

FIELD WATER QUALITY ANALYSES

Purpose

The Environmental Stewardship is responsible for acquiring water quality analytical measurements during the course of field work. This procedure outlines the requirements for field analytical measurements provided by ENV personnel and are standard operating procedures for 40CFR136 NPDES programs for permits under section 402 of the Clean Water Act of 1977, as amended (CWA), and/or for reports required to be submitted under NPDES permits or other requests for quantitative or qualitative effluent data under parts 122 to 125 of title 40.

Scope

This procedure applies to ENV staff and contract personnel. Samples obtained for analysis will consist of water. The conventions set forth in this document have been established to ensure that ENV data quality objectives (DQO) are met and that data obtained from different personnel are comparable.

In this procedure

This procedure addresses the following major topics:

| Topic | See Page |
|--|-----------------|
| 1. General Information About This Procedure | 3 |
| 2. Analysis Requests and Sample Shipment | 5 |
| 3. Quality Assurance Requirements | 6 |
| 4. Analytical and Quality Control Requirements | 9 |
| 5. Analytical Data Deliverable Requirements | 11 |
| Field Measurement Methods – | 12 |
| 6. Electrical Conductance | |
| 7. Reduction-Oxidation Potential | 16 |
| 8. Turbidity | 21 |
| 9. pH | 24 |
| 10. Titrimetric Sulfite | 26 |
| 11. Total Residual Chlorine | 28 |
| 12. Alkalinity | 31 |
| 13. Dissolved Oxygen | 35 |
| 14. Lessons Learned | 37 |
| 15. Records Resulting from this Procedure | 38 |

Integrated work management

The work specified in this procedure is conducted with applicable Integrated Work Documents, in accordance with LANL IMP 300-00-00, Integrated Work Management for Work Activities.

Signatures

First authorization review date is one year from division leader signature below.

| | |
|--|-------------------------|
| Prepared by: <u>Signature on file</u> B. Turney, ENV-WQH | Date: <u>7/28/05</u> |
| Concurred by: <u>Signature on file</u> K. Greene, ENV-ECR | Date: <u>7/28/05</u> |
| Approved by: <u>Signature on file</u> A. Dorries, ENV-ECR Group Leader | Date: <u>7/28/05</u> |
| Approved by: <u>Signature on file</u> S. Rae, ENV-WQH Group Leader | Date: <u>7/29/05</u> |
| Approved by: <u>Signature on file</u> K. Hargis, ENV Division Leader | Date: <u>7/29/05</u> |

1. General Information About This Procedure

Attachments

| Number | Attachment Title | No. of pages |
|--------|--|--------------|
| 1 | Standard Half-cell Potentials and Eh of ZoBells Solution | 1 |

History of revision

This table lists the revision history and effective dates of this procedure.

| Revision | Date | Description Of Changes |
|----------|------|---|
| 0 | 7/05 | New document. Supersedes RRES-WQH-054.1 and ECR-06.02 |

Who requires training to this procedure

All ENV staff and contract personnel who take water quality analytical measurements.

Training method

The training method for this procedure may include “self-study” (reading), on the job training, and proficiency testing depending on the experience of the personnel. Training is documented in accordance with the Group’s implementing procedure for training.

Prerequisites

In addition to training to this procedure, the following training is also required prior to performing this procedure:

- HAZCOM
- RRES-ES-Field, *General Field Safety for All*

References

The following documents are referenced in this procedure:

- U.S. Geological Survey, 1997 to present, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, 2 v., variously paged. [Also available online at <http://pubs.water.usgs.gov/twri9A>. Chapters originally were published from 1997-1999; updates and revisions are ongoing and are summarized at: <http://water.usgs.gov/owq/FieldManual/mastererrata.html>]
- ENV-DO-207, *Handling, Packaging, and Shipping of Samples*
- ENV-DO-IMP, *Integrated Management Plan for the Environmental Stewardship Division*

1. General Information About This Procedure, continued

| | | |
|--------------------|---------------------|---|
| Definitions | | |
| | Alkalinity | Alkalinity is a measure of the capacity of water to neutralize a strong acid. |
| | Duplicate | A duplicate is a sample split taken by the sampling team and submitted as a sample for the purpose of assessing both sampling and analytical precision. |
| | Field sheet | The term field sheet refers to any form used to describe the work in a particular batch of samples. Field sheets may present the data acquired or be a cover sheet for those data. |
| | Field sheet review | Field sheet review is a process for verification of compliance with requirements in the analysis documentation. |
| | MDL | Method Detection Limit. |
| | Reagent | