Ohio | Environmental Protection Agency

Ted Strickland, Governor
Lee Fisher, Lt. Governor
Chris Korleski, Director

1PC0001320101216

GREENE YELLOW SPRINGS WWTP JACKSON, JOSHUA | 2010/12/16

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Yellow Springs
Corresp.

Ohio | Environmental Protection Agency

Ted Strickland, Governor
Lee Fisher, Lt. Governor
Chris Korleski, Director

December 16, 2010

Village of Yellow Springs
Attn: Mr. Mark Cundiff
100 Dayton Street
Yellow Springs, OH 45387

RE: Village of Yellow Springs WWTW/Compliance Evaluation Inspection Report NPDES Permit No. OH0028215/OEPA PERMIT NO. 1PC00013*ID

Dear Mr. Cundiff:

On December 13, 2010, I conducted an NPDES Compliance Evaluation Inspection at the Village of Yellow Springs wastewater treatment works (WWTW). Joe Bates (Operator of Record) and Brad Ault were present during the inspection. The purpose of the inspection was to check on the construction progress and observe how the WWTW was operating.

All evaluated areas received "Satisfactory" ratings; however, there are comments for the Village to address located throughout the report.

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

Cc: Joe Bates, Village of Yellow Springs (w/report)

Enclosure

Southwest District Office
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**
1PC00013*ID	OH0028215	12/13/2010	C	S	1

Section B: Facility Data		
Name and Location of Facility Inspected	**Entry Time**	**Permit Effective Date**
Village of Yellow Springs WWTW 3835 Grinnell Road Yellow Springs, Greene County	11:30 a.m.	10/1/2010
	Exit Time	**Permit Expiration Date**
	2:15 p.m.	9/30/2015
Name(s) and Title(s) of On-Site Representatives	**Phone Number(s)**	
Joe Bates, Operator of Record	937-767-7208	
Name, Address and Title of Responsible Official	**Phone Number**	
Mark Cundiff, Village Manager Village of Yellow Springs 100 Dayton Street Yellow Springs, OH 45387	937-7671279	

Section C: Areas Evaluated During Inspection
(S = Satisfactory, M = Marginal, U = Unsatisfactory, N = Not Evaluated)

S	Permit	S	Flow Measurement	N	Pretreatment
S	Records/Reports	S	Laboratory	S	Compliance Schedule
S	Operations & Maintenance	S	Effluent/Receiving Waters	S	Self-Monitoring Program
S	Facility Site Review	S	Sludge Storage/Disposal	N	Other
S	Collection System				

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

See attached findings.

Inspector	Reviewer
12-16-10	12/16/10
Joshua Jackson Date Division of Surface Water Southwest District Office	Martyn Burt Date Compliance & Enforcement Supervisor Division of Surface Water Southwest District Office

Permit # : 1PC00013*IL
NPDES #: OH0028215

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.....	Y
(c) Permittee is taking actions to resolve violations.....	Y
(d) Permittee has a compliance schedule.....	Y
(e) Compliance schedule contained in...Administrative Orders	
(f) Permittee is in compliance with schedule.....	Y
(g) Has biomonitoring shown toxicity in discharge since last inspection	N

Comments/Status:

Section G: Operation & Maintenance

Treatment Works:

Treatment facility properly operated and maintained

(a) Standby power available.....generator ☐ or dual feed ☐..... N/E

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

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

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

(c) All treatment units in service other than backup units..... N/E

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

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

(f) Operation and maintenance manual provided and maintained..... N/E

(g) Any plant bypasses since last inspection..... N/E

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

Comments/Status:

WWTW has been under construction for most of 2010. It is anticipated that construction will be completed within the next two months.

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 book. Needs to be consecutive numbering and Joe Bates stated that he would make the changes.

(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..... N
  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)... Y
  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:

Mr. Bates has documented when he comes into work and when he leaves for the day. He has not documented all the times that he physically leaves the plant grounds (to check on the pump station or out for lunch, etc.). He stated that he would make the appropriate changes.

