Ohio | Environmental Protection Agency

John R. Kasich, Governor
Mary Taylor, Lt. Governor
Scott J. Nally, Director

February 14, 2012

Mayor & Council
57 South Fairfield Street
Leesburg, Ohio 45135

RE: Village of Leesburg WWTW/Compliance Evaluation Inspection
NPDES Permit No. OH0050881/OEPA PERMIT NO. 1PB00106*GD

Ladies & Gentlemen:

On February 8, 2012, I conducted a NPDES Compliance Evaluation Inspection at the Village of Leesburg wastewater treatment works (WWTW). Mr. Phil Weyrich was present during the inspection and represented the Village. The purpose of the inspection was to evaluate compliance with the terms and conditions of the NPDES Permit. A copy of the report is provided within.

The Village is in Significant Non-compliance with the requirements of the NPDES permit (total recoverable copper violations). The Village must take immediate steps to address the issues causing non-compliance; please see the discussion within the report. Also pay special attention to the "items requiring correction" in bold type, as there are associated compliance schedules.

Thank you and your staff for time extended during the inspection process. If you have any questions, please feel free to contact me by phone at (937) 285-6029 or by e-mail at joshua.jackson@epa.state.oh.us.

Respectfully,

Joshua Jackson
Environmental Specialist II
Division of Surface Water

Ec: Phil Weyrich, Village of Leesburg (w/attachments)

Enclosures

JJ/ca

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401 East Fifth Street
Dayton, OH 45402-2911

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OhioEPA

State of Ohio Environmental Protection Agency
Southwest District Office

NPDES Compliance Inspection Report

Section A: National Data System Coding					
Permit #	**NPDES#**	**Month/Day/Year**	**Inspection Type**	**Inspector**	**Facility Type**
1PB00106*GD	OH0050881	2/8/2012	C	S	1

Section B: Facility Data		
Name and Location of Facility Inspected	**Entry Time**	**Permit Effective Date**
Village of Leesburg WWTW 7 East Street Leesburg, Highland County	9:25 a.m.	2/1/2011
	Exit Time	**Permit Expiration Date**
		1/31/2016
Name(s) and Title(s) of On-Site Representatives	**Phone Number(s)**	
Phil Weyrich, ORC	937-673-0263 937-780-6115 (WWTW)	
Name, Address and Title of Responsible Official	**Phone Number**	
Mayor & Council 57 South Fairfield Street Leesburg, OH 45135	937-780-6928	

Section C: Areas Evaluated During Inspection (S = Satisfactory, M = Marginal, U = Unsatisfactory, N = Not Evaluated)					
S	Permit	M	Flow Measurement	N	Pretreatment
S	Records/Reports	S	Laboratory	S	Compliance Schedule
S	Operations & Maintenance	U	Effluent/Receiving Waters	S	Self-Monitoring Program
S	Facility Site Review	S	Sludge Storage/Disposal	N	Other
U	Collection System				

Section D: Summary of Findings (Attach additional sheets if necessary)

See Attached Report.

Inspector	Reviewer
2-14-2012	Martyn G Burt 2/14/2012
Joshua Jackson Division of Surface Water Southwest District Office Date	Martyn Burt Compliance & Enforcement Supervisor Division of Surface Water Southwest District Office Date

Sections E thru K: Complete on all inspections as appropriate
Y – Yes, N – No, N/A – Not Applicable, N/E – Not Evaluated

Section E: Permit Verification

Inspection observations verify the permit

(a) Correct name and mailing address of permittee	Y
(b) Flows and loadings conform with NPDES permit.....	Y
(c) Treatment processes are as described in permit application...	Y
(d) All discharges are permitted.....	Y
(e) Number and location of discharge points are as described in permit.....	Y
(f) Storm water discharges properly permitted.....	N/A

Comments/Status:

Section F: Compliance

(a) Any significant violations since the last inspection.....	Y
(b) Appropriate Non-compliance notification of violations.....	N
(c) Permittee is taking actions to resolve violations.....	N
(d) Permittee has a compliance schedule.....	N
(e) Compliance schedule contained in...N/A	
(f) Permittee is in compliance with schedule.....	N/A
(g) Has biomonitoring shown toxicity in discharge since last inspection	N

Comments/Status:

See discussion on the significant violations in the attached report.

Section G: Operation & Maintenance

Treatment Works:

Treatment facility properly operated and maintained

(a) Standby power available.....generator ☒ or dual feed ☐..... Y

i. What does the back-up power source operate.....

The generator operates every component on the WWTW grounds. When power is lost to the WWTW, there is an automatic switchover to the generator.

ii. How often is the generator tested under load.....

1/week

(b) Which components have an alarm system available for power or equipment failures.....

High level alarms for influent channel of SBR and influent pump station to the WWTW. Alarm when the emergency equalization pumps are on.
There is an autodialer for these alarms.

(c) All treatment units in service other than backup units..... Y

(d) What method is used for scheduling routine & preventative maintenance (calendar, software, etc.).....

There is no PM schedule. Receipts for equipment repair/maintenance are kept on file.

(e) Any major equipment breakdown since last inspection..... N

(f) Operation and maintenance manual provided and maintained..... Y

(g) Any plant bypasses since last inspection..... Y

(h) Any plant upsets since last inspection..... N

Comments/Status:

Once flows are around 0.8 MGD, the tertiary filters start to backwash (alternate) continuously to the point where one of the eq basins starts to back-up. At this point, Mr. Weyrich begins to bypass the tertiary filters.

Section G: Operation & Maintenance con't

Record Keeping/Operator of Record:

(a) Wastewater Treatment Works classification (OAC 3745-7)..... II
(b) Operator of Record holds unexpired license of class required by Permit..... Y
(c) Copy of certificate of Operator of Record displayed on-site..... Y
(d) Has the Operator of Record submitted an ORC Notification form.. Y
(e) Minimum operator staffing requirements fulfilled (OAC 3745-7).... Y
(f) If a Staffing Reduction plan has been approved, are the stipulations of the plan being met.....N/A
(g) Operator of Record log book provided..... Y
(h) Format of log book (e.g. computer log, hard bound book)

Hard Bound.

(i) Log book kept onsite (in an area protected from weather)..... Y
(j) Log book contains the following:
  I. Identification of treatment works..... Y
  II. Date/times of arrival/departure for Operator of Record and any other operator required by OAC 3745-7..... Y
  iii. Daily record of operator and maintenance activities (including preventative maintenance, repairs and request for repairs, process control test results, etc.)..... Y
  iv. Laboratory results (unless documented on bench sheets)... N
  v. Identification of person making entries..... Y
(k) Has the Operator of Record submitted written notifications to the permittee, Ohio EPA and, if applicable, any local environmental agencies when a collection system overflow, treatment plant bypass or effluent limit violation has occurred..... Y

Comments/Status:

Two random weeks from the Operator of Record logbook were reviewed in order to verify that the logbook was kept in accordance to Ohio Admininstrative Code 3745-7 and that the ORC was working the required staffing hours for this facility. Everything appeared to be in order.

Section G: Operation & Maintenance con't

Collection System:

(a) Are there pump stations in the collection system..... Y
- i. How many publicly-owned pump stations equipped with permanent standby power or equivalent.....5
- ii. How many pump stations have telemetered alarms.....2
- iii. How many pump stations have operable alarms.....5

(b) Any chronic collection system overflows since last inspection..... N
(c) Regulatory agency notified of all overflows..... N/A
(d) Are there CSOs in the collection system..... N
if so, what is the LTCP status.....

(e) How are CSOs monitored (chalk, block, level sensor, etc.).....

(f) Portable pumps available for collection system maintenance..... N/E
(g) RDII Program established and active..... N
(h) Any WIB complaint received since last inspection..... N
(i) Is there a WIB response plan..... N
(j) Is any portion of the collection system at or near dry weather capacity..... N/E

Comments/Status:

Inflow and infiltration program discussion in the attached report.

Section H: Sludge Management

(a) Method of Sludge Disposal... ☒Land Application
☐Haul to Another NPDES Permitee
☐Haul to a Mixed Solid Waste Landfill

(b) Has amount of sludge generated changed significantly since the last inspection..... N

(c) How much sludge storage is provided at the plant.....

>4 months

(d) Records kept in accordance with State and Federal law (5 years according to OAC 3745-40-06)..... Y

(e) Any complaints received in last year regarding sludge..... N

(f) 5/8" screen at headworks for facilities that land apply sludge..... N/A

(g) Are sludge application sites inspected to verify compliance with NPDES permit..... N/A

(h) Is a contractor used for sludge disposal..... Y
If so, what is the name of the contractor.....

Waste Management hauls roll-off boxes (filled with sludge cake) from the WWTW to a mixed solid waste landfill.

Comments/Status:

Mr. Weyrich should keep sludge files in separate file folders in order to streamline records retrieval.

Section I: Self-Monitoring Program

Flow Measurement:

(a) Primary/Secondary flow measuring devices (e.g. weir with ultrasonic level sensor):

Magnetic Meter

(b) Flow meter calibrated annually ..... N
(Date of last calibration: 2010)

(c) 24-hour recording instruments operated and maintained..... N

(d) Flow measurement equipment adequate to handle full range of flows..... N

(e) All discharged flow is measured..... Y

Comments/Status:

See discussion of flow meter issues in the attached report.

Section I: Self-Monitoring Program (con't)

Sampling:

(a) Sampling location(s) are as specified by permit..... Y
(b) Parameters and sampling frequency agree with permit..... Y
(c) Permittee uses required sampling method..... Y
(see GLC page)
(d) Monitoring records (i.e., flow, pH, DO) maintained for a minimum of three years including all original strip chart recordings (i.e, continuous monitoring instrumentation, calibration and maintenance records)..... Y

Comments/Status:

Section I: Self-Monitoring Program (con't)

Laboratory:

General

(a) Does the Quality Assurance Manual contain written Standard Operating Procedures (SOP's) for all analysis performed onsite..... Y
(b) Do SOP's include the following if applicable..... N

- Title
- Scope and Application
- Summary
- Sample Handling and Preservation
- Interferences
- Apparatus and Materials
- Reagents
- Procedure
- Calculations
- Quality Control
- Maintenance
- Corrective Action
- Reference (Parent Method)

Note: Standard Methods 1020A establishes that "Quality assurance (QA) is the definitive program for laboratory operation that specifies the measure required to produce defensible data of know precision and accuracy. Standard operating procedures are to be used in the laboratory in sufficient detail that a competent analyst unfamiliar with the method can conduct a reliable review and/or obtain acceptable results." SOPs should be developed for each analytical procedure.

(c) EPA approved analytical testing procedures used (40 CFR 136.3).. Y

(d) If alternate analytical procedures are used, proper approval has been obtained..... N/A
(e) Analyses being performed more frequently than required by permit. N
(f) If (e) is yes, are results in permittee's self-monitoring report..... N/A
(g) Satisfactory calibration and maintenance of instruments/equipment. Y (see score from GLC page)
(h) Commercial laboratory used..... Y
Parameters analyzed by commercial lab: All parameter with the exception of temperture, pH and dissolved oxygen.

Lab name: MASI

Comments/Status:

See GLC form for discussion on laboratory and sampling.
Mr. Weyrich prepared SOPs for DO, temperature and pH but they did not provide all the required information/headings. I will provide Mr. Weyrich with an example SOP for pH. He should then prepare SOPs for pH, DO, temperture and sample collection by no later than July 31, 2012..

Section J: Effluent/Receiving Water Observations

Outfall # 001
Outfall Description: Sampling occurs after disinfection. There was no discharge at the time of the inspection (batch discharges)

Receiving Stream: Lees Creek
Receiving Stream Description: No observable solids attributed to the WWTW.

Comments/Status:

Section K: Multimedia Observations

(a) Are there indications of sloppy housekeeping or poor maintenance in work and storage areas or laboratories..... N
(b) Do you notice staining or discoloration of soils, pavement or floors.. N
(c) Do you notice distressed (unhealthy, discolored, dead) vegetation.. N
(d) Do you see unidentified dark smoke or dust clouds coming from sources other than smokestacks..... N
(e) Do you notice any unusual odors or strong chemical smells..... N
(f) Do you see any open or unmarked drums, unsecured liquids, or damaged containment facilities..... N

If any of the above are observed, ask the following questions:

(1) What is the cause of the condition?
(2) Is the observed condition or source a waste product?
(3) Where is the suspected contaminant normally disposed?
(4) Is this disposal permitted?
(5) How long has the condition existed and when did it begin?

Comments/Status:

Inspection Findings
(Items for Correction in Bold Type)

Sewage Collection System Infiltration/Inflow

According to the 2010 U.S. Census, the Village of Leesburg has a population of around 1,300. The Village of Highland, who conveys sewage to the Village of Leesburg wastewater treatment works (WWTW), has a population of approximately 300. The Leesburg WWTW was upgraded in 2007, and with these improvements the average daily design capacity was expanded from 0.16 MGD to 0.4 MGD. According to the design report from the contract engineer, the WWTW would be able to treat a maximum daily flow of 1.0 MGD and a peak instantaneous flow of 1.6 MGD.

After performing a review of the 2011 discharge monitoring report data submitted by the Village of Leesburg, the average daily discharge flow from the WWTW was 0.32 MGD. There were two days in March when flows averaged just over 1.2 MGD. When comparing this data with the average daily flow that the Leesburg WTP delivers into the water distribution system (~0.1 MGD) plus the sewage conveyed from the Village of Highland (~30,000-50,000 gpd), one can see there is anywhere between a 4:1 – 12:1 difference between the drinking water supplied to homes and business and the wastewater received at the WWTW. All of this translates to extraneous water inflow and/or infiltration in the Leesburg collection system during wet weather conditions.

To further prove the point, discharge flows from the Leesburg WWTW were around 0.35 MGD on the day of the inspection, yet there had been no precipitation for days (wet antecedent conditions). Although the existing WWTW is designed to accommodate some wet weather flows, operations staff have bypassed tertiary filters this past year when influent flows exceed 0.8 MGD. With just over 40,000 feet of gravity sanitary sewers in the Leesburg sewage collection system and much of it consisting of vitrified clay pipe, the Village must initiate and sustain an Inflow & Infiltration Reduction Program with the goal of reducing wet weather flows in sewage collection system and WWTW. Towards that end, the following must be completed by the associated compliance dates:

1. Currently, there is no ability to record influent or effluent flow rates over a 24-hour period of time. A flow recorder is invaluable in determining how the collection system reacts to a precipitation event in terms of intensity and duration. **An influent or effluent flow recorder must be installed and on-line at the WWTW no later than May 1, 2012.**
2. The Village must prepare an I&I Reduction Plan that will outline a long-term, systematic approach for CCTVing all vitrified clay pipe (or any other pipe material suspected of being in disrepair) in the Village. This should entail investigating several thousand feet of sewer each year. Once the

yearly investigation is completed, sections of pipe should be prioritized for improvements the following year (unless the condition of the sewer lines do not warrant repair). The improvements could include, sewer replacement, sewer re-lining or disconnecting clean water connections (such as downspouts or storm sewers) from the sanitary sewer system. The plan should also point out that documentation of all sewage collection system investigation and improvements will be kept on file at the WWTW for Ohio EPA review.

An acceptable I&I Reduction Plan shall be submitted to this office no later than July 1, 2012. The Village of Leesburg shall initiate sewage collection investigation this year and Ohio EPA will review the status of the program during subsequent inspections.

Tertiary Filter Bypassing

As mentioned above, during/after certain wet weather events Mr. Weyrich will begin bypassing tertiary filters at the WWTW when influent flows are around 0.8 MGD. This is because the two filters will begin to backwash constantly (alternating backwash cycles), which in turn directs more flow to a headworks that is already taken on a large amount of flow. If Mr. Weyrich does not bypass the tertiary filters, the eq basin will overflow.

According to the design report provided by the engineer when the Permit to Install for the WWTW upgrades was submitted to Ohio EPA, the tertiary filters are designed for a peak flow of 1.6 MGD *for each filter.* **The Village must consult the manufacturers/design engineer and provide a standard operating procedure for the tertiary filters in order to maximize the treatment capacity. This standard operating procedure must be submitted to this office no later than May 1, 2012.**

Village of Leesburg Wastewater Treatment Works (WWTW)
EFFLUENT LIMIT VIOLATIONS
(Period of Review: January – December 2011)

7D = Weekly 30D = Monthly
1D = Daily Conc. = Concentration (mg/l) – for metals (ug/l)
Qty.= Quantity (Kg/Day)

Reporting Period	Station	Parameter	Limit Type	Limit	Reported Value
February 2011	001	Copper, Total Recoverable	30D Conc	22	32.
February 2011	001	Copper, Total Recoverable	30D Qty	0.03	.04651
March 2011	001	Total Suspended Solids	7D Qty	27	44.4794
April 2011	001	Total Suspended Solids	30D Qty	18	18.5923
April 2011	001	Copper, Total Recoverable	30D Conc	22	26.
April 2011	001	Copper, Total Recoverable	30D Qty	0.03	.04015

April 2011	001	Total Suspended Solids	7D Qty	27	47.4676
May 2011	001	Copper, Total Recoverable	30D Conc	22	25.
May 2011	001	Copper, Total Recoverable	30D Qty	0.03	.044
June 2011	001	Copper, Total Recoverable	30D Conc	22	27.
June 2011	001	Copper, Total Recoverable	30D Qty	0.03	.03209
August 2011	001	Copper, Total Recoverable	30D Conc	22	30.
October 2011	001	Copper, Total Recoverable	30D Conc	22	187.
October 2011	001	Copper, Total Recoverable	30D Qty	0.03	.14227
October 2011	001	Copper, Total Recoverable	1D Conc	35	187.
October 2011	001	Copper, Total Recoverable	1D Qty	0.05	.14227
November 2011	001	Copper, Total Recoverable	30D Conc	22	38.
November 2011	001	Copper, Total Recoverable	30D Qty	0.03	.03265
November 2011	001	Copper, Total Recoverable	1D Conc	35	38.
November 2011	001	Total Suspended Solids	7D Qty	27	33.7981
December 2011	001	Total Suspended Solids	30D Qty	18	20.2951
December 2011	001	CBOD 5 day	30D Qty	15	15.2204
December 2011	001	Copper, Total Recoverable	30D Conc	22	32.
December 2011	001	Copper, Total Recoverable	1D Qty	0.05	.06916
December 2011	001	Copper, Total Recoverable	30D Qty	0.03	.06916
December 2011	001	Total Suspended Solids	7D Conc	18	20.
December 2011	001	Total Suspended Solids	7D Qty	27	46.4306
December 2011	001	CBOD 5 day	7D Conc	15	17.5
December 2011	001	CBOD 5 day	7D Qty	23	41.3984

Significant Non-Compliance

As you can see from the effluent violation table shown above, the Village is in Significant Non-Compliance (SNC) for total recoverable copper. SNC is a designation given to facilities that report significant violations (40% or 20% exceedance, depending on the pollutant of concern, of the NPDES permit monthly limit) for two or more months in two consecutive quarters. The Village must take immediate steps in order to return to compliance or Ohio EPA Southwest District Office will pursue an enforcement action against the Village of Leesburg.

Wastewater operations staff has taken preliminary steps toward finding the cause of the high copper values. On two different occasions, July and October 2011, Mr. Weyrich has pulled grab samples at all the lift stations in the sewage collection system. The results of the sampling identified areas that warrant further investigation. It is also worth noting that more than half of the Village (areas not tributary to a lift station) was not part of the initial sampling run.

By no later than May 1, 2012, the Village of Leesburg shall complete the following tasks:

1. **Purchase or rent time-proportioned, composite sampling equipment to be used in an extensive sampling of the sewage collection system**

in order to further the copper investigation. While grab samples offer good preliminary data, they are only a "snapshot" of the conditions in the collection system. Time-proportioned composite samples will provide 24-hour characterization data.

2. **Identify locations within the collection system for composite sampling. These areas should include a "background" sample, which would be downstream of residential users only. Please feel free to contact myself or Ms. Marianne Piekutowski (Pretreatment Coordinator) of this office for assistance in this phase.**
3. **Conduct composite sampling of the target areas and provide results to the Ohio EPA Southwest District Office.**

After this work is completed, Ohio EPA will evaluate the data and meet with the Village to discuss the next steps.

Maintenance and Safety Items

During the inspection, it was noted that the outdoor lights mounted on the SBR are not working. According to the Mr. Weyrich, there is an issue with the electrical conduit located on the interior walls of the SBR.
Ohio EPA considers this a safety hazard, especially when the operator may need to work in that area at night. The Village must correct this issue without delay. All outdoor lights on the SBR must be fully operational no later than April 13, 2012.

During the inspection process it was also brought out that the waste activated sludge line, located on the interior wall of the SBR, has frozen on several occasions in the past. Since this conduit is an integral piece of the treatment process, it must be protected from conditions that would prohibit its use. The Village shall take steps to protect this line from freezing by no later than April 13, 2012.

Operator of Record for the Sewage Collection System Required

Ohio Administrative Code (OAC) 3745-7-02(A)(2) states:
Each person owning or operating a treatment works or sewerage system, except as provided for in paragraph (E) of this rule, shall designate one or more operator of record to oversee the technical operation of the treatment works, sewerage system, or each wastewater treatment facility. Each operator of record shall have a valid certification of a class equal to or greater than the classification of the treatment works, sewerage system, or wastewater treatment facility.

OAC 3745-7-04(B)(1) goes on to state:
Each sewerage system that is a tributary to a class I treatment works shall be classified as a class I sewerage system. Each sewerage system that is a

tributary to a class II, III, or IV treatment works shall be classified as a class II sewerage system.

Since the Village of Leesburg WWTW is a Class II facility, the sewage collection system is rated Class II. An Operator of Record is required for the collection system and shall hold a Wastewater Operator or Collection System license no less than a level of Class II. **The Village shall submit a complete Operator of Record (ORC) Notification Form for the sewage collection system to the Ohio EPA Southwest District Office in order to show compliance with OAC 3745-7. The completed form shall be submitted by no later than March 2, 2012. A blank copy of this form has been provided for your convenience.**

Annual Flow Meter Calibration

Accurate discharge flow monitoring is one of the foundational requirements of the NPDES permitting program. Pollutant loading-based limitations are discharge flow driven, as are waste load allocations to meet Ohio water quality standards. Therefore, it is paramount that the Village report accurate and defensible data to Ohio EPA. Towards that end, the Village shall conduct annual calibrations of the effluent flow meter by a qualified source and maintain a record of the calibration event on file.
Since the last calibration of the effluent flow meter was performed in 2010, the Village of Leesburg must contract with a qualified professional to calibrate the flow meter no later than March 9, 2012. The Village has been given a rating of "Marginal" for the "Flow Monitoring" section of the report.

General Lab Criteria

Criteria	Standard Methods Requirement			Rating
pH Meter		Acceptable?		
• Calibration Frequency / Documentation	• Calibration verification required for testing over long period of time (e.g. 12 hrs.), or after a large number of samples (every 10 samples)[3]	☒ Yes	☐ No	A
	• Logbook maintained[2]	☒ Yes	☐ No	
• Minimum of 2 point calibration	• Calibration per manufacturer specification and calibration buffers must bracket anticipated result[7]	☒ Yes	☐ No	
• Slope Documentation / Acceptability	• Slope acceptable range indicated on benchsheet[2]	☒ Yes	☐ No	
• Buffer Expiration Date	• Buffers must not be expired	☒ Yes	☐ No	
• Other	• Instrument manual available	☒ Yes	☐ No	
	• Teflon covered magnetic stirrer or equivalent for mixing[8]	☒ Yes	☐ No	
Comments:				

Criteria	Standard Methods Requirement			Rating
Dissolved Oxygen Meter		Acceptable?		
• Calibration Method	• Air or known DO calibration method[10]	☒ Yes	☐ No	A
	• Calibration per manufacturer specification[10]	☒ Yes	☐ No	
• Calibration Frequency / Documentation	• Logbook maintained[2]	☒ Yes	☐ No	
	• Calibration verification required at least once each day the meter is used.[3]	☒ Yes	☐ No	
• Other	• Small to no bubble present under membrane (must be smaller than the lead in number 2 pencil)[11]	☒ Yes	☐ No	
	• Instrument manual available	☒ Yes	☐ No	
Comments:				

General Lab Criteria

Criteria	Standard Methods Requirement			Rating
Refrigerator		Acceptable?		
• Temperature Recordkeeping	• Temperature Log (thermometer accurate to 0.5 Celsius).[5]	☐ Yes	☒ No	M
• Temperature Calibration / Documentation	• Thermometer calibrated annually with NIST traceable thermometer[1, 2]	☒ Yes	☐ No	
• Other	• Thermometer held in water bath. [1]	☒ Yes	☐ No	
	• Refrigerator temperature ≤6° Celsius.[13]	☒ Yes	☐ No	
	• Do not store volatile solvents, food, or beverages.[14]	☒ Yes	☐ No	

Comments: Thermometers were accurate to 1.0 degree Celsius. Mr. Weyrich will replace all sampler thermometers immediately

Criteria	Standard Methods Requirement			Rating
Bench sheets		Acceptable?		
• General criteria	• Date(s)[2]	☒ Yes	☐ No	A
	• Analyst initials[2]	☒ Yes	☐ No	
	• Blue or black ink pen[2]	☒ Yes	☐ No	
	• Calibration information[2]	☒ Yes	☐ No	
	• Equations, calculations, units for all measurements, notations, and results present[2]	☒ Yes	☐ No	
	• Corrections, single line through, initialed and dated[2]	☒ Yes	☐ No	

Comments:

General Lab Criteria

Criteria	Standard Methods Requirement			Rating
Final Effluent Temperature Monitoring		Acceptable?		
• General Criteria	• Thermometer calibrated annually with NIST traceable thermometer [1,2]	☐ Yes	☒ No	**M**
	• Thermometer accurate to 0.1° Celsius[5]	☒ Yes	☐ No	
	• Log book being maintained [2]	☒ Yes	☐ No	

Comments: Mr. Weyrich will send in the DO meter/thermometer in for calibration/certification.

Number of Criteria Rated:		
	Acceptable	
	Marginal	
	Unacceptable	
	Total Number of Areas Rated	

Acceptable Ratings – No action required (recommend SOP's written or updated, perform DMRQA's for all onsite analysis, recommend voluntary lab analyst certification, written response not required).

Marginal Ratings – Improvements required, written response required (recommend SOP's be written or updated, recommend they perform DMRQA's for all onsite analysis, recommend voluntary lab analyst certification, require deficiencies to be addressed in written response).

Unsatisfactory Rating - Improvements required, written response required, NOV issued (recommend SOP's be written or updated, recommend they perform DMRQA's for all onsite analysis, recommend voluntary lab analyst certification, require deficiencies to be addressed in written response to NOV).

Consider recommending PAI Audit from DES when:	>60% of ratings are Marginal >45% of ratings are a combination of Marginal or Unacceptable >30% of ratings are Unacceptable

Notation of Referenced Method

1 Method 9020-B, Item 3
2 Method 1020-A, Item 1
3 Method 1020-B, Item 10
4 Method 2540-B, Item 2
5 Method 2550-B, Item 1
6 Method 1020-A, Item 1
7 Method 4500-H B, Item 4
8 Method 4500-H B, Item 2
9 Method 1020-B, Item 2
10 Method 4500-O B, Item 3
11 Method 4500-O G, Item 3
12 Method 5210-B, Item 5
13 CFR 136.3, Table II
14 Method 1060A, Item 1
15 Method 4500-Cl I, Item 2
16 Method 4500-Cl I, Item 4
17 Method 4500-NH3 D, Item 4
18 Method 4500-NH3 D, Item 2
19 Method 1060-B, Item 2
20 Method 1060-B, Item 1
21 Method 9222D, Item 1
22 Method 9223 B, Item 2
23 Method 9223 B, Item 3
24 Method 1603, Item 2
25 Method 9030-B, Item 3
26 Method 9020 B, Table IV

Equipment Logbook Content - all maintenance performed on a piece of equipment should be documented in the logbook. This should include parts replacement and routine maintenance activities. Entries should include date, maintenance performed and initials of person making entry.

General Lab Criteria

Preservation and Holding Times

Parameter	Container	Min. Sample Size (mL)	Sample Type	Preservation	Maximum Storage Time	
					Recommended	Regulatory
BOD / CBOD	P, G	1000	G, C	Refrigerate ≤6° C	6h	48h
TSS	P, G	200	G, C	Refrigerate ≤6° C	7 d	7 d
pH	P, G	50	G	Analyze immediately	0.25h	0.25 h
NH3-N	P, G	500	G, C	Analyze as soon as possible or add H_2SO_4 to pH <2, Refrigerate ≤6° C	7 d	28 d
TRC	P, G	500	G	Analyze immediately	0.25h	0.25 h
DO (electrode)	G, BOD Bottle	300	G	Analyze immediately	0.25h	0.25 h
Temperature	P, G	--	G	Analyze immediately	0.25h	0.25 h
Metals, general	P, G	1000	G, C	For dissolved filter immediately and add HNO_3 to pH <2	6 months	6 months
Purgeables by purge and trap	G (PTFE lined lid)	40 (X2)	G	HCl to pH<2, Refrigerate ≤6° C	7 d	14 d
Base/Neutrals and acids	G (solvent rinsed or baked)	1000	C, G	Refrigerate ≤6° C	7 d	7 days until extraction 40 days after extraction
Pesticides	G (PTFE lined lid)	1000	C	Refrigerate ≤6° C	7 d	7 days until extraction 40 days after extraction
Fecal Coliform / E-Coli	G, P (Sterilized)	100	G	Refrigerate ≤10° C If chlorine present, add sodium thiosulfate tablet	6 hrs transport Start analysis within 2 hrs of receipt in lab.	
Oil and Grease	G	1000	G	HCl or H_2SO_4 to pH <2, Refrigerate ≤6° C	28 d	28 d

Approved Standard Methods

CBOD / BOD 5 Day	Std Methods 5210-B
Ammonia, Selective Electrode Method	Std Methods 4500-NH3 D
Total Residual Chlorine, DPD Colorimetric Method	Std Methods 4500-Cl G
Total Suspended Solids, Dried at 103-105 °C	Std Methods 2540-D
Dissolved Oxygen, Membrane Electrode Method	Std Method 4500-O G
pH, Electrometric Method	Std Methods 4500-H+ B
Fecal Coliform, Membrane Filter Procedure	Std Methods 9222D
Escherichia Coli, Enzyme Substrate Test	Std Method 9223B
Escherichia Coli Membrane Filtration Procedure	EPA Method 1603
Oil and Grease	USEPA 1664A or Std Methods 5520B
Metals, general	USEPA 200, Std Methods 3111B or C, or 3120B
Volatiles (Purgeables by purge and trap)	USEPA 6210, Std Methods 624
Semi-Volatiles (Base/Neutrals and acids)	USEPA 6410, Std Methods 625
Pesticides	USEPA 6410 and 6630, Std Methods 608

Ohio | Environmental Protection Agency
Division of Drinking and Ground Waters
Operator Certification Unit

Operator of Record (ORC) Notification Form

Ohio Environmental Protection Agency
Division of Drinking and Ground Waters
Operator Certification Unit
50 West Town St, Suite 700
P.O. Box 1049
Columbus, OH 43216-1049

Phone: (614) 644-2752
1- 866 - 411-OPCT (6728)
Fax: (614) 644-2909
email: opcert@epa.state.oh.us
website: http://www.epa.ohio.gov/ddagw/opcert.aspx

I. SYSTEM INFORMATION

Name of System: _____ Phone Number: _____

PWS ID/NPDES Permit #:_____ STU #:_____ Classification:_____

_____ _____
Name of Facility Owner or Permittee, Title (Print) Facility Owner or Permittee (Signature)

II. SYSTEM TYPE (Check only one of the following. Use additional sheets if necessary.)

Public Water System (PWS)	Distribution System	Treatment Works	Collection System
☐	☐	☐	☐

III. OPERATOR OF RECORD INFORMATION

Add Additional (A), Existing (E), New (N) or Remove (R)	Effective Date	Name of Operator of Record	Certification Number & Expiration Date	I verify that I am the onsite certified operator responsible for the technical operation of the above referenced facility. I have a valid certification of a class equal to or greater than the classification of the above referenced facility. (Signature of certified operator)*

* A signature by an operator of record who is being removed is not required.
(Attach additional sheets if necessary.)

Amount of time an ORC spends onsite at the Facility: _____ hours/week _____ days/week

For Internal Use Only	
Reviewed by:	Date of SDWIS update:
Date of Compliance Status Letter:	

pH

OHIO EPA METHOD 120.1
STD METHODS 18th, 19th, & 20th ed. 4500-H^+ B

STORET NO. 00403

1. SCOPE AND APPLICATION:

This method is used for the measurement of pH in natural surface water, treated and untreated sewage, and industrial wastewater. It may also be used for potable and ground water. However, severe limitations are encountered in extremely acid or alkaline samples.

2. SUMMARY OF METHOD:

The samples are measured at room temperature while stirring using a pH meter and electrode that has been calibrated using two known pH buffers that encompass the expected pH of the samples. The pH, defined as -log[H^+], is measured potentiometrically. The meter is calibrated to read in standard pH units.

3. SAMPLE HANDLING AND PRESERVATION:

3.1 Samples are cooled to 4°C immediately after collection in the field. No preservatives are added.

3.2 A minimum sample volume of one quart collected in a polyethylene or glass container is required.

3.3 Samples should be submitted to the laboratory immediately and the pH measured as soon as possible. Sample pH should be obtained within 24 hours of the time of collection.

4. INTERFERENCES:

4.1 Results are subject to error when extreme pH values (below 1 or greater than 10) are encountered. The pH meter manufacturer instructions should be consulted when such values are expected.

4.2 Grease or oil in the sample can coat the electrode and cause a sluggish response. If the electrode is contaminated in this manner, clean by gently washing with a detergent solution, rinsing with tap water, 10% hydrochloric acid and finally reagent water. Be sure the electrode filling hole is closed during this cleaning operation.

5. APPARATUS:

5.1 Electronic pH meter with a pH readout having a temperature compensation and a slope adjustment: Orion 520A pH meter

5.2 Combination glass and reference electrode: Ross 80-03/81-72 Sure-Flow electrode

5.3 Magnetic stir plate and Teflon-coated magnetic stir bars

5.4 100 mL beakers

6. REAGENTS:

6.1 Reagent water: Prepare by passing distilled water through a deionization system. Use distilled deionized water for the preparation of all reagents and to rinse the probe. Currently, water of this quality is prepared by using a Barnstead Nanopure system (minimum resistance of 18.0 MΩ).

6.2 Commercially prepared pH 2.00, 4.00, 7.00 and 10.00 buffers are available to calibrate the pH meter. Unopened buffers are acceptable for use until their expiration date (one year from receipt if not labeled with an expiration date) but should be discarded once they have been open for three months.

6.3 Buffers for pH values that fall outside the 4 to 10 range may be prepared in the laboratory according to instructions in *Standard Methods for the Examination of Water and Wastewater*, 18th Ed.(1992), p.4-67 or CRC Handbook of Chemistry and Physics, 63rd Ed. These buffers are also commercially available.

6.4 Reference electrode filling solution: Orion # 81-00-07; electrode storage solution: Orion #SE40-1 or 1.0 g KCl per 200 mL of pH buffer 7

6.5 Quality Control Sample: This solution is a pH 7.00 buffer that is from a different manufacturer or lot than that of the calibration buffers. It is purchased ready to use.

7. PROCEDURE:

7.1 Electrode Use:

7.1.1 If a new pH electrode is being put into operation, refer to the manufacturer instructions to prepare it for use. New electrodes must be soaked prior to use. If it requires that a filling solution be added, the solution must cover the coil and be at least one inch above the sample level that the electrode is immersed in. Once an electrode has been put into service the glass membrane must not be exposed to the air for extended periods of time or be allowed to dry out.

7.1.2 If the electrode has a solution fill cap, remove the cap when using the electrode and replace it when probe is not in use.

7.2 Meter Calibration:

7.2.1 Calibration must be done daily or anytime the pH meter is used. Turn on the pH meter and allow it to warm up for 30 minutes. Refer to the manufacturer instructions for information on using the instrument. Check probe filling solution level. If there are air bubbles in the probe tip or chamber, shake down the probe like a thermometer. If crystals have formed inside or around filling solution hole, rinse with distilled water and replace solution with Orion #810007, 3M KCl. Do not use solutions containing silver.

7.2.2 Calibrate the 520A meter using autocalibration with two buffers. This procedure is outlined in the instrument manual. (Manual calibration with two buffers may also be selected if desired).

7.2.3 For samples expected to have a pH above 7, calibrate with buffers pH 7.00 and 10.00. For samples expected to have a pH between 4 and 7, calibrate with buffers pH 4.00 and 7.00. For samples expected to have a pH below 4, calibrate with buffers pH 2.00 and 4.00.

7.2.4 Press "calibrate."

7.2.5 Press "2" to indicate the number of buffers used to calibrate. Press "yes."

7.2.6 Place a stir bar and the probe in the first buffer and start the stirrer. Enter the buffer value if the one indicated by the meter is not correct. Press "yes."

7.2.7 Rinse the probe with reagent water and blot dry. Be sure not to wipe the probe as this will leave a static charge that will create error in the results. Repeat step 7.2.6 for the second buffer.

7.2.8 The meter will then display the electrode slope. The slope must be between 80 and 120%. If it is not, recalibrate. Record this value on the bench sheet.

7.2.9 The meter will automatically go into "MEASURE" mode.

7.3 Sample Determinations

7.3.1 For best results, samples and buffers should be within a 2°C range.

7.3.2 Rinse the pH electrode with reagent water and blot dry with a tissue. Pour approximately 50 mL of sample into a 100 mL beaker and add a magnetic stir bar. Immerse probe in sample and gently stir.

7.3.3 Wait for the reading to stabilize (indicated by the meter changing from "measuring" to "ready") and record the reading to the nearest 0.01 pH unit.

7.3.4 Between samples, rinse the pH electrode with reagent water and blot dry with a tissue.

8. DATA TREATMENT:

The pH values of the samples are read directly from the meter display. Results are to be reported to the nearest 0.01 pH unit. Sample results must fall between the calibration buffer values. For samples that fall outside the original calibration, recalibrate with appropriate buffer values and reanalyze.

9. QUALITY CONTROL:

9.1 The Instrument Performance Check (IPC) (calibration buffer pH 7.00) must be analyzed after every 10 samples and at the end of a sample run. If the buffer does not maintain within 0.05 pH unit, discontinue analysis and recalibrate. Reanalyze the samples after the last acceptable IPC and before a failing IPC until precision criteria is met.

9.2 At least one Quality Control Sample (QCS) (pH 7.00 buffer from a manufacturer different than that used for calibration) is analyzed following the calibration. Periodic reanalysis of the QCS is recommended. Results obtained must be within 0.05 pH unit.

9.3 Audit samples supplied by a NIST accredited PT vendor will be analyzed biannually. Results will be reported to the quality assurance officer who will submit them to the PT vendor for evaluation.

9.4 Duplicates are analyzed on 10% of samples in any analytical batch. The allowable difference of duplicate samples for is 0.14 pH unit. Samples with results outside the limits must be repeated as well as additional samples in the analytical batch.

9.5 Repeat any field blank with pH results outside the range of 6-9. If the repeat analysis does not confirm earlier results, repeat other samples in the analytical batch.

9.6 Repeat field duplicates with relative difference greater than 0.14 pH unit.

9.7 A QC summary should be completed immediately after sample analysis. All data must be submitted to the QA office for approval.

9.8 Results for any samples analyzed past the 24-hour holding time will be qualified using the appropriate qualifier.

10. REFERENCES:

Standard Methods for the Examination of Water and Wastewater, 18th, 19th, and 20th editions, 4500-H^+ B.

11. REVISIONS:

11.1 Added section 10 for References.

11.2 Altered title from "US EPA Method 150.1" to read "STD METHODS 18th, 19th, & 20th ed. 4500-H^+ B."

4500-H^+ pH VALUE*

4500-H^+ A. Introduction

1. Principles

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, e.g., acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control, is pH-dependent. pH is used in alkalinity and carbon dioxide measurements and many other acid-base equilibria. At a given temperature the *intensity* of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Alkalinity and acidity are the acid- and base-neutralizing capacities of a water and usually are expressed as milligrams $CaCO_3$ per liter. Buffer capacity is the amount of strong acid or base, usually expressed in moles per liter, needed to change the pH value of a 1-L sample by 1 unit. pH as defined by Sorenson[1] is $-\log [H^+]$; it is the "intensity" factor of acidity. Pure water is very slightly ionized and at equilibrium the ion product is

$$[H^+][OH^-] = K_w = 1.01 \times 10^{-14} \text{ at } 25°C \quad (1)$$

and

$$[H^+] = [OH^-] = 1.005 \times 10^{-7}$$

where:

$[H^+]$ = activity of hydrogen ions, moles/L,
$[OH^-]$ = activity of hydroxyl ions, moles/L, and
K_w = ion product of water.

Because of ionic interactions in all but very dilute solutions, it is necessary to use the "activity" of an ion and not its molar concentration. Use of the term pH assumes that the activity of the hydrogen ion, a_{H^+}, is being considered. The *approximate* equivalence to molarity, $[H^+]$ can be presumed only in very dilute solutions (ionic strength <0.1).

A logarithmic scale is convenient for expressing a wide range of ionic activities. Equation 1 in logarithmic form and corrected to reflect activity is:

$$(-\log_{10} a_{H^+}) + (-\log_{10} a_{OH^-}) = 14 \quad (2)$$

or

$$pH + pOH = pK_w$$

where:

pH† = $\log_{10} a_{H^+}$ and
pOH = $\log_{10} a_{OH^-}$.

Equation 2 states that as pH increases pOH decreases correspondingly and vice versa because pK_w is constant for a given temperature. At 25°C, pH 7.0 is neutral, the activities of the hydrogen and hydroxyl ions are equal, and each corresponds to an approximate activity of 10^{-7} moles/L. The neutral point is temperature-dependent and is pH 7.5 at 0°C and pH 6.5 at 60°C.

The pH value of a highly dilute solution is approximately the same as the negative common logarithm of the hydrogen ion concentration. Natural waters usually have pH values in the range of 4 to 9, and most are slightly basic because of the presence of bicarbonates and carbonates of the alkali and alkaline earth metals.

2. Reference

1. SORENSON, S. 1909. Über die Messung und die Bedeutung der Wasserstoff ionen Konzentration bei Enzymatischen Prozessen. *Biochem. Z.* 21:131.

* Approved by Standard Methods Committee, 2000.

† p designates $-\log_{10}$ of a number.

4500-H^+ B. Electrometric Method

1. General Discussion

a. Principle: The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, the glass electrode commonly is used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

Because single ion activities such as a_{H^+} cannot be measured, pH is defined operationally on a potentiometric scale. The pH measuring instrument is calibrated potentiometrically with an indicating (glass) electrode and a reference electrode using National Institute of Standards and Technology (NIST) buffers having assigned values so that:

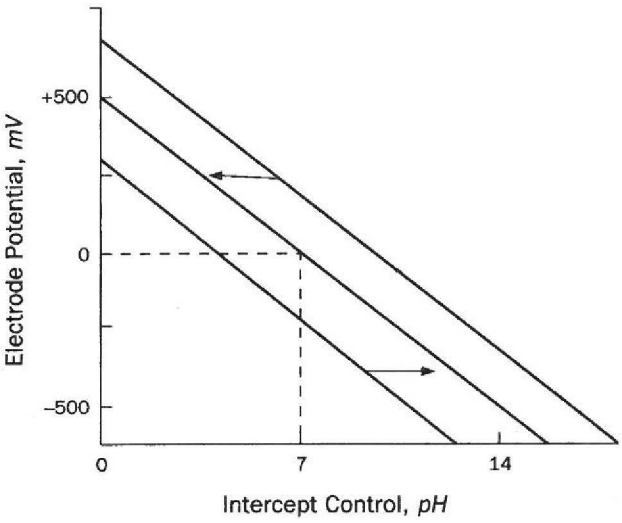

Figure 4500-H⁺:1. Electrode potential vs. pH. Intercept control shifts response curve laterally.

$$pH_B = -\log_{10} a_{H^+}$$

where:

pH_B = assigned pH of NIST buffer.

The operational pH scale is used to measure sample pH and is defined as:

$$pH_x = pH_B \pm \frac{F(E_x - E_s)}{2.303\ RT}$$

where:

pH_x = potentiometrically measured sample pH,
F = Faraday: 9.649×10^4 coulomb/mole,
E_x = sample emf, V,
E_s = buffer emf, V,
R = gas constant; 8.314 joule/(mole °K), and
T = absolute temperature, °K.

NOTE: Although the equation for pH_x appears in the literature with a plus sign, the sign of emf readings in millivolts for most pH meters manufactured in the U.S. is negative. The choice of negative sign is consistent with the IUPAC Stockholm convention concerning the sign of electrode potential.[1,2]

The activity scale gives values that are higher than those on Sorenson's scale by 0.04 units:

$$pH\ (activity) = pH\ (Sorenson) + 0.04$$

The equation for pH_x assumes that the emf of the cells containing the sample and buffer is due solely to hydrogen ion activity unaffected by sample composition. In practice, samples will have varying ionic species and ionic strengths, both affecting H^+ activity. This imposes an experimental limitation on pH measurement; thus, to obtain meaningful results, the differences between E_x and E_s should be minimal. Samples must be dilute aqueous solutions of simple solutes (<0.2*M*). (Choose buffers to bracket the sample.) Determination of pH cannot be made accurately in nonaqueous media, suspensions, colloids, or high-ionic-strength solutions.

b. Interferences: The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at pH > 10. Reduce this error by using special "low sodium error" electrodes.

pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. In the first instance, the Nernstian slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH buffers have a specified pH at indicated temperatures.

Always report temperature at which pH is measured.

2. Apparatus

a. pH meter consisting of potentiometer, a glass electrode, a reference electrode, and a temperature-compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test solution. Many pH meters are capable of reading pH or millivolts and some have scale expansion that permits reading to 0. 001 pH unit, but most instruments are not that precise.

For routine work use a pH meter accurate and reproducible to 0.1 pH unit with a range of 0 to 14 and equipped with a temperature-compensation adjustment.

Although manufacturers provide operating instructions, the use of different descriptive terms may be confusing. For most instruments, there are two controls: intercept (set buffer, asymmetry, standardize) and slope (temperature, offset); their functions are shown diagramatically in Figures 4500-H⁺:1 and 2. The intercept control shifts the response curve laterally to pass through the isopotential point with no change in slope. This

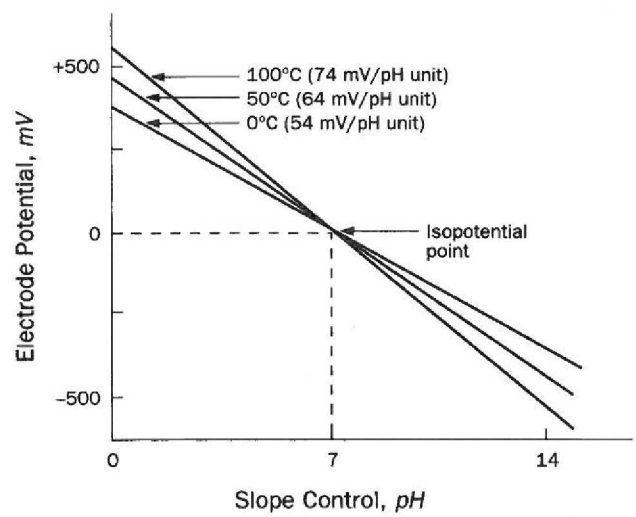

Figure 4500-H⁺:2. Typical pH electrode response as a function of temperature.

TABLE 4500-H^+:I. PREPARATION OF pH STANDARD SOLUTIONS[3]

Standard Solution (molality)	pH at 25°C	Weight of Chemicals Needed/1000 mL Pure Water at 25°C
Primary standards:		
Potassium hydrogen tartrate (saturated at 25°C)	3.557	> 7 g $KHC_4H_4O_6$*
0.05 potassium dihydrogen citrate	3.776	11.41 g $KH_2C_6H_5O_7$
0.05 potassium hydrogen phthalate	4.004	10.12 g $KHC_8H_4O_4$
0.025 potassium dihydrogen phosphate + 0.025 disodium hydrogen phosphate	6.863	3.387 g KH_2PO_4 + 3.533 g Na_2HPO_4†
0.008 695 potassium dihydrogen phosphate + 0.030 43 disodium hydrogen phosphate	7.415	1.179 g KH_2PO_4 + 4.303 g Na_2HPO_4†
0.01 sodium borate decahydrate (borax)	9.183	3.80 g $Na_2B_4O_7 \cdot 10H_2O$†
0.025 sodium bicarbonate + 0.025 sodium carbonate	10.014	2.092 g $NaHCO_3$ + 2.640 g Na_2CO_3
Secondary standards:		
0.05 potassium tetroxalate dihydrate	1.679	12.61 g $KH_3C_4O_8 \cdot 2H_2O$
Calcium hydroxide (saturated at 25°C)	12.454	> 2 g $Ca(OH)_2$*

* Approximate solubility.
† Prepare with freshly boiled and cooled distilled water (carbon-dioxide-free).

permits bringing the instrument on scale (0 mV) with a pH 7 buffer that has no change in potential with temperature.

The slope control rotates the emf/pH slope about the isopotential point (0 mV/pH 7). To adjust slope for temperature without disturbing the intercept, select a buffer that brackets the sample with pH 7 buffer and adjust slope control to pH of this buffer. The instrument will indicate correct millivolt change per unit pH at the test temperature.

b. Reference electrode consisting of a half cell that provides a constant electrode potential. Commonly used are calomel and silver: silver-chloride electrodes. Either is available with several types of liquid junctions.

The liquid junction of the reference electrode is critical because at this point the electrode forms a salt bridge with the sample or buffer and a liquid junction potential is generated that in turn affects the potential produced by the reference electrode. Reference electrode junctions may be annular ceramic, quartz, or asbestos fiber, or the sleeve type. The quartz type is most widely used. The asbestos fiber type is not recommended for strongly basic solutions. Follow the manufacturer's recommendation on use and care of the reference electrode.

Refill nonsealed electrodes with the correct electrolyte to proper level and make sure junction is properly wetted.

c. Glass electrode: The sensor electrode is a bulb of special glass containing a fixed concentration of HCl or a buffered chloride solution in contact with an internal reference electrode. Upon immersion of a new electrode in a solution the outer bulb surface becomes hydrated and exchanges sodium ions for hydrogen ions to build up a surface layer of hydrogen ions. This, together with the repulsion of anions by fixed, negatively charged silicate sites, produces at the glass-solution interface a potential that is a function of hydrogen ion activity in solution.

Several types of glass electrodes are available. Combination electrodes incorporate the glass and reference electrodes into a single probe. Use a "low sodium error" electrode that can operate at high temperatures for measuring pH over 10 because standard glass electrodes yield erroneously low values. For measuring pH below 1 standard glass electrodes yield erroneously high values; use liquid membrane electrodes instead.

d. Beakers: Preferably use polyethylene or TFE* beakers.

e. Stirrer: Use either a magnetic, TFE-coated stirring bar or a mechanical stirrer with inert plastic-coated impeller.

f. Flow chamber: Use for continuous flow measurements or for poorly buffered solutions.

3. Reagents

a. General preparation: Calibrate the electrode system against standard buffer solutions of known pH. Because buffer solutions may deteriorate as a result of mold growth or contamination, prepare fresh as needed for accurate work by weighing the amounts of chemicals specified in Table 4500-H^+:I, dissolving in distilled water at 25°C, and diluting to 1000 mL. This is particularly important for borate and carbonate buffers.

Boil and cool distilled water having a conductivity of less than 2 μmhos/cm. To 50 mL add 1 drop of saturated KCl solution suitable for reference electrode use. If the pH of this test solution is between 6.0 and 7.0, use it to prepare all standard solutions.

Dry KH_2PO_4 at 110 to 130°C for 2 h before weighing but do not heat unstable hydrated potassium tetroxalate above 60°C nor dry the other specified buffer salts.

Although ACS-grade chemicals generally are satisfactory for preparing buffer solutions, use certified materials available from the National Institute of Standards and Technology when the greatest accuracy is required. For routine analysis, use commercially available buffer tablets, powders, or solutions of tested quality. In preparing buffer solutions from solid salts, insure complete solution.

As a rule, select and prepare buffer solutions classed as primary standards in Table 4500-H^+:I; reserve secondary standards for extreme situations encountered in wastewater measurements. Consult Table 4500- H^+:II for accepted pH of standard buffer solutions at temperatures other than 25°C. In routine use, store buffer solutions and samples in polyethylene bottles. Replace buffer solutions every 4 weeks.

* Teflon or equivalent

b. Saturated potassium hydrogen tartrate solution: Shake vigorously an excess (5 to 10 g) of finely crystalline $KHC_4H_4O_6$ with 100 to 300 mL distilled water at 25°C in a glass-stoppered bottle. Separate clear solution from undissolved material by decantation or filtration. Preserve for 2 months or more by adding one thymol crystal (8 mm diam) per 200 mL solution.

c. Saturated calcium hydroxide solution: Calcine a well-washed, low-alkali grade $CaCO_3$ in a platinum dish by igniting for 1 h at 1000°C. Cool, hydrate by slowly adding distilled water with stirring, and heat to boiling. Cool, filter, and collect solid $Ca(OH)_2$ on a fritted glass filter of medium porosity. Dry at 110°C, cool, and pulverize to uniformly fine granules. Vigorously shake an excess of fine granules with distilled water in a stoppered polyethylene bottle. Let temperature come to 25°C after mixing. Filter supernatant under suction through a sintered glass filter of medium porosity and use filtrate as the buffer solution. Discard buffer solution when atmospheric CO_2 causes turbidity to appear.

d. Auxiliary solutions: 0.1*N* NaOH, 0.1*N* HCl, 5*N* HCl (dilute five volumes 6*N* HCl with one volume distilled water), and acid potassium fluoride solution (dissolve 2 g KF in 2 mL conc H_2SO_4 and dilute to 100 mL with distilled water).

4. Procedure

a. Instrument calibration: In each case follow manufacturer's instructions for pH meter and for storage and preparation of electrodes for use. Recommended solutions for short-term storage of electrodes vary with type of electrode and manufacturer, but generally have a conductivity greater than 4000 μmhos/cm. Tap water is a better substitute than distilled water, but pH 4 buffer is best for the single glass electrode and saturated KCl is preferred for a calomel and Ag/AgCl reference electrode. Saturated KCl is the preferred solution for a combination electrode. Keep electrodes wet by returning them to storage solution whenever pH meter is not in use.

Before use, remove electrodes from storage solution, rinse, blot dry with a soft tissue, place in initial buffer solution, and set the isopotential point (¶ 2*a* above). Select a second buffer within 2 pH units of sample pH and bring sample and buffer to same temperature, which may be the room temperature, a fixed temperature such as 25°C, or the temperature of a fresh sample. Remove electrodes from first buffer, rinse thoroughly with distilled water, blot dry, and immerse in second buffer. Record temperature of measurement and adjust temperature dial on meter so that meter indicates pH value of buffer at test temperature (this is a slope adjustment).

Use the pH value listed in the tables for the buffer used at the test temperature. Remove electrodes from second buffer, rinse thoroughly with distilled water and dry electrodes as indicated above. Immerse in a third buffer below pH 10, approximately 3 pH units different from the second; the reading should be within 0.1 unit for the pH of the third buffer. If the meter response shows a difference greater than 0.1 pH unit from expected value, look for trouble with the electrodes or potentiometer (see ¶s 5*a* and *b* below).

The purpose of standardization is to adjust the response of the glass electrode to the instrument. When only occasional pH measurements are made standardize instrument before each measurement. When frequent measurements are made and the instrument is stable, standardize less frequently. If sample pH

TABLE 4500-H$^+$:II. STANDARD pH VALUES[3]

	Primary Standards							Secondary Standards	
Temperature °C	Tartrate (Saturated)	Citrate (0.05*M*)	Phthalate (0.05*M*)	Phosphate (1:1)	Phosphate (1:3.5)	Borax (0.01*M*)	Bicarbonate-Carbonate (0.025*M*)	Tetroxalate (0.05*M*)	Calcium Hydroxide (Saturated)
0			4.003	6.982	7.534	9.460	10.321	1.666	
5			3.998	6.949	7.501	9.392	10.248	1.668	
10			3.996	6.921	7.472	9.331	10.181	1.670	
15			3.996	6.898	7.449	9.276	10.120	1.672	
20			3.999	6.878	7.430	9.227	10.064	1.675	
25	3.557	3.776	4.004	6.863	7.415	9.183	10.014	1.679	12.454
30	3.552		4.011	6.851	7.403	9.143	9.968	1.683	
35	3.549		4.020	6.842	7.394	9.107	9.928	1.688	
37			4.024	6.839	7.392	9.093			
40	3.547		4.030	6.836	7.388	9.074	9.891	1.694	
45	3.547		4.042	6.832	7.385	9.044	9.859	1.700	
50	3.549		4.055	6.831	7.384	9.017	9.831	1.707	
55	3.554		4.070					1.715	
60	3.560		4.085					1.723	
70	3.580		4.12					1.743	
80	3.609		4.16					1.766	
90	3.650		4.19					1.792	
95	3.674		4.21					1.806	

values vary widely, standardize for each sample with a buffer having a pH within 1 to 2 pH units of the sample.

b. Sample analysis: Establish equilibrium between electrodes and sample by stirring sample to insure homogeneity; stir gently to minimize carbon dioxide entrainment. For buffered samples or those of high ionic strength, condition electrodes after cleaning by dipping them into sample for 1 min. Blot dry, immerse in a fresh portion of the same sample, and read pH.

With dilute, poorly buffered solutions, equilibrate electrodes by immersing in three or four successive portions of sample. Take a fresh sample to measure pH.

5. Trouble Shooting

a. Potentiometer: To locate trouble source disconnect electrodes and, using a short-circuit strap, connect reference electrode terminal to glass electrode terminal. Observe change in pH when instrument calibration knob is adjusted. If potentiometer is operating properly, it will respond rapidly and evenly to changes in calibration over a wide scale range. A faulty potentiometer will fail to respond, will react erratically, or will show a drift upon adjustment. Switch to the millivolt scale on which the meter should read zero. If inexperienced, do not attempt potentiometer repair other than maintenance as described in instrument manual.

b. Electrodes: If potentiometer is functioning properly, look for the instrument fault in the electrode pair. Substitute one electrode at a time and cross-check with two buffers that are about 4 pH units apart. A deviation greater than 0.1 pH unit indicates a faulty electrode. Glass electrodes fail because of scratches, deterioration, or accumulation of debris on the glass surface. Rejuvenate electrode by alternately immersing it three times each in 0.1*N* HCl and 0.1*N* NaOH. If this fails, immerse tip in KF solution for 30 s. After rejuvenation, soak in pH 7.0 buffer overnight. Rinse and store in pH 7.0 buffer. Rinse again with distilled water before use. Protein coatings can be removed by soaking glass electrodes in a 10% pepsin solution adjusted to pH 1 to 2.

To check reference electrode, oppose the emf of a questionable reference electrode against another one of the same type that is known to be good. Using an adapter, plug good reference electrode into glass electrode jack of potentiometer; then plug questioned electrode into reference electrode jack. Set meter to read millivolts and take readings with both electrodes immersed in the same electrolyte (KCl) solution and then in the same buffer solution. The millivolt readings should be 0 ± 5 mV for both solutions. If different electrodes are used, i.e., silver: silver-chloride against calomel or vice versa, the reading will be 44 ± 5 mV for a good reference electrode.

Reference electrode troubles generally are traceable to a clogged junction. Interruption of the continuous trickle of electrolyte through the junction causes increase in response time and drift in reading. Clear a clogged junction by applying suction to the tip or by boiling tip in distilled water until the electrolyte flows freely when suction is applied to tip or pressure is applied to the fill hole. Replaceable junctions are available commercially.

6. Precision and Bias

By careful use of a laboratory pH meter with good electrodes, a precision of ±0.02 pH unit and an accuracy of ±0.05 pH unit can be achieved. However, ±0.1 pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions. For this reason, report pH values to the nearest 0.1 pH unit. A synthetic sample of a Clark and Lubs buffer solution of pH 7.3 was analyzed electrometrically by 30 laboratories with a standard deviation of ±0.13 pH unit.

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where:

A = weight of dried residue + dish, mg,
B = weight of dish,
C = weight of wet sample + dish, mg, and
D = weight of residue + dish after ignition, mg.

5. Precision and Bias

Precision and bias data are not now available.

6. Bibliography

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2550 TEMPERATURE*

2550 A. Introduction

Temperature readings are used in the calculation of various forms of alkalinity, in studies of saturation and stability with respect to calcium carbonate, in the calculation of salinity, and in general laboratory operations. In limnological studies, water temperatures as a function of depth often are required. Elevated temperatures resulting from discharges of heated water may have significant ecological impact. Identification of source of water supply, such as deep wells, often is possible by temperature measurements alone. Industrial plants often require data on water temperature for process use or heat-transmission calculations.

* Approved by Standard Methods Committee, 2000.

2550 B. Laboratory and Field Methods

1. Laboratory and Other Non-Depth Temperature Measurements

Normally, temperature measurements may be made with any good mercury-filled Celsius thermometer. As a minimum, the thermometer should have a scale marked for every 0.1°C, with markings etched on the capillary glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. Periodically check the thermometer against a precision thermometer certified by the National Institute of Standards and Technology (NIST, formerly National Bureau of Standards)* that is used with its certificate and correction chart. For field operations use a thermometer having a metal case to prevent breakage.

A total immersion thermometer is designed to indicate temperatures correctly when the bulb and the entire liquid column are exposed to the temperature being measured, except for a minimal emergent length. A partial-immersion thermometer has a line around it at the immersion distance from the bottom. It indicates correctly when the bulb and the liquid column to that line are exposed to the temperature being measured and the emergent stem is at ambient temperature.

* Some commercial thermometers may be as much as 3°C in error.

2. Depth Temperature Measurements

Depth temperature required for limnological studies may be measured with a reversing thermometer, thermophone, or thermistor. The thermistor is most convenient and accurate; however, higher cost may preclude its use. Calibrate any temperature measurement devices with a NIST-certified thermometer before field use. Make readings with the thermometer or device immersed in water long enough to permit complete equilibration. Report results to the nearest 0.1 or 1.0°C, depending on need.

The thermometer commonly used for depth measurements is of the reversing type. It often is mounted on the sample collection apparatus so that a water sample may be obtained simultaneously. Correct readings of reversing thermometers for changes due to differences between temperature at reversal and temperature at time of reading. Calculate as follows:

$$\Delta T = \left[\frac{(T^1 - t)(T^1 + V_0)}{K}\right] \times \left[1 + \frac{(T^1 - t)(T^1 + V_0)}{K}\right] + L$$

where:

ΔT = correction to be added algebraically to uncorrected reading,
T^1 = uncorrected reading at reversal,

t = temperature at which thermometer is read,
V_0 = volume of small bulb end of capillary up to 0°C graduation,
K = constant depending on relative thermal expansion of mercury and glass (usual value of K = 6100), and
L = calibration correction of thermometer depending on T^1.

If series observations are made it is convenient to prepare graphs for a thermometer to obtain ΔT from any values of T^1 and t.

3. Bibliography

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2560 PARTICLE COUNTING AND SIZE DISTRIBUTION*

2560 A. Introduction

1. General Discussion

Particles are ubiquitous in natural waters and in water and wastewater treatment streams. Particle counting and size distribution analysis can help to determine the makeup of natural waters, treatment plant influent, process water, and finished water. Similarly, it can aid in designing treatment processes, making decisions about changes in operations, and/or determining process efficiency. Methods for measuring particle size distribution included herein depend on electronic measurement devices because manual methods are likely to be too slow for routine analysis. However, when particle size analysis is to include size distribution of large (>500-μm) aggregates, use direct microscopic counting and sizing. Principles of various types of instruments capable of producing both size and number concentration information on particulate dispersions are included. Unless explicitly stated otherwise, the term "size distribution" means an absolute size distribution, i.e., one that includes the number concentration or count.

In most particle-counting instruments, particles pass though a sensing zone where they are measured individually; the only exception included is the static type of light-scattering instrument. Instruments create an electronic pulse (voltage, current, or resistance) that is proportional to a characteristic size of the particle. The instrument responses (pulse height, width, or area) are classified by magnitude and counted in each class to yield the particle size distribution.

2. Selection of Method

Three instrument types are included: electrical sensing zone instruments, light-blockage instruments, and light-scattering instruments.

Select instrument consistent with expected use of the particle size analysis. Instruments vary in the particle characteristic being sensed, lower and upper size limits of detection, degree of resolution of the size distribution, particle number concentration range that can be measured accurately, amount of shear to which a sample is subjected before measurement, amount of sample preparation, operator skill required, and the ease with which data can be obtained and manipulated into the desired forms. See Sections 2560B.1, C.1, and D.1, and manufacturers' literature for information on characteristics of each type of instrumentation.

Some instruments can be set up for either continuous-flow or batch sampling. Others can be used only for batch analysis. For instruments usable in both modes, check that no systematic differences in particle size distributions occur between continuous-flow measurements and batch samples taken at or near the intake point for continuous-flow samples.

3. Sample Collection and Handling

a. Batch samples: Use extreme care in obtaining, handling, and preparing batch samples to avoid changing total particle count and size distribution.

Choose representative times and locations for sampling. Ensure that particles are not subjected to greater physical forces during collection than in their natural setting. Collect samples from a body of water with submerged vessels to minimize turbulence and bubble entrainment. If sampling from particular depths, use standard samplers designed for that purpose. For flowing systems, make sure that the velocity into the opening of the sampling device is the same as that of the flowing stream (isokinetic sampling) and that the opening

* Approved by Standard Methods Committee, 2000.
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4500-O OXYGEN (DISSOLVED)*

4500-O A. Introduction

1. Significance

Dissolved oxygen (DO) levels in natural and wastewaters depend on the physical, chemical, and biochemical activities in the water body. The analysis for DO is a key test in water pollution and waste treatment process control.

2. Selection of Method

Two methods for DO analysis are described: the Winkler or iodometric method and its modifications and the electrometric method using membrane electrodes. The iodometric method[1] is a titrimetric procedure based on the oxidizing property of DO while the membrane electrode procedure is based on the rate of diffusion of molecular oxygen across a membrane.[2] The choice of procedure depends on the interferences present, the accuracy desired, and, in some cases, convenience or expedience.

3. References

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* Approved by Standard Methods Committee, 2001.

4500-O B. Iodometric Methods

1. Principle

The iodometric test is the most precise and reliable titrimetric procedure for DO analysis. It is based on the addition of divalent manganese solution, followed by strong alkali, to the sample in a glass-stoppered bottle. DO rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides of higher valency states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of thiosulfate.

The titration end point can be detected visually, with a starch indicator, or electrometrically, with potentiometric or dead-stop techniques.[1] Experienced analysts can maintain a precision of ± 50 μg/L with visual end-point detection and a precision of ± 5 μg/L with electrometric end-point detection.[1,2]

The liberated iodine also can be determined directly by simple absorption spectrophotometers.[3] This method can be used on a routine basis to provide very accurate estimates for DO in the microgram-per-liter range provided that interfering particulate matter, color, and chemical interferences are absent.

2. Selection of Method

Before selecting a method consider the effect of interferences, particularly oxidizing or reducing materials that may be present in the sample. Certain oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Most organic matter is oxidized partially when the oxidized manganese precipitate is acidified, thus causing negative errors.

Several modifications of the iodometric method are given to minimize the effect of interfering materials.[2] Among the more commonly used procedures are the azide modification,[4] the permanganate modification,[5] the alum flocculation modification,[6] and the copper sulfate-sulfamic acid flocculation modification.[7,8] The azide modification (C) effectively removes interference caused by nitrite, which is the most common interference in biologically treated effluents and incubated BOD samples. Use the permanganate modification (D) in the presence of ferrous iron. When the sample contains 5 or more mg ferric iron salts/L, add potassium fluoride (KF) as the first reagent in the azide modification or after the permanganate treatment for ferrous iron. Alternately, eliminate Fe(III) interference by using 85 to 87% phosphoric acid (H_3PO_4) instead of sulfuric acid (H_2SO_4) for acidification. This procedure has not been tested for Fe(III) concentrations above 20 mg/L.

Use the alum flocculation modification (E) in the presence of suspended solids that cause interference and the copper sulfate-sulfamic acid flocculation modification (F) on activated-sludge mixed liquor.

3. Collection of Samples

Collect samples very carefully. Methods of sampling are highly dependent on source to be sampled and, to a certain extent, on method of analysis. Do not let sample remain in contact with air or be agitated, because either condition causes a change in its gaseous content. Samples from any depth in streams, lakes, or reservoirs, and samples of boiler water, need special precautions to eliminate changes in pressure and temperature. Procedures and equipment have been developed for sampling waters under pressure and unconfined waters (e.g., streams,

rivers, and reservoirs). Sampling procedures and equipment needed are described in American Society for Testing and Materials Special Technical Publication No. 148-1 and in U.S. Geological Survey Water Supply Paper No. 1454.

Collect surface water samples in narrow-mouth glass-stoppered BOD bottles of 300-mL capacity with tapered and pointed ground-glass stoppers and flared mouths. Avoid entraining or dissolving atmospheric oxygen. In sampling from a line under pressure, attach a glass or rubber tube to the tap and extend to bottom of bottle. Let bottle overflow two or three times its volume and replace stopper so that no air bubbles are entrained.

Suitable samplers for streams, ponds, or tanks of moderate depth are of the APHA type shown in Figure 4500-O:1. Use a Kemmerer-type sampler for samples collected from depths greater than 2 m. Bleed sample from bottom of sampler through a tube extending to bottom of a 250- to 300-mL BOD bottle. Fill bottle to overflowing (overflow for approximately 10 s), and prevent turbulence and formation of bubbles while filling. Record sample temperature to nearest degree Celsius or more precisely.

4. Preservation of Samples

Determine DO immediately on all samples containing an appreciable oxygen or iodine demand. Samples with no iodine demand may be stored for a few hours without change after adding manganous sulfate ($MnSO_4$) solution, alkali-iodide solution, and H_2SO_4, followed by shaking in the usual way. Protect stored samples from strong sunlight and titrate as soon as possible.

For samples with an iodine demand, preserve for 4 to 8 h by adding 0.7 mL conc H_2SO_4 and 1 mL sodium azide solution (2 g NaN_3/100 mL distilled water) to the BOD bottle. This will arrest biological activity and maintain DO if the bottle is stored at the temperature of collection or water-sealed and kept at 10 to 20°C. As soon as possible, complete the procedure, using 2 mL $MnSO_4$ solution, 3 mL alkali-iodide solution, and 2 mL conc H_2SO_4.

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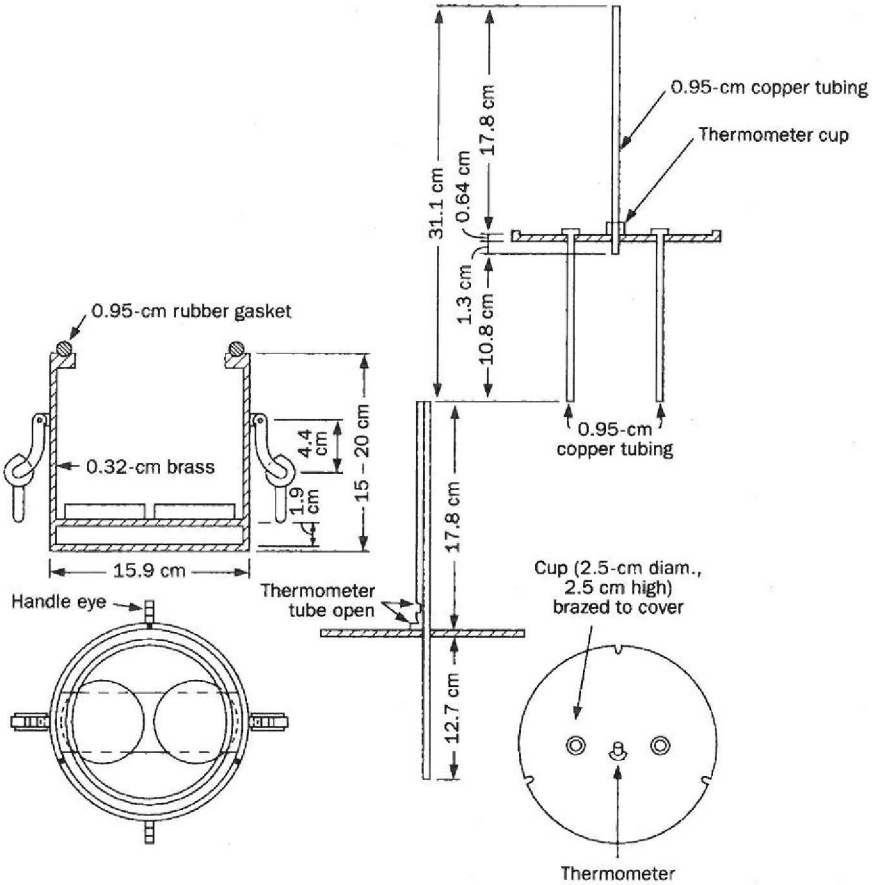

Figure 4500-O:1. DO and BOD sampler assembly.

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4500-O C. Azide Modification

1. General Discussion

Use the azide modification for most wastewater, effluent, and stream samples, especially if samples contain more than 50 μg NO_2^--N/L and not more than 1 mg ferrous iron/L. Other reducing or oxidizing materials should be absent. If 1 mL KF solution is added before the sample is acidified and there is no delay in titration, the method is applicable in the presence of 100 to 200 mg ferric iron/L.

2. Reagents

a. Manganous sulfate solution: Dissolve 480 g $MnSO_4 \cdot 4H_2O$, 400 g $MnSO_4 \cdot 2H_2O$, or 364 g $MnSO_4 \cdot H_2O$ in distilled water, filter, and dilute to 1 L. The $MnSO_4$ solution should not give a color with starch when added to an acidified potassium iodide (KI) solution.

b. Alkali-iodide-azide reagent:

1) For saturated or less-than-saturated samples—Dissolve 500 g NaOH (or 700 g KOH) and 135 g NaI (or 150 g KI) in distilled water and dilute to 1 L. Add 10 g NaN_3 dissolved in 40 mL distilled water. Potassium and sodium salts may be used interchangeably. This reagent should not give a color with starch solution when diluted and acidified.

2) For supersaturated samples—Dissolve 10 g NaN_3 in 500 mL distilled water. Add 480 g sodium hydroxide (NaOH) and 750 g sodium iodide (NaI), and stir until dissolved. There will be a white turbidity due to sodium carbonate (Na_2CO_3), but this will do no harm. CAUTION—*Do not acidify this solution because toxic hydrazoic acid fumes may be produced.*

c. Sulfuric acid, H_2SO_4, conc: One milliliter is equivalent to about 3 mL alkali-iodide-azide reagent.

d. Starch: Use either an aqueous solution or soluble starch powder mixtures.

To prepare an aqueous solution, dissolve 2 g laboratory-grade soluble starch and 0.2 g salicylic acid, as a preservative, in 100 mL hot distilled water.

e. Standard sodium thiosulfate titrant: Dissolve 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in distilled water. Add 1.5 mL 6*N* NaOH or 0.4 g solid NaOH and dilute to 1000 mL. Standardize with bi-iodate solution.

f. Standard potassium bi-iodate solution, 0.0021*M:* Dissolve 812.4 mg $KH(IO_3)_2$ in distilled water and dilute to 1000 mL.

Standardization—Dissolve approximately 2 g KI, free from iodate, in an erlenmeyer flask with 100 to 150 mL distilled water. Add 1 mL 6*N* H_2SO_4 or a few drops of conc H_2SO_4 and 20.00 mL standard bi-iodate solution. Dilute to 200 mL and titrate liberated iodine with thiosulfate titrant, adding starch toward end of titration, when a pale straw color is reached. When the solutions are of equal strength, 20.00 mL 0.025*M* $Na_2S_2O_3$ should be required. If not, adjust the $Na_2S_2O_3$ solution to 0.025*M*.

3. Procedure

a. To the sample collected in a 250- to 300-mL bottle, add 1 mL $MnSO_4$ solution, followed by 1 mL alkali-iodide-azide reagent. If pipets are dipped into sample, rinse them before returning them to reagent bottles. Alternatively, hold pipet tips just above liquid surface when adding reagents. Stopper carefully to exclude air bubbles and mix by inverting bottle a few times. When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernate above the manganese hydroxide floc, add 1.0 mL conc H_2SO_4. Restopper and mix by inverting several times until dissolution is complete. Titrate a volume corresponding to 200 mL original sample after correction for sample loss by displacement with reagents. Thus, for a total of 2 mL (1 mL each) of $MnSO_4$ and alkali-iodide-azide reagents in a 300-mL bottle, titrate $200 \times 300/(300 - 2) = 201$ mL.

b. Titrate with 0.025*M* $Na_2S_2O_3$ solution to a pale straw color. Add a few drops of starch solution and continue titration to first disappearance of blue color. If end point is overrun, back-titrate with 0.0021*M* bi-iodate solution added dropwise, or by adding a measured volume of treated sample. Correct for amount of bi-iodate solution or sample. Disregard subsequent recolorations due to the catalytic effect of nitrite or to traces of ferric salts that have not been complexed with fluoride.

4. Calculation

a. For titration of 200 mL sample, 1 mL 0.025*M* $Na_2S_2O_3$ = 1 mg DO/L.

b. To express results as percent saturation at 101.3 kPa, use the solubility data in Table 4500-O:I. Equations for correcting sol-

TABLE 4500-O:I SOLUBILITY OF OXYGEN IN WATER EXPOSED TO WATER-SATURATED AIR AT ATMOSPHERIC PRESSURE (101.3 kPa)[1]

Temperature °C	Oxygen Solubility mg/L Chlorinity: 0	5.0	10.0	15.0	20.0	25.0	Temperature °C	Oxygen Solubility mg/L Chlorinity: 0	5.0	10.0	15.0	20.0	25.0
0.0	14.621	13.728	12.888	12.097	11.355	10.657	26.0	8.113	7.711	7.327	6.962	6.615	6.285
1.0	14.216	13.356	12.545	11.783	11.066	10.392	27.0	7.968	7.575	7.201	6.845	6.506	6.184
2.0	13.829	13.000	12.218	11.483	10.790	10.139	28.0	7.827	7.444	7.079	6.731	6.400	6.085
3.0	13.460	12.660	11.906	11.195	10.526	9.897	29.0	7.691	7.317	6.961	6.621	6.297	5.990
4.0	13.107	12.335	11.607	10.920	10.273	9.664	30.0	7.559	7.194	6.845	6.513	6.197	5.896
5.0	12.770	12.024	11.320	10.656	10.031	9.441	31.0	7.430	7.073	6.733	6.409	6.100	5.806
6.0	12.447	11.727	11.046	10.404	9.799	9.228	32.0	7.305	6.957	6.624	6.307	6.005	5.717
7.0	12.139	11.442	10.783	10.162	9.576	9.023	33.0	7.183	6.843	6.518	6.208	5.912	5.631
8.0	11.843	11.169	10.531	9.930	9.362	8.826	34.0	7.065	6.732	6.415	6.111	5.822	5.546
9.0	11.559	10.907	10.290	9.707	9.156	8.636	35.0	6.950	6.624	6.314	6.017	5.734	5.464
10.0	11.288	10.656	10.058	9.493	8.959	8.454	36.0	6.837	6.519	6.215	5.925	5.648	5.384
11.0	11.027	10.415	9.835	9.287	8.769	8.279	37.0	6.727	6.416	6.119	5.835	5.564	5.305
12.0	10.777	10.183	9.621	9.089	8.586	8.111	38.0	6.620	6.316	6.025	5.747	5.481	5.228
13.0	10.537	9.961	9.416	8.899	8.411	7.949	39.0	6.515	6.217	5.932	5.660	5.400	5.152
14.0	10.306	9.747	9.218	8.716	8.242	7.792	40.0	6.412	6.121	5.842	5.576	5.321	5.078
15.0	10.084	9.541	9.027	8.540	8.079	7.642	41.0	6.312	6.026	5.753	5.493	5.243	5.005
16.0	9.870	9.344	8.844	8.370	7.922	7.496	42.0	6.213	5.934	5.667	5.411	5.167	4.933
17.0	9.665	9.153	8.667	8.207	7.770	7.356	43.0	6.116	5.843	5.581	5.331	5.091	4.862
18.0	9.467	8.969	8.497	8.049	7.624	7.221	44.0	6.021	5.753	5.497	5.252	5.017	4.793
19.0	9.276	8.792	8.333	7.896	7.483	7.090	45.0	5.927	5.665	5.414	5.174	4.944	4.724
20.0	9.092	8.621	8.174	7.749	7.346	6.964	46.0	5.835	5.578	5.333	5.097	4.872	4.656
21.0	8.915	8.456	8.021	7.607	7.214	6.842	47.0	5.744	5.493	5.252	5.021	4.801	4.589
22.0	8.743	8.297	7.873	7.470	7.087	6.723	48.0	5.654	5.408	5.172	4.947	4.730	4.523
23.0	8.578	8.143	7.730	7.337	6.963	6.609	49.0	5.565	5.324	5.094	4.872	4.660	4.457
24.0	8.418	7.994	7.591	7.208	6.844	6.498	50.0	5.477	5.242	5.016	4.799	4.591	4.392
25.0	8.263	7.850	7.457	7.083	6.728	6.390							

NOTE:

1. The table provides three decimal places to aid interpolation. When computing saturation values to be used with measured values, such as in computing DO deficit in a receiving water, precision of measured values will control choice of decimal places to be used.
2. Equations are available to compute DO concentration in fresh water[1-3] and in seawater[1] at equilibrium with water-saturated air. Figures and tables also are available.[3]

   Calculate the equilibrium oxygen concentration, C^*, from equation:

$$\ln C^* = -139.344\,11 + (1.575\,701 \times 10^5/T) - (6.642\,308 \times 10^7/T^2) + (1.243\,800 \times 10^{10}/T^3) - (8.621\,949 \times 10^{11}/T^4) - \mathrm{Chl}\,[(3.1929) \times 10^{-2}) - (1.9428 \times 10^1/T) + (3.8673 \times 10^3/T^2)]$$

   where:

   C^* = equilibrium oxygen concentration at 101.325 kPa, mg/L,
   T = temperature (°K) = °C + 273.150, (°C is between 0.0 and 40.0 in the equation; the table is accurate up to 50.0), and
   Chl = Chlorinity (see definition in Note 4, below).

   Example 1: At 20°C and 0.000 Chl, ln C^* = 2.207 442 and C^* = 9.092 mg/L;
   Example 2: At 20°C and 15.000 ChL,

$$\ln C^* = (2.207\,442) - 15.000\,(0.010\,657) = 2.0476 \text{ and } C^* = 7.749 \text{ mg/L}.$$

   When salinity is used, replace the chlorinity term (−Chl[. . .]) by:

$$-S(1.7674 \times 10^{-2}) - (1.0754 \times 10^1/T) + (2.1407 \times 10^3/T^2)$$

   where:

   S = salinity (see definition in Note 4, below).

3. For nonstandard conditions of pressure:

$$C_p = C^*P\left[\frac{(1 - P_{wv}/P)(1 - \theta P)}{(1 - P_{wv})(1 - \theta)}\right]$$

   where:

   C_p = equilibrium oxygen concentration at nonstandard pressure, mg/L,
   C^* = equilibrium oxygen concentration at standard pressure of 1 atm, mg/L.
   P = nonstandard pressure, atm,
   P_{wv} = partial pressure of water vapor, atm, computed from: $\ln P_{wv} = 11.8571 - (3840.70/T) - (216\,961/T^2)$,
   T = temperature, °K,
   $\theta = 0.000\,975 - (1.426 \times 10^{-5}t) + (6.436 \times 10^{-8}t^2)$, and
   t = temperature, °C.

   N.B.: Although not explicit in the above, the quantity in brackets in the equation for C_p has dimensions of atm^{-1} per Reference 4, so that P multiplied by this quantity is dimensionless.

   Also, the equation for ln P_{wv} is strictly valid for fresh water only, but for practical purposes no error is made by neglecting the effect of salinity. An equation for P_{wv} that includes the salinity factor may be found in Reference 1.

   Example 3: At 20°C, 0.000 Chl, and 0.700 atm,

$$C_p = C^*\,P\,(0.990\,092) = 6.30 \text{ mg/L}.$$

4. Definitions:

   Salinity: Although salinity has been defined traditionally as the total solids in water after all carbonates have been converted to oxides, all bromide and iodide have been replaced by chloride, and all organic matter has been oxidized (see Section 2520), the new scale used to define salinity is based on the electrical conductivity of seawater relative to a specified solution of KCl in water.[5] The scale is dimensionless and the traditional dimension of parts per thousand (i.e., g/kg of solution) no longer applies.

   Chlorinity: Chlorinity is defined in relation to salinity as follows:

$$\text{Salinity} = 1.806\,55 \times \text{chlorinity}$$

   Although chlorinity is not equivalent to chloride concentration, the factor for converting a chloride concentration in seawater to include bromide, for example, is only 1.0045 (based on the relative molecular weights and amounts of the two ions). Therefore, for practical purposes, chloride concentration (in g/kg of solution) is nearly equal to chlorinity in seawater. For wastewater, it is necessary to know the ions responsible for the solution's electrical conductivity to correct for their effect on oxygen solubility and use of the tabular value. If this is not done, the equation is inappropriate unless the relative composition of the wastewater is similar to that of seawater.

ubilities to barometric pressures other than mean sea level and for various chlorinities are given below the table.

5. Precision and Bias

DO can be determined with a precision, expressed as a standard deviation, of about 20 μg/L in distilled water and about 60 μg/L in wastewater and secondary effluents. In the presence of appreciable interference, even with proper modifications, the standard deviation may be as high as 100 μg/L. Still greater errors may occur in testing waters having organic suspended solids or heavy pollution. Avoid errors due to carelessness in collecting samples, prolonging the completion of test, or selecting an unsuitable modification.

6. References

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4500-O D. Permanganate Modification

1. General Discussion

Use the permanganate modification only on samples containing ferrous iron. Interference from high concentrations of ferric iron (up to several hundred milligrams per liter), as in acid mine water, may be overcome by the addition of 1 mL potassium fluoride (KF) and azide, provided that the final titration is made immediately after acidification.

This procedure is ineffective for oxidation of sulfite, thiosulfate, polythionate, or the organic matter in wastewater. The error with samples containing 0.25% by volume of digester waste from the manufacture of sulfite pulp may amount to 7 to 8 mg DO/L. With such samples, use the alkali-hypochlorite modification.[1] At best, however, the latter procedure gives low results, the deviation amounting to 1 mg/L for samples containing 0.25% digester wastes.

2. Reagents

All the reagents required for Method C, and in addition:

a. Potassium permanganate solution: Dissolve 6.3 g $KMnO_4$ in distilled water and dilute to 1 L.

b. Potassium oxalate solution: Dissolve 2 g $K_2C_2O_4 \cdot H_2O$ in 100 mL distilled water; 1 mL will reduce about 1.1 mL permanganate solution.

c. Potassium fluoride solution: Dissolve 40 g $KF \cdot 2H_2O$ in distilled water and dilute to 100 mL.

3. Procedure

a. To a sample collected in a 250- to 300-mL bottle add, below the surface, 0.70 mL conc H_2SO_4, 1 mL $KMnO_4$ solution, and 1 mL KF solution. Stopper and mix by inverting. Never add more than 0.7 mL conc H_2SO_4 as the first step of pretreatment. Add acid with a 1-mL pipet graduated to 0.1 mL. Add sufficient $KMnO_4$ solution to obtain a violet tinge that persists for 5 min. If the permanganate color is destroyed in a shorter time, add additional $KMnO_4$ solution, but avoid large excesses.

b. Remove permanganate color completely by adding 0.5 to 1.0 mL $K_2C_2O_4$ solution. Mix well and let stand in the dark to facilitate the reaction. Excess oxalate causes low results; add only enough $K_2C_2O_4$ to decolorize the $KMnO_4$ completely without an excess of more than 0.5 mL. Complete decolorization in 2 to 10 min. If it is impossible to decolorize the sample without adding a large excess of oxalate, the DO result will be inaccurate.

c. From this point the procedure closely parallels that in Section 4500-O.C.3. Add 1 mL $MnSO_4$ solution and 3 mL alkali-iodide-azide reagent. Stopper, mix, and let precipitate settle a short time; acidify with 2 mL conc H_2SO_4. When 0.7 mL acid, 1 mL KF solution, 1 mL $KMnO_4$ solution, 1 mL $K_2C_2O_4$ solution, 1 mL $MnSO_4$ solution, and 3 mL alkali-iodide-azide (or a total of 7.7 mL reagents) are used in a 300-mL bottle, take $200 \times 300/(300 - 7.7) = 205$ mL for titration.

This correction is slightly in error because the $KMnO_4$ solution is nearly saturated with DO and 1 mL would add about 0.008 mg oxygen to the DO bottle. However, because precision of the method (standard deviation, 0.06 mL thiosulfate titration, or 0.012 mg DO) is 50% greater than this error, a correction is unnecessary. When substantially more $KMnO_4$ solution is used routinely, use a solution several times more concentrated so that 1 mL will satisfy the permanganate demand.

4. Reference

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4500-O E. Alum Flocculation Modification

1. General Discussion

Samples high in suspended solids may consume appreciable quantities of iodine in acid solution. The interference due to solids may be removed by alum flocculation.

2. Reagents

All the reagents required for the azide modification (Section 4500-O.C.2) and in addition:

a. Alum solution: Dissolve 10 g aluminum potassium sulfate, $AlK(SO_4)_2 \cdot 12H_2O$, in distilled water and dilute to 100 mL.

b. Ammonium hydroxide, NH_4OH, conc.

3. Procedure

Collect sample in a glass-stoppered bottle of 500 to 1000 mL capacity, using the same precautions as for regular DO samples. Add 10 mL alum solution and 1 to 2 mL conc NH_4OH. Stopper and invert gently for about 1 min. Let sample settle for about 10 min and siphon clear supernate into a 250- to 300-mL DO bottle until it overflows. Avoid sample aeration and keep siphon submerged at all times. Continue sample treatment as in Section 4500-O.C.3 or an appropriate modification.

4500-O F. Copper Sulfate-Sulfamic Acid Flocculation Modification

1. General Discussion

This modification is used for biological flocs such as activated sludge mixtures, which have high oxygen utilization rates.

2. Reagents

All the reagents required for the azide modification (Section 4500-O.C.2) and, in addition:

Copper sulfate-sulfamic acid inhibitor solution: Dissolve 32 g technical-grade NH_2SO_2OH without heat in 475 mL distilled water. Dissolve 50 g $CuSO_4 \cdot 5H_2O$ in 500 mL distilled water. Mix the two solutions and add 25 mL conc acetic acid.

3. Procedure

Add 10 mL $CuSO_4$-NH_2SO_2OH inhibitor to a 1-L glass-stoppered bottle. Insert bottle in a special sampler designed so that bottle fills from a tube near bottom and overflows only 25 to 50% of bottle capacity. Collect sample, stopper, and mix by inverting. Let suspended solids settle and siphon relatively clear supernatant liquor into a 250- to 300-mL DO bottle. Continue sample treatment as rapidly as possible by the azide (Section 4500-O.C.3) or other appropriate modification.

4500-O G. Membrane Electrode Method

1. General Discussion

Various modifications of the iodometric method have been developed to eliminate or minimize effects of interferences; nevertheless, the method still is inapplicable to a variety of industrial and domestic wastewaters.[1] Moreover, the iodometric method is not suited for field testing and cannot be adapted easily for continuous monitoring or for DO determinations in situ.

Polarographic methods using the dropping mercury electrode or the rotating platinum electrode have not been reliable always for the DO analysis in domestic and industrial wastewaters because impurities in the test solution can cause electrode poisoning or other interferences.[2,3] With membrane-covered electrode systems these problems are minimized, because the sensing element is protected by an oxygen-permeable plastic membrane that serves as a diffusion barrier against impurities.[4–6] Under steady-state conditions the current is directly proportional to the DO concentration.*

Membrane electrodes of the polarographic[4] as well as the galvanic[5] type have been used for DO measurements in lakes and reservoirs,[8] for stream survey and control of industrial effluents,[9,10] for continuous monitoring of DO in activated sludge units,[11] and for estuarine and oceanographic studies.[12] Being completely submersible, membrane electrodes are suited for analysis in situ. Their portability and ease of operation and maintenance make them particularly convenient for field applications. In laboratory investigations, membrane electrodes have been used for continuous DO analysis in bacterial cultures, including the BOD test.[5,13]

Membrane electrodes provide an excellent method for DO analysis in polluted waters, highly colored waters, and strong waste effluents. They are recommended for use especially under

* Fundamentally, the current is directly proportional to the activity of molecular oxygen.[7]

conditions that are unfavorable for use of the iodometric method, or when that test and its modifications are subject to serious errors caused by interferences.

a. Principle: Oxygen-sensitive membrane electrodes of the polarographic or galvanic type are composed of two solid metal electrodes in contact with supporting electrolyte separated from the test solution by a selective membrane. The basic difference between the galvanic and the polarographic systems is that in the former the electrode reaction is spontaneous (similar to that in a fuel cell), while in the latter an external source of applied voltage is needed to polarize the indicator electrode. Polyethylene and fluorocarbon membranes are used commonly because they are permeable to molecular oxygen and are relatively rugged.

Membrane electrodes are commercially available in some variety. In all these instruments the "diffusion current" is linearly proportional to the concentration of molecular oxygen. The current can be converted easily to concentration units (e.g., milligrams per liter) by a number of calibration procedures.

Membrane electrodes exhibit a relatively high temperature coefficient largely due to changes in the membrane permeability.[6] The effect of temperature on the electrode sensitivity, ϕ (microamperes per milligram per liter), can be expressed by the following simplified relationship:[6]

$$\log \phi = 0.43\, mt + b$$

where:

t = temperature, °C,
m = constant that depends on the membrane material, and
b = constant that largely depends on membrane thickness.

If values of ϕ and m are determined for one temperature (ϕ_0 and t_0), it is possible to calculate the sensitivity at any desired temperature (ϕ and t) as follows:

$$\log \phi = \log \phi_0 + 0.43\, m\,(t - t_0)$$

Nomographic charts for temperature correction can be constructed easily[7] and are available from some manufacturers. An example is shown in Figure 4500-O:2, in which, for simplicity, sensitivity is plotted versus temperature on semilogarithmic coordinates. Check one or two points frequently to confirm original calibration. If calibration changes, the new calibration should be parallel to the original, provided that the same membrane material is used.

Temperature compensation also can be made automatically by using thermistors in the electrode circuit.[4] However, thermistors may not compensate fully over a wide temperature range. For certain applications where high accuracy is required, use calibrated nomographic charts to correct for temperature effect.

To use the DO membrane electrode in estuarine waters or in wastewaters with varying ionic strength, correct for effect of salting-out on electrode sensitivity.[6,7] This effect is particularly significant for large changes in salt content. Electrode sensitivity varies with salt concentration according to the following relationship:

$$\log \phi_S = 0.43\, m_S C_S + \log \phi_0$$

where:

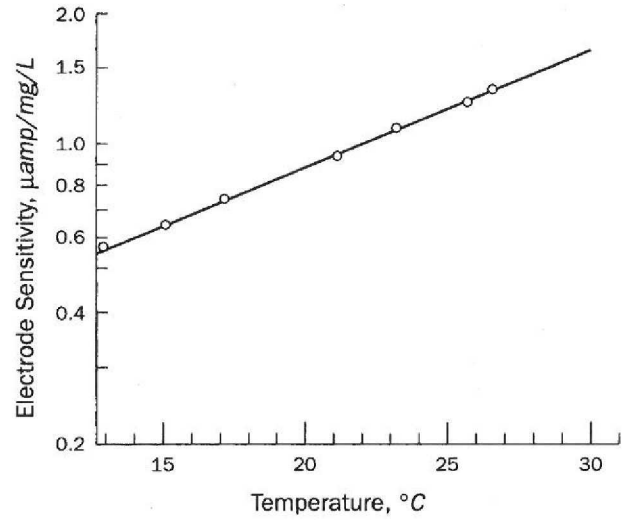

Figure 4500-O:2. Effect of temperature on electrode sensitivity.

ϕ_S, ϕ_0 = sensitivities in salt solution and distilled water, respectively,
C_S = salt concentration (preferably ionic strength), and
m_S = constant (salting-out coefficient).

If ϕ_0 and m_S are determined, it is possible to calculate sensitivity for any value of C_S. Conductivity measurements can be used to approximate salt concentration (C_S). This is particularly applicable to estuarine waters. Figure 4500-O:3 shows calibration curves for sensitivity of varying salt solutions at different temperatures.

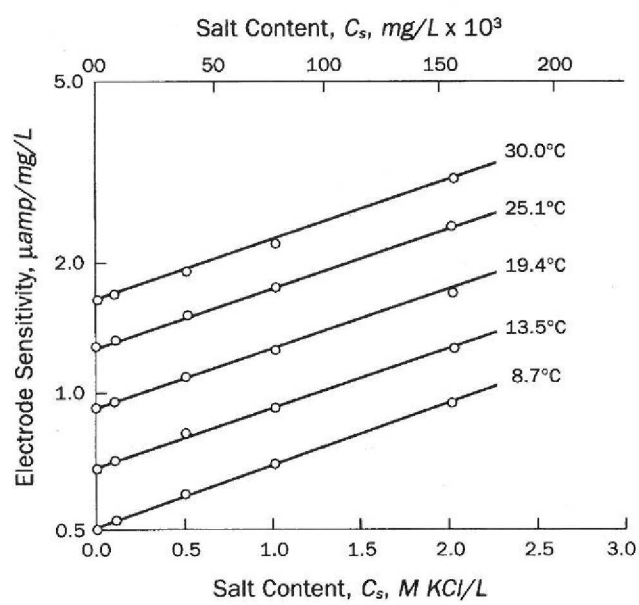

Figure 4500-O:3. The salting-out effect at different temperatures.

b. Interference: Plastic films used with membrane electrode systems are permeable to a variety of gases besides oxygen, although none is depolarized easily at the indicator electrode. Prolonged use of membrane electrodes in waters containing such gases as hydrogen sulfide (H_2S) tends to lower cell sensitivity. Eliminate this interference by frequently changing and calibrating the membrane electrode.

c. Sampling: Because membrane electrodes offer the advantage of analysis in situ they eliminate errors caused by sample handling and storage. If sampling is required, use the same precautions suggested for the iodometric method.

2. Apparatus

Oxygen-sensitive membrane electrode, polarographic or galvanic, with appropriate meter.

3. Procedure

a. Calibration: Follow manufacturer's calibration procedure exactly to obtain guaranteed precision and accuracy. Generally, calibrate membrane electrodes by reading against air or a sample of known DO concentration (determined by iodometric method) as well as in a sample with zero DO. (Add excess sodium sulfite, Na_2SO_3, and a trace of cobalt chloride, $CoCl_2$, to bring DO to zero.) Preferably calibrate with samples of water under test. Avoid an iodometric calibration where interfering substances are suspected. The following illustrate the recommended procedures:

1) Fresh water—For unpolluted samples where interfering substances are absent, calibrate in the test solution or distilled water, whichever is more convenient.

2) Salt water—Calibrate directly with samples of seawater or waters having a constant salt concentration in excess of 1000 mg/L.

3) Fresh water containing pollutants or interfering substances—Calibrate with distilled water because erroneous results occur with the sample.

4) Salt water containing pollutants or interfering substances—Calibrate with a sample of clean water containing the same salt content as the sample. Add a concentrated potassium chloride (KCl) solution (see Conductivity, Section 2510 and Table 2510:I) to distilled water to produce the same specific conductance as that in the sample. For polluted ocean waters, calibrate with a sample of unpolluted seawater.

5) Estuary water containing varying quantities of salt—Calibrate with a sample of uncontaminated seawater or distilled or tap water. Determine sample chloride or salt concentration and revise calibration to account for change of oxygen solubility in the estuary water.[7]

b. Sample measurement: Follow all precautions recommended by manufacturer to insure acceptable results. Take care in changing membrane to avoid contamination of sensing element and also trapping of minute air bubbles under the membrane, which can lead to lowered response and high residual current. Provide sufficient sample flow across membrane surface to overcome erratic response (see Figure 4500-O:4 for a typical example of the effect of stirring).

c. Validation of temperature effect: Check frequently one or two points to verify temperature correction data.

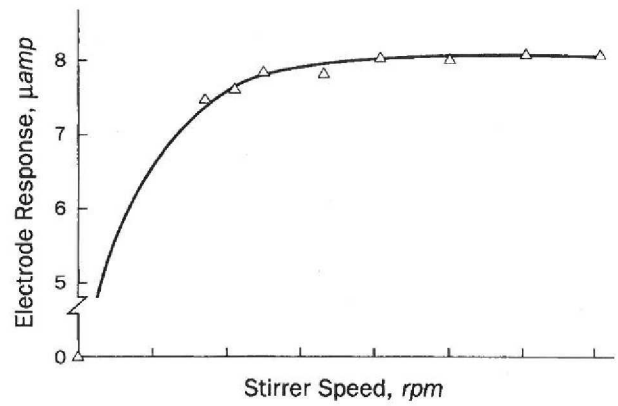

Figure 4500-O:4. Typical trend of effect of stirring on electrode response.

4. Precision and Bias

With most commercially available membrane electrode systems an accuracy of ±0.1 mg DO/L and a precision of ±0.05 mg DO/L can be obtained.

5. References

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figures, puts the limit on the number of places that justifiably may be carried in the sum or difference. Thus the sum

```
   0.0072
  12.02
   4.0078
  25.9
4886
4927.9350
```

must be rounded off to "4928," no decimals, because one of the addends, 4886, has no decimal places. Notice that another addend, 25.9, has only three significant figures and yet it does not set a limit to the number of significant figures in the answer.

The preceding discussion is necessarily oversimplified. The reader is referred to mathematical texts for more detailed discussion.

1060 COLLECTION AND PRESERVATION OF SAMPLES*

1060 A. Introduction

It is an old axiom that the result of any testing method can be no better than the sample on which it is performed. It is beyond the scope of this publication to specify detailed procedures for the collection of all samples because of varied purposes and analytical procedures. Detailed information is presented in specific methods. This section presents general considerations, applicable primarily to chemical analyses. See appropriate sections for samples to be used in toxicity testing and microbiological, biological, and radiological examinations.

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and yet large enough for analytical purposes while still accurately representing the material being sampled. This objective implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the material being sampled, and that the sample will be handled in such a way that no significant changes in composition occur before the tests are made.

Frequently the objective of sampling and testing is to demontrate whether continuing compliance with specific regulatory requirements has been achieved. Samples are presented to the laboratory for specific determinations with the sampler being responsible for collecting a valid and representative sample. Because of the increasing importance placed on verifying the accuracy and representativeness of data, greater emphasis is placed on proper sample collection, tracking, and preservation techniques. Often, laboratory personnel help in planning a sampling program, in consultation with the user of the test results. Such consultation is essential to ensure selecting samples and analytical methods that provide a sound and valid basis for answering the questions that prompted the sampling and that will meet regulatory and/or project-specific requirements.

This section addresses the collection and preservation of water and wastewater samples; the general principles also apply to the sampling of solid or semisolid matrices.

1. General Requirements

Obtain a sample that meets the requirements of the sampling program and handle it so that it does not deteriorate or become contaminated or compromised before it is analyzed.

Ensure that all sampling equipment is clean and quality-assured before use. Use sample containers that are clean and free of contaminants. Bake at 450°C all bottles to be used for organic-analysis sampling.

Fill sample containers without prerinsing with sample; prerinsing results in loss of any pre-added preservative and sometimes can bias results high when certain components adhere to the sides of the container. Depending on determinations to be performed, fill the container full (most organic compound determinations) or leave space for aeration, mixing, etc. (microbiological and inorganic analyses). If a bottle already contains preservative, take care not to overfill the bottle, as preservative may be lost or diluted. Except when sampling for analysis of volatile organic compounds, leave an air space equivalent to approximately 1% of the container volume to allow for thermal expansion during shipment.

Special precautions (discussed below) are necessary for samples containing organic compounds and trace metals. Because many constituents may be present at low concentrations (micrograms or nanograms per liter), they may be totally or partially lost or easily contaminated when proper sampling and preservation procedures are not followed.

Composite samples can be obtained by collecting over a period of time, depth, or at many different sampling points. The details of collection vary with local conditions, so specific recommendations are not universally applicable. Sometimes it is more informative to analyze numerous separate samples instead of one composite so that variability, maxima, and minima can be determined.

Because of the inherent instability of certain properties and compounds, composite sampling for some analytes is not recommended where quantitative values are desired (examples include oil and grease, acidity, alkalinity, carbon dioxide, chlorine residual, iodine, hexavalent chromium, nitrate, volatile organic compounds, radon-222, dissolved oxygen, ozone, temperature, and pH). In certain cases, such as for BOD, composite samples

* Joint Task Group: 20th Edition—Lawrence H. Keith (chair), Clifford G. Annis, Gary L. DeKock, Carleton P. Edmunds, Scott J. Mickelson, Mark Wyzalek.

are routinely required by regulatory agencies. Refrigerate composite samples for BOD and nitrite.

Sample carefully to ensure that analytical results represent the actual sample composition. Important factors affecting results are the presence of suspended matter or turbidity, the method chosen for removing a sample from its container, and the physical and chemical changes brought about by storage or aeration. Detailed procedures are essential when processing (blending, sieving, filtering) samples to be analyzed for trace constituents, especially metals and organic compounds. Some determinations can be invalidated by contamination during processing. Treat each sample individually with regard to the substances to be determined, the amount and nature of turbidity present, and other conditions that may influence the results.

