) 788-1080.
June 6, 1991.

16. Request Reviewed By (CRL use only):
Date:

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for Special Analytical Services. Should you have any questions or need any assistance, please contact your local Regional representative at the Sample Management Office.