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.....1
- ii. How many pump stations have telemetered alarms.....1
- iii. How many pump stations have operable alarms.....1

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

Comments/Status:

The NPDES permit requires the Village to submit a Capacity, Management, Operation and Maintenance (CMOM) program and submit the written components of this program to Ohio EPA/SWDO by no later than May 1, 2012.
The Village has a known sanitary sewer overflow location at the main lift station located off U.S. 68. There has not been any documented overflows from the lift station since the last inspection. It is worth noting, however, that conditions have been unusually dry.
The Village purchased/installed an autodialer system and a flow meter so conditions at the lift station can be monitored remotely. Staff will be notified imediately if there are problems with the pumps,a power outage, and/or high wet well occurrence.

Section H: Sludge Management

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

*if one of the selected methods is land application, complete applicable charts.

Class B Sewage Sludge (monitoring station 581)

Pathogen Reduction Alternative	84370 Vector Attraction Reduction Options									
	Option 1 -38% Volatile Solids Reduction	Option 2 -Anaerobic Bench Scale Analysis	Option 3 – Aerobic Bench Scale Analysis	Option 4 – Specific Oxygen Uptake Rate	Option 5 – Aerobic Time and Temperature	Option 6 – Alkali Addition	Option 7 – >75% Percent Solids without Unstabilized	Option 8 - >75% Percent Solids with Unstabilized	Option 9 – Land Injection	Option 10 – Immediate Incorporation
Alternative 1 - Geometric Mean of Seven Fecal Samples (84369)	☐	☐	☐	☒	☐	☐	☐	☐	☐	☐

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

(c) How much sludge storage is provided at the plant.....
75 days of liquid storage in digesters plus sludge storage pad for cake storage

(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..... Y

(g) Are sludge application sites inspected to verify compliance with NPDES permit..... Y

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

Comments/Status:

Reviewed most recent fecal coliform sludge samples and SOUR test. All results were within acceptable range.

Section I: Self-Monitoring Program

Flow Measurement:

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

90-degree weir with ultrasonic level sensor

(b) Flow meter calibrated annually ..... Y
(Date of last calibration: 12-18-2009)

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

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

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

Comments/Status:

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:

The Village purchased NIST thermometers for the influent and effluent automatic sampler refrigeration units. At the time of the inspection, both refrigeration units were within the acceptable range. Village personnel document temperature readings in the sampler refrigeration units daily. I instructed Mr. Bates to take a reading at the beginning and end of a sampling event.

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..... Y

- 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..... Y

(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

(h) Commercial laboratory used..... Y
Parameters analyzed by commercial lab: Everything but Do, Cl2 residual, temperature and pH

Lab name: Belmont Labs

Comments/Status:

The SOP prepared for pH testing was reviewed during the inspection. Overall, the SOP was well-written but it did fail to mention certain items such as 1) utilizing a stirrer for laboratory measurement readings (see "Apparatus" section of the attached Standard Method 4500 for pH and 2) one of the "References" should be Standard Method 4500 and a copy should be kept in the laboratory. Please make the appropriate changes.
A NIST traceable thermometer should be used to calibrate the thermometer utilized for final effluent sampling (annually). The correction value (if any) should be noted on or near the final effluent thermometer.

Permit # : 1PC00013*ID
NPDES #: OH0028215

Section J: Effluent/Receiving Water Observations

Outfall # 001
Outfall Description: Located after chlorine contact tank. Effluent was clear, without noticable solids

Receiving Stream: Unnamed tributary to Yellow Springs Creek
Receiving Stream Description: As observed from the cascade from Grinnell Road, no observable solids.