Carefully consider the technique for collecting a representative sample and define it in the sampling plan. For metals it often is appropriate to collect both a filtered and an unfiltered sample to differentiate between total and dissolved metals present in the matrix. Be aware that some metals may partially sorb to filters. Beforehand, determine the acid requirements to bring the pH to <2 on a separate sample. Add the same relative amount of acid to all samples; use ultrapure acid preservative to prevent contamination. Be sure that the dilution caused by acidifying is negligible or sufficiently reproducible for a dilution correction factor. When filtered samples are to be collected, filter them, if possible, in the field, or at the point of collection before preservation with acid. Filter samples in a laboratory-controlled environment if field conditions could cause error or contamination; in this case filter as soon as possible. Often slight turbidity can be tolerated if experience shows that it will cause no interference in gravimetric or volumetric tests and that its influence can be corrected in colorimetric tests, where it has potentially the greatest interfering effect. Sample collector must state whether or not the sample has been filtered.

Make a record of every sample collected and identify every bottle with a unique sample number, preferably by attaching an appropriately inscribed tag or label. Document sufficient information to provide positive sample identification at a later date, including the unique sample identification number, the name of the sample collector, the date, hour, exact location, and, if possible, sample type (e.g., grab or composite), and any other data that may be needed for correlation, such as water temperature, weather conditions, water level, stream flow, post-collection conditions, etc. If space for all pertinent information for label or attached tag is insufficient, record information in a bound sample log book at the sampling site at the time of sample collection. Use waterproof ink to record all information (preferably with black, non-solvent-based ink). Fix sampling points by detailed description in the sampling plan, by maps, or with the aid of stakes, buoys, or landmarks in a manner that will permit their identification by other persons without reliance on memory or personal guidance. Global positioning systems (GPS) also are used and supply accurate sampling position data. Particularly when sample results are expected to be involved in litigation, use formal "chain-of-custody" procedures (see ¶ B.2 below), which trace sample history from collection to final reporting.

Before collecting samples from distribution systems, flush lines with three to five pipe volumes (or until water is being drawn from the main source) to ensure that the sample is representative of the supply, taking into account the volume of pipe to be flushed and the flow velocity. If the distribution system volume is unavailable, flush with tap fully open for at least 2 to 3 min before sampling. An exception to these guidelines, i.e., collecting a first draw sample, is when information on areas of reduced or restricted flow is desired or when samples for lead in drinking water are being collected.

Although well pumping protocols depend on the objectives of an investigation and other factors such as well characteristics and available equipment, a general rule is to collect samples from wells only after the well has been purged sufficiently (usually with three to ten well volumes) to ensure that the sample represents the groundwater. Purging stagnant water is critical. Sometimes it will be necessary to pump at a specified rate to achieve a characteristic drawdown, if this determines the zones from which the well is supplied; record purging rate and drawdown, if necessary. By using methods with minimal drawdown, purging volumes can be reduced significantly.

When samples are collected from a river or stream, observed results may vary with depth, stream flow, and distance from each shore. Selection of the number and distribution of sites at which samples should be collected depends on study objectives, stream characteristics, available equipment, and other factors. If equipment is available, take an integrated sample from top to bottom in the middle of the main channel of the stream or from side to side at mid-depth. If only grab or catch samples can be collected, preferably take them at various points of equal distance across the stream; if only one sample can be collected, take it in the middle of the main channel of the stream and at mid-depth. Integrated samples are described further in ¶ B.1*c* below.

Rivers, streams, lakes, and reservoirs are subject to considerable variations from normal causes such as seasonal stratification, diurnal variations, rainfall, runoff, and wind. Choose location, depth, and frequency of sampling depending on local conditions and the purpose of the investigation.

Use the following examples for general guidance. Avoid areas of excessive turbulence because of potential loss of volatile constituents and of potential presence of denser-than-air toxic vapors. Avoid sampling at weirs if possible because such locations tend to favor retrieval of lighter-than-water, immiscible compounds. Generally, collect samples beneath the surface in quiescent areas and open sampling container below surface with the mouth directed toward the current to avoid collecting surface scum unless oil and grease is a constituent of interest; then collect water at the surface. If composite samples are required, ensure that sample constituents are not lost during compositing because of improper handling of portions being composited. If samples will be analyzed for organic constituents, refrigerate composited portions. Do not composite samples for VOC analysis because some of the components will be lost through volatilization.

2. Safety Considerations

Because sample constituents may be toxic, take adequate precautions during sampling and sample handling. Toxic substances can enter through the skin and eyes and, in the case of vapors, also through the lungs. Ingestion can occur via direct contact of toxic materials with foods or by adsorption of vapors onto foods. Precautions may be limited to wearing gloves or may include coveralls, aprons, or other protective apparel. Often, the degree of protection provided by chemical protective clothing

(CPC) is specific for different manufacturers and their product models[1]; ensure that the clothing chosen will offer adequate protection. Always wear eye protection (e.g., safety glasses with side shields or goggles). When toxic vapors may be present, sample only in well-ventilated areas, or use an appropriate respirator or self-contained breathing apparatus. In a laboratory, open sample containers in a fume hood. Never have food in the laboratory, near samples, or near sampling locations; always wash hands thoroughly before handling food.[2]

Always prohibit eating, drinking, or smoking near samples, sampling locations, and in the laboratory. Keep sparks, flames, and excessive heat sources away from samples and sampling locations. If flammable compounds are suspected or known to be present and samples are to be refrigerated, use only specially designed *explosion-proof* refrigerators.[2]

Collect samples safely, avoiding situations that may lead to accidents. When in doubt as to the level of safety precautions needed, consult a knowledgeable industrial hygienist or safety professional. Samples with radioactive contaminants may require other safety considerations; consult a health physicist.

Label adequately any sample known or suspected to be hazardous because of flammability, corrosivity, toxicity, oxidizing chemicals, or radioactivity, so that appropriate precautions can be taken during sample handling, storage, and disposal.

3. References

1. FORSBERG, K. & L.H. KEITH. 1998. Instant Gloves and CPC Database. Instant Reference Sources, Inc. Austin, Tex.
2. WATER POLLUTION CONTROL FEDERATION. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.

1060 B. Collection of Samples

1. Types of Samples

a. Grab samples: Grab samples are single samples collected at a specific spot at a site over a short period of time (typically seconds or minutes). Thus, they represent a "snapshot" in both space and time of a sampling area. Discrete grab samples are taken at a selected location, depth, and time. Depth-integrated grab samples are collected over a predetermined part or the entire depth of a water column, at a selected location and time in a given body of water.

A sample can represent only the composition of its source at the time and place of collection. However, when a source is known to be relatively constant in composition over an extended time or over substantial distances in all directions, then the sample may represent a longer time period and/or a larger volume than the specific time and place at which it was collected. In such circumstances, a source may be represented adequately by single grab samples. Examples are protected groundwater supplies, water supplies receiving conventional treatment, some well-mixed surface waters, but rarely, wastewater streams, rivers, large lakes, shorelines, estuaries, and groundwater plumes.

When a source is known to vary with time, grab samples collected at suitable intervals and analyzed separately can document the extent, frequency, and duration of these variations. Choose sampling intervals on the basis of the expected frequency of changes, which may vary from as little as 5 min to as long as 1 h or more. Seasonal variations in natural systems may necessitate sampling over months. When the source composition varies in space (i.e., from location to location) rather than time, collect samples from appropriate locations that will meet the objectives of the study (for example, upstream and downstream from a point source, etc.).

The same principles apply to sampling wastewater sludges, sludge banks, and muds, although these matrices are not specifically addressed in this section. Take every possible precaution to obtain a representative sample or one conforming to a sampling program.

b. Composite samples: Composite samples should provide a more representative sampling of heterogeneous matrices in which the concentration of the analytes of interest may vary over short periods of time and/or space. Composite samples can be obtained by combining portions of multiple grab samples or by using specially designed automatic sampling devices. Sequential (time) composite samples are collected by using continuous, constant sample pumping or by mixing equal water volumes collected at regular time intervals. Flow-proportional composites are collected by continuous pumping at a rate proportional to the flow, by mixing equal volumes of water collected at time intervals that are inversely proportional to the volume of flow, or by mixing volumes of water proportional to the flow collected during or at regular time intervals.

Advantages of composite samples include reduced costs of analyzing a large number of samples, more representative samples of heterogeneous matrices, and larger sample sizes when amounts of test samples are limited. Disadvantages of composite samples include loss of analyte relationships in individual samples, potential dilution of analytes below detection levels, increased potential analytical interferences, and increased possibility of analyte interactions. In addition, use of composite samples may reduce the number of samples analyzed below the required statistical need for specified data quality objectives or project-specific objectives.

Do not use composite samples with components or characteristics subject to significant and unavoidable changes during storage. Analyze individual samples as soon as possible after collection and preferably at the sampling point. Examples are dissolved gases, residual chlorine, soluble sulfide, temperature, and pH. Changes in components such as dissolved oxygen or carbon dioxide, pH, or temperature may produce secondary changes in certain inorganic constituents such as iron, manganese, alkalinity, or hardness. Some organic analytes also may be changed by changes in the foregoing components. Use time-composite samples only for determining components that can be demonstrated to remain unchanged under the conditions of sample collection, preservation, and storage.

Collect individual portions in a wide-mouth bottle every hour (in some cases every half hour or even every 5 min) and mix at

the end of the sampling period or combine in a single bottle as collected. If preservatives are used, add them to the sample bottle initially so that all portions of the composite are preserved as soon as collected.

Automatic sampling devices are available; however, do not use them unless the sample is preserved as described below. Composite samplers running for extended periods (weeks to months) should undergo routine cleaning of containers and sample lines to minimize sample growth and deposits.

c. Integrated (discharge-weighted) samples: For certain purposes, the information needed is best provided by analyzing mixtures of grab samples collected from different points simultaneously, or as nearly so as possible, using discharge-weighted methods such as equal-width increment (EWI) or equal discharge-increment (EDI) procedures and equipment. An example of the need for integrated sampling occurs in a river or stream that varies in composition across its width and depth. To evaluate average composition or total loading, use a mixture of samples representing various points in the cross-section, in proportion to their relative flows. The need for integrated samples also may exist if combined treatment is proposed for several separate wastewater streams, the interaction of which may have a significant effect on treatability or even on composition. Mathematical prediction of the interactions among chemical components may be inaccurate or impossible and testing a suitable integrated sample may provide more useful information.

Both lakes and reservoirs show spatial variations of composition (depth and horizontal location). However, there are conditions under which neither total nor average results are especially useful, but local variations are more important. In such cases, examine samples separately (i.e., do not integrate them).

Preparation of integrated samples usually requires equipment designed to collect a sample water uniformly across the depth profile. Knowledge of the volume, movement, and composition of the various parts of the water being sampled usually is required. Collecting integrated samples is a complicated and specialized process that must be described adequately in a sampling plan.

2. Chain-of-Custody Procedures

Properly designed and executed chain-of-custody forms will ensure sample integrity from collection to data reporting. This includes the ability to trace possession and handling of the sample from the time of collection through analysis and final disposition. This process is referred to as "chain-of-custody" and is required to demonstrate sample control when the data are to be used for regulation or litigation. Where litigation is not involved, chain-of-custody procedures are useful for routine control of samples.

A sample is considered to be under a person's custody if it is in the individual's physical possession, in the individual's sight, secured and tamper-proofed by that individual, or secured in an area restricted to authorized personnel. The following procedures summarize the major aspects of chain of custody. More detailed discussions are available.[1,2]

a. Sample labels (including bar-code labels): Use labels to prevent sample misidentification. Gummed paper labels or tags generally are adequate. Include at least the following information: a unique sample number, sample type, name of collector, date and time of collection, place of collection, and sample preservative. Also include date and time of preservation for comparison to date and time of collection. Affix tags or self-adhesive labels to sample containers before, or at the time of, sample collection.

b. Sample seals: Use sample seals to detect unauthorized tampering with samples up to the time of analysis. Use self-adhesive paper seals that include at least the following information: sample number (identical with number on sample label), collector's name, and date and time of sampling. Plastic shrink seals also may be used.

Attach seal in such a way that it is necessary to break it to open the sample container or the sample shipping container (e.g., a cooler). Affix seal to container before sample leaves custody of sampling personnel.

c. Field log book: Record all information pertinent to a field survey or sampling in a bound log book. As a minimum, include the following in the log book: purpose of sampling; location of sampling point; name and address of field contact; producer of material being sampled and address, if different from location; type of sample; and method, date, and time of preservation. If the sample is wastewater, identify process producing waste stream. Also provide suspected sample composition, including concentrations; number and volume of sample(s) taken; description of sampling point and sampling method; date and time of collection; collector's sample identification number(s); sample distribution and how transported; references such as maps or photographs of the sampling site; field observations and measurements; and signatures of personnel responsible for observations. Because sampling situations vary widely, it is essential to record sufficient information so that one could reconstruct the sampling event without reliance on the collector's memory. Protect log book and keep it in a safe place.

d. Chain-of-custody record: Fill out a chain-of-custody record to accompany each sample or group of samples. The record includes the following information: sample number; signature of collector; date, time, and address of collection; sample type; sample preservation requirements; signatures of persons involved in the chain of possession; and inclusive dates and times of possession.

e. Sample analysis request sheet: The sample analysis request sheet accompanies samples to the laboratory. The collector completes the field portion of such a form that includes most of the pertinent information noted in the log book. The laboratory portion of such a form is to be completed by laboratory personnel and includes: name of person receiving the sample, laboratory sample number, date of sample receipt, condition of each sample (i.e., if it is cold or warm, whether the container is full or not, color, if more than one phase is present, etc.), and determinations to be performed.

f. Sample delivery to the laboratory: Deliver sample(s) to laboratory as soon as practicable after collection, typically within 2 d. Where shorter sample holding times are required, make special arrangements to insure timely delivery to the laboratory. Where samples are shipped by a commercial carrier, include the waybill number in the sample custody documentation. Insure that samples are accompanied by a completed chain-of-custody record and a sample analysis request sheet. Deliver sample to sample custodian.

g. Receipt and logging of sample: In the laboratory, the sample custodian inspects the condition and seal of the sample and reconciles label information and seal against the chain-of-custody record before the sample is accepted for analysis. After acceptance, the custodian assigns a laboratory number, logs

sample in the laboratory log book and/or computerized laboratory information management system, and stores it in a secured storage room or cabinet or refrigerator at the specified temperature until it is assigned to an analyst.

h. Assignment of sample for analysis: The laboratory supervisor usually assigns the sample for analysis. Once the sample is in the laboratory, the supervisor or analyst is responsible for its care and custody.

i. Disposal: Hold samples for the prescribed amount of time for the project or until the data have been reviewed and accepted. Document the disposition of samples. Ensure that disposal is in accordance with local, state, and U.S. EPA approved methods.

3. Sampling Methods

a. Manual sampling: Manual sampling involves minimal equipment but may be unduly costly and time-consuming for routine or large-scale sampling programs. It requires trained field technicians and is often necessary for regulatory and research investigations for which critical appraisal of field conditions and complex sample collection techniques are essential. Manually collect certain samples, such as waters containing oil and grease.

b. Automatic sampling: Automatic samplers can eliminate human errors in manual sampling, can reduce labor costs, may provide the means for more frequent sampling,[3] and are used increasingly. Be sure that the automatic sampler does not contaminate the sample. For example, plastic components may be incompatible with certain organic compounds that are soluble in the plastic parts or that can be contaminated (e.g., from phthalate esters) by contact with them. If sample constituents are generally known, contact the manufacturer of an automatic sampler regarding potential incompatibility of plastic components.

Program an automatic sampler in accordance with sampling needs. Carefully match pump speeds and tubing sizes to the type of sample to be taken.

c. Sorbent sampling: Use of solid sorbents, particularly membrane-type disks, is becoming more frequent. These methods offer advantages of rapid, inexpensive sampling if the analytes of interest can be adsorbed and desorbed efficiently and the water matrix is free of particulates that plug the sorbent.

4. Sample Containers

The type of sample container used is of utmost importance. Test sample containers and document that they are free of analytes of interest, especially when sampling and analyzing for very low analyte levels. Containers typically are made of plastic or glass, but one material may be preferred over the other. For example, silica, sodium, and boron may be leached from soft glass but not plastic, and trace levels of some pesticides and metals may sorb onto the walls of glass containers.[4] Thus, hard glass containers* are preferred. For samples containing organic compounds, do not use plastic containers except those made of fluorinated polymers such as polytetrafluoroethylene (PTFE).[3]

Some sample analytes may dissolve (be absorbed) into the walls of plastic containers; similarly, contaminants from plastic containers may leach into samples. Avoid plastics wherever possible because of potential contamination from phthalate esters. Container failure due to breakdown of the plastic is possible. Therefore, use glass containers for all organics analyses such as volatile organics, semivolatile organics, pesticides, PCBs, and oil and grease. Some analytes (e.g., bromine-containing compounds and some pesticides, polynuclear aromatic compounds, etc.) are light-sensitive; collect them in amber-colored glass containers to minimize photodegradation. Container caps, typically plastic, also can be a problem. Do not use caps with paper liners. Use foil or PTFE liners but be aware that metal liners can contaminate samples collected for metals analysis and they may also react with the sample if it is acidic or alkaline. Serum vials with PTFE-lined rubber or plastic septa are useful.

In rare situations it may be necessary to use sample containers not specifically prepared for use, or otherwise unsuitable for the particular situation; thoroughly document these deviations. Documentation should include type and source of container, and the preparation technique, e.g., acid washed with reagent water rinse. For QA purposes the inclusion of a bottle blank may be necessary.

5. Number of Samples

Because of variability from analytical and sampling procedures (i.e., population variability), a single sample is insufficient to reach any reasonable desired level of confidence. If an overall standard deviation (i.e., the standard deviation of combined sampling and analysis) is known, the required number of samples for a mobile matrix such as water may be estimated as follows:[4]

$$N \geq \left(\frac{ts}{U}\right)^2$$

where:

N = number of samples,
t = Student-t statistic for a given confidence level,
s = overall standard deviation, and
U = acceptable level of uncertainty.

To assist in calculations, use curves such as those in Figure 1060:1. As an example, if s is 0.5 mg/L, U is ± 0.2 mg/L, and a 95% confidence level is desired, approximately 25 to 30 samples must be taken.