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 Report
(Items for Correction in Bold Type)

The Village of Yellow Springs wastewater treatment works (WWTW) is designed to treat an average daily of 0.6 million gallons/day. A review of the discharge monitoring reports (DMRs) for June 2010 – October 2010 shows an average daily flow of 0.37 MGD.
The Village started construction of the WWTW upgrade in October 2009 (Ohio EPA Permit to Install was issued to the Village on July 1, 2009). The Director's Final Findings & Orders issued to the Village on March 12, 2010, requires construction completed and the WWTW operational by no later than May 1, 2011. In general, this upgrade will include installation/construction of the following salient features:

- Earthen overflow basin (Overflow box will divert influent flow in excess of 3.93 MGD to the overflow basin until flows subside. Wastewater in the overflow basin will then be pumped back to the head of the plant.)
- Mechanical fine screen (6.0 MGD capacity – ¼ inch openings)
- Grit Removal (4.0 MGD capacity – "Vortex")
- Conversion of existing extended aeration activated sludge system to a biological nutrient removal plant (~500,000 gallons of tank volume)
- Conversion of existing aerobic digester and sludge storage tank to a "Sequencing Falcultative Digester"
- Side stream Phosphorus treatment for digester supernatant and sludge dewatering filtrate
- Back-up Generator (350 KW – which will power all essential equipment)
- Supervisor Control and Data Acquisition (SCADA) system via DeviceNet.

The main purpose of the inspection was to check on the construction progress and observe how the WWTW was operating. According to Mr. Bates, the construction of the new facilities should be completed by February 1, 2011 (if not sooner). Most of the new equipment is installed and operating. The SCADA system is the main component that has not been installed, but work on the system will occur within the next 2-3 weeks.

The WWTW appeared to be performing well, as the aeration basins had a good color with no objectionable odors. One clarifer had been taken out of service so that operational staff could repair a cable utilized for stabilizing and centering the rotating arm. It was expected to be brought back on-line that same day. The effluent from the remaining clarifier was clear.

An aluminum baffle had been installed in the chlorine contact tank to prevent any floating solids from flowing out of the WWTW. The baffle appeared to be effective, as the picture below shows. Several insects had expired due to the very cold conditions and they were held in one area as a result of the baffle. Operational staff use a net to clear the quiescent area of any trapped floatables.

EFFLUENT LIMIT VIOLATIONS
(Period of Review: June 2010 – October 2010)

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

Reporting Period	Parameter	Limit Type	Limit	Reported Value
June 2010	Nitrogen, Ammonia (NH3)	30D Conc	0.7	.89775
June 2010	Nitrogen, Ammonia (NH3)	7D Conc	1.1	1.835
June 2010	Nitrogen, Ammonia (NH3)	30D Qty	1.6	2.09798
June 2010	Nitrogen, Ammonia (NH3)	7D Qty	2.4	2.6397

June 2010	Phosphorus, Total (P)	30D Conc	1.0	1.6125
June 2010	Phosphorus, Total (P)	30D Qty	2.3	4.12224
June 2010	Nitrogen, Ammonia (NH3)	7D Conc	1.1	1.235
June 2010	Nitrogen, Ammonia (NH3)	7D Qty	2.4	4.92945
June 2010	Phosphorus, Total (P)	7D Conc	1.5	4.97
June 2010	Phosphorus, Total (P)	7D Qty	3.4	14.1838
July 2010	Phosphorus, Total (P)	30D Conc	1.0	1.449
July 2010	Phosphorus, Total (P)	7D Conc	1.5	3.65
July 2010	Phosphorus, Total (P)	7D Qty	3.4	5.0702
August 2010	Phosphorus, Total (P)	30D Conc	1.0	4.58
August 2010	Phosphorus, Total (P)	30D Qty	2.3	5.48949
August 2010	Phosphorus, Total (P)	7D Conc	1.5	4.49
August 2010	Phosphorus, Total (P)	7D Qty	3.4	5.59124
August 2010	pH	1D Conc	6.5	6.3
August 2010	Dissolved Oxygen	1D Conc	6.0	5.63
August 2010	Phosphorus, Total (P)	7D Conc	1.5	6.46
August 2010	Phosphorus, Total (P)	7D Qty	3.4	7.7999
August 2010	Phosphorus, Total (P)	7D Conc	1.5	6.49
August 2010	Phosphorus, Total (P)	7D Qty	3.4	7.46765
September 2010	Phosphorus, Total (P)	30D Conc	1.0	5.33
September 2010	Phosphorus, Total (P)	7D Conc	1.5	4.93
September 2010	Phosphorus, Total (P)	30D Qty	2.3	6.09751
September 2010	Phosphorus, Total (P)	7D Qty	3.4	5.42237
September 2010	Phosphorus, Total (P)	7D Conc	1.5	7.38
September 2010	Phosphorus, Total (P)	7D Qty	3.4	9.02246
September 2010	Phosphorus, Total (P)	7D Conc	1.5	5.47
September 2010	Phosphorus, Total (P)	7D Qty	3.4	6.45963
September 2010	Phosphorus, Total (P)	7D Conc	1.5	3.94
September 2010	Phosphorus, Total (P)	7D Qty	3.4	4.1607
October 2010	Phosphorus, Total (P)	30D Conc	1.0	4.36
October 2010	Phosphorus, Total (P)	7D Conc	1.5	3.98
October 2010	Phosphorus, Total (P)	30D Qty	2.28	4.46267
October 2010	Phosphorus, Total (P)	7D Qty	3.41	3.99204
October 2010	Phosphorus, Total (P)	7D Conc	1.5	4.49
October 2010	Phosphorus, Total (P)	7D Qty	3.41	4.60555
October 2010	Phosphorus, Total (P)	7D Conc	1.5	4.83
October 2010	Phosphorus, Total (P)	7D Qty	3.41	4.77148
October 2010	Phosphorus, Total (P)	7D Conc	1.5	4.14
October 2010	Phosphorus, Total (P)	7D Qty	3.41	4.48159

*The phosphorus violations were attributed to the lack of any phosphorus treatment during the construction process. Once the SCADA system is installed and the remaining Bio-Phos equipment is brought on-line, the WWTW should be able to begin biologically removing phosphorus from the waste stream.

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:

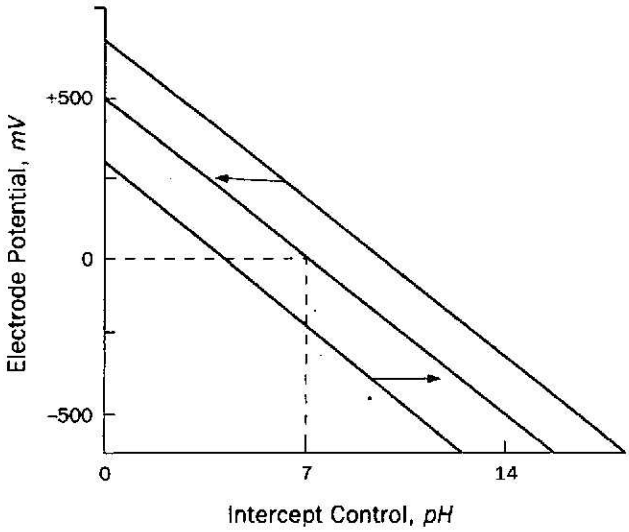

Figure 4500-H⁺:1. Electrode potential vs. pH. Intercept control shifts response curve laterally.

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

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

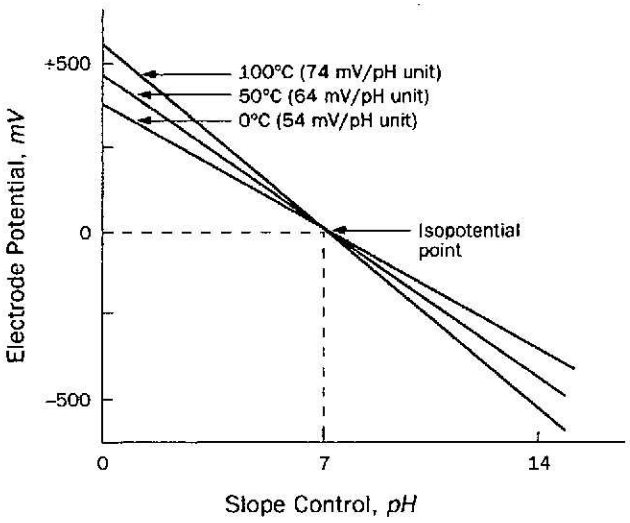

Figure 4500-H⁺:2. Typical pH electrode response as a function of temperature.

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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