The above equation assumes that total error (population variability) is known. Total variability consists of all sources of variability, including: the distribution of the analytes of interest within the sampling site, collection, preservation, preparation, and analysis of samples, and data handling and reporting. In simpler terms, error (variability) can be divided into sampling and analysis components. Sampling error due to population variability (including heterogeneous distribution of analytes in the environmental matrix) usually is much larger than analytical error components. Unfortunately, sampling error usually is not available and the analyst is left with only the published error of the measurement system (typically obtained by using a reagent water matrix under the best analytical conditions).

More accurate equations are available.[5] These are based on the Z distribution for determining the number of samples needed to estimate a mean concentration when variability is estimated in absolute terms using the standard deviation. The coefficient of variation (relative standard deviation) is used when variability is estimated in relative terms.

The number of random samples to be collected at a site can be influenced partly by the method that will be used. The values for

* Pyrex or equivalent.

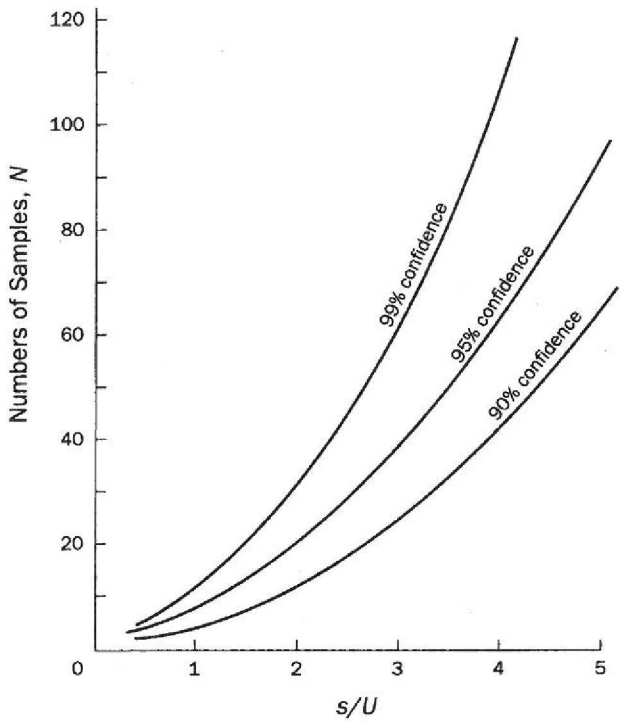

Figure 1060:1. Approximate number of samples required in estimating a mean concentration. Source: Methods for the Examination of Waters and Associated Materials: General Principles of Sampling and Accuracy of Results. 1980. Her Majesty's Stationery Off., London, England.

standard deviation (SD) or relative standard deviation (RSD) may be obtained from each of the methods or in the literature.[6] However, calculations of estimated numbers of samples needed based only on this information will result in underestimated numbers of samples because only the analytical variances are considered, and the typically larger variances from the sampling operations are not included. Preferably, determine and use SDs or RSDs from overall sampling and analysis operations.

For estimates of numbers of samples needed for systematic sampling (e.g., drilling wells for sampling groundwater or for systematically sampling large water bodies such as lakes), equations are available[7] that relate number of samples to shape of grid, area covered, and space between nodes of grid. The grid spacing is a complex calculation that depends on the size and shape of any contaminated spot (such as a groundwater plume) to be identified, in addition to the geometric shape of the sampling grid.

See individual methods for types and numbers of quality assurance (QA) and quality control (QC) samples, e.g., for normal-level (procedural) or low-level (contamination) bias or for precision, involving sampling or laboratory analysis (either overall or individually). Estimates of numbers of QC samples needed to achieve specified confidence levels also can be calculated. Rates of false positives (Type I error) and false negatives (Type II error) are useful parameters for estimating required numbers of QC samples. A false positive is the incorrect conclusion that an analyte is present when it is absent. A false negative is the incorrect conclusion that an analyte is absent when it is present. If the frequency of false positives or false negatives desired to be detected is less than 10%, then

$$n = \frac{\ln \alpha}{\ln (1 - Y)}$$

where:

α = (1 − desired confidence level), and
Y = frequency to detect (<10%).

If the frequency that is desirable to detect is more than 10%, iterative solution of a binomial equation is necessary.[5,8]

Equations are available as a computer program† for computing sample number by the Z distribution, for estimating samples needed in systematic sampling, and for estimating required number of QC samples.

6. Sample Volumes

Collect a 1-L sample for most physical and chemical analyses. For certain determinations, larger samples may be necessary. Table 1060:I lists volumes ordinarily required for analyses, but it is strongly recommended that the laboratory that will conduct the analyses also be consulted to verify the analytical needs of sampling procedures as they pertain to the goals and data quality objective of an investigation.

Do not use samples from the same container for multiple testing requirements (e.g., organic, inorganic, radiological, bacteriological, and microscopic examinations) because methods of collecting and handling are different for each type of test. Always collect enough sample volume in the appropriate container in order to comply with sample handling, storage, and preservation requirements.

7. References

1. U.S. Environmental Protection Agency. 1986. Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, 3rd ed. Publ. No. SW-846, Off. Solid Waste and Emergency Response, Washington, D.C.
2. U.S. Environmental Protection Agency. 1982. NEIC Policies and Procedures. EPA-330/9/78/001/-R (rev. 1982).
3. Water Pollution Control Federation. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.
4. Methods for the Examination of Waters and Associated Materials: General Principles of Sampling and Accuracy of Results. 1980. Her Majesty's Stationery Off., London, England.
5. Keith, L.H., G.L. Patton, D.L. Lewis & P.G. Edwards. 1996. Determining numbers and kinds of analytical samples. Chapter 1 *in* Principles of Environmental Sampling, 2nd ed. ACS Professional Reference Book, American Chemical Soc., Washington, D.C.

† DQO-PRO, available (free) by downloading from American Chemical Society Division of Environmental Chemistry home page at http://acs.environmental.duq.edu/acsenv/envchem.htm, and also as part of the tutorial, Reliable Environmental Sampling and Analysis, Instant Reference Sources, Inc., http://instantref.com/inst.ref.htm.

TABLE 1060:I. SUMMARY OF SPECIAL SAMPLING AND HANDLING REQUIREMENTS*

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	Preservation§	Maximum Storage Recommended	Maximum Storage Regulatory‖
Acidity	P, G(B)	100	g	Refrigerate	24 h	14 d
Alkalinity	P, G	200	g	Refrigerate	24 h	14 d
BOD	P, G	1000	g, c	Refrigerate	6 h	48 h
Boron	P (PTFE) or quartz	1000	g, c	HNO_3 to pH <2	28 d	6 months
Bromide	P, G	100	g, c	None required	28 d	28 d
Carbon, organic, total	G (B)	100	g, c	Analyze immediately; or refrigerate and add HCl, H_3PO_4, or H_2SO_4 to pH <2	7 d	28 d
Carbon dioxide	P, G	100	g	Analyze immediately	0.25 h	N.S.
COD	P, G	100	g, c	Analyze as soon as possible, or add H_2SO_4 to pH <2; refrigerate	7 d	28 d
Chloride	P, G	50	g, c	None required	N.S.	28 d
Chlorine, total, residual	P, G	500	g	Analyze immediately	0.25 h	0.25 h
Chlorine dioxide	P, G	500	g	Analyze immediately	0.25 h	N.S.
Chlorophyll	P, G	500	g	Unfiltered, dark, 4°C Filtered, dark, −20°C (Do not store in frost-free freezer)	24–48 h 28 d	
Color	P, G	500	g, c	Refrigerate	48 h	48 h
Specific conductance	P, G	500	g, c	Refrigerate	28 d	28 d
Cyanide						
Total	P, G	1000	g, c	Add NaOH to pH >12, refrigerate in dark#	24 h	14 d; 24 h if sulfide present
Amenable to chlorination	P, G	1000	g, c	Add 0.6 g ascorbic acid if chlorine is present and refrigerate	stat	14 d; 24 h if sulfide present
Fluoride	P	100	g, c	None required	28 d	28 d
Hardness	P, G	100	g, c	Add HNO_3 or H_2SO_4 to pH <2	6 months	6 months
Iodine	P, G	500	g	Analyze immediately	0.25 h	N.S.
Metals, general	P(A), G(A)	1000	g, c	For dissolved metals filter immediately, add HNO_3 to pH <2	6 months	6 months
Chromium VI	P(A), G(A)	1000	g	Refrigerate	24 h	24 h
Copper by colorimetry*			g, c			
Mercury	P(A), G(A)	1000	g, c	Add HNO_3 to pH <2, 4°C, refrigerate	28 d	28 d
Nitrogen						
Ammonia	P, G	500	g, c	Analyze as soon as possible or add H_2SO_4 to pH <2, refrigerate	7 d	28 d
Nitrate	P, G	100	g, c	Analyze as soon as possible; refrigerate	48 h	48 h (28 d for chlorinated samples)
Nitrate + nitrite	P, G	200	g, c	Add H_2SO_4 to pH <2, refrigerate	1–2 d	28 d
Nitrite	P, G	100	g, c	Analyze as soon as possible; refrigerate	none	48 h
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate, add H_2SO_4 to pH <2	7 d	28 d
Odor	G	500	g	Analyze as soon as possible; refrigerate	6 h	N.S.
Oil and grease	G, wide-mouth calibrated	1000	g	Add HCl or H_2SO_4 to pH <2, refrigerate	28 d	28 d
Organic compounds						
MBAs	P, G	250	g, c	Refrigerate	48 h	N.S.
Pesticides*	G(S), PTFE-lined cap	1000	g, c	Refrigerate, add 1000 mg ascorbic acid/L if residual chlorine present	7 d	7 d until extraction; 40 d after extraction
Phenols	P, G, PTFE-lined cap	500	g, c	Refrigerate, add H_2SO_4 to pH <2	*	28 d until extraction
Purgeables* by purge and trap	G, PTFE-lined cap	2 × 40	g	Refrigerate; add HCl to pH <2; add 1000 mg ascorbic acid/L if residual chlorine present	7 d	14 d

TABLE 1060:I. CONT.

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	Preservation§	Maximum Storage Recommended	Maximum Storage Regulatory‖
Base/neutrals & acids	G(S) amber	1000	g, c	Refrigerate	7 d	7 d until extraction; 40 d after extraction
Oxygen, dissolved	G, BOD bottle	300	g			
Electrode				Analyze immediately	0.25 h	0.25 h
Winkler				Titration may be delayed after acidification	8 h	8 h
Ozone	G	1000	g	Analyze immediately	0.25 h	N.S.
pH	P, G	50	g	Analyze immediately	0.25 h	0.25 h
Phosphate	G(A)	100	g	For dissolved phosphate filter immediately; refrigerate	48 h	N.S.
Phosphorus, total	P, G	100	g, c	Add H_2SO_4 to pH <2 and refrigerate	28 d	
Salinity	G, wax seal	240	g	Analyze immediately or use wax seal	6 months	N.S.
Silica	P (PTFE) or quartz	200	g, c	Refrigerate, do not freeze	28 d	28 d
Sludge digester gas	G, gas bottle	—	g	—	N.S.	
Solids[9]	P, G	200	g, c	Refrigerate	7 d	2–7 d; see cited reference
Sulfate	P, G	100	g, c	Refrigerate	28 d	28 d
Sulfide	P, G	100	g, c	Refrigerate; add 4 drops 2*N* zinc acetate/100 mL; add NaOH to pH >9	28 d	7 d
Temperature	P, G	—	g	Analyze immediately	0.25 h	0.25 h
Turbidity	P, G	100	g, c	Analyze same day; store in dark up to 24 h, refrigerate	24 h	48 h

* For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible.
† P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents or baked.
‡ g = grab; c = composite.
§ Refrigerate = storage at 4°C ± 2°C; in the dark; analyze immediately = analyze usually within 15 min of sample collection.
‖ See citation[10] for possible differences regarding container and preservation requirements. N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.
If sample is chlorinated, see text for pretreatment.

6. KEITH, L.H. 1996. Compilation of EPA's Sampling and Analysis Methods, 2nd ed. Lewis Publ./CRC Press, Boca Raton, Fla.
7. GILBERT, R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York, N.Y.
8. GRANT, E.L. & R.S. LEAVENWORTH. 1988. Statistical Quality Control, 6th ed. McGraw-Hill, Inc., New York, N.Y.
9. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1996. 40 CFR Part 136, Table II.
10. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1992. Rules and Regulations. 40 CFR Parts 100-149.

1060 C. Sample Storage and Preservation

Complete and unequivocal preservation of samples, whether domestic wastewater, industrial wastes, or natural waters, is a practical impossibility because complete stability for every constituent never can be achieved. At best, preservation techniques only retard chemical and biological changes that inevitably continue after sample collection.

1. Sample Storage before Analysis

a. Nature of sample changes: Some determinations are more affected by sample storage than others. Certain cations are subject to loss by adsorption on, or ion exchange with, the walls of glass containers. These include aluminum, cadmium, chromium, copper, iron, lead, manganese, silver, and zinc, which are best collected in a separate clean bottle and acidified with nitric acid to a pH below 2.0 to minimize precipitation and adsorption on container walls. Also, some organics may be subject to loss by adsorption to the walls of glass containers.

Temperature changes quickly; pH may change significantly in a matter of minutes; dissolved gases (oxygen, carbon dioxide) may be lost. Because changes in such basic water quality properties may occur so quickly, determine temperature, reduction-oxidation potential, and dissolved gases in situ and pH, specific conductance,

turbidity, and alkalinity immediately after sample collection. Many organic compounds are sensitive to changes in pH and/or temperature resulting in reduced concentrations during storage.

Changes in the pH-alkalinity-carbon dioxide balance may cause calcium carbonate to precipitate, decreasing the values for calcium and total hardness.

Iron and manganese are readily soluble in their lower oxidation states but relatively insoluble in their higher oxidation states; therefore, these cations may precipitate or they may dissolve from a sediment, depending on the redox potential of the sample. Microbiological activity may affect the nitrate-nitrite-ammonia content, phenol or BOD concentration, or the reduction of sulfate to sulfide. Residual chlorine is reduced to chloride. Sulfide, sulfite, ferrous iron, iodide, and cyanide may be lost through oxidation. Color, odor, and turbidity may increase, decrease, or change in quality. Sodium, silica, and boron may be leached from the glass container. Hexavalent chromium may be reduced to trivalent chromium.

Biological activity taking place in a sample may change the oxidation state of some constituents. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well-known nitrogen and phosphorus cycles are examples of biological influences on sample composition.

Zero head-space is important in preservation of samples with volatile organic compounds and radon. Avoid loss of volatile materials by collecting sample in a completely filled container. Achieve this by carefully filling the bottle so that top of meniscus is above the top of the bottle rim. It is important to avoid spillage or air entrapment if preservatives such as HCl or ascorbic acid have already been added to the bottle. After capping or sealing bottle, check for air bubbles by inverting and gently tapping it; if one or more air bubbles are observed then, if practical, discard the sample and repeat refilling bottle with new sample until no air bubbles are observed (this cannot be done if bottle contained preservatives before it was filled).

Serum vials with septum caps are particularly useful in that a sample portion for analysis can be taken through the cap by using a syringe,[1] although the effect of pressure reduction in the head-space must be considered. Pulling a sample into a syringe under vacuum can result in low bias data for volatile compounds and the resulting headspace precludes taking further subsamples.

b. Time interval between collection and analysis: In general, the shorter the time that elapses between collection of a sample and its analysis, the more reliable will be the analytical results. For certain constituents and physical values, immediate analysis in the field is required. For composited samples it is common practice to use the time at the end of composite collection as the sample collection time.

Check with the analyzing laboratory to determine how much elapsed time may be allowed between sample collection and analysis; this depends on the character of the sample and the stability of the target analytes under the conditions of storage. Many regulatory methods limit the elapsed time between sample collection and analysis (see Table 1060:I). Changes caused by growth of microorganisms are greatly retarded by keeping the sample at a low temperature (<4°C but above freezing). When the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, follow the preservation practices given in Table 1060:I. Record time elapsed between sampling and analysis, and which preservative, if any, was added.

2. Preservation Techniques

To minimize the potential for volatilization or biodegradation between sampling and analysis, keep samples as cool as possible without freezing. Preferably pack samples in crushed or cubed ice or commercial ice substitutes before shipment. Avoid using dry ice because it will freeze samples and may cause glass containers to break. Dry ice also may effect a pH change in samples. Keep composite samples cool with ice or a refrigeration system set at 4°C during compositing. Analyze samples as quickly as possible on arrival at the laboratory. If immediate analysis is not possible, preferably store at 4°C.[1]

No single method of preservation is entirely satisfactory; choose the preservative with due regard to the determinations to be made. Use chemical preservatives only when they do not interfere with the analysis being made. When they are used, add them to the sample bottle initially so that all sample portions are preserved as soon as collected. Because a preservation method for one determination may interfere with another one, samples for multiple determinations may need to be split and preserved separately. All methods of preservation may be inadequate when applied to suspended matter. Do not use formaldehyde as a preservative for samples collected for chemical analysis because it affects many of the target analytes.

Methods of preservation are relatively limited and are intended generally to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce volatility of constituents.

Preservation methods are limited to pH control, chemical addition, the use of amber and opaque bottles, refrigeration, filtration, and freezing. Table 1060:I lists preservation methods by constituent. See Section 7010B for sample collection and preservation requirements for radionuclides.

The foregoing discussion is by no means exhaustive and comprehensive. Clearly it is impossible to prescribe absolute rules for preventing all possible changes. Additional advice will be found in the discussions under individual determinations, but to a large degree the dependability of an analytical determination rests on the experience and good judgment of the person collecting the sample. Numbers of samples required for confidence levels in data quality objectives, however, rely on statistical equations such as those discussed earlier.

3. Reference

1. WATER POLLUTION CONTROL FEDERATION. 1986. Removal of Hazardous Wastes in Wastewater Facilities—Halogenated Organics. Manual of Practice FD-11, Water Pollution Control Fed., Alexandria, Va.

4. Bibliography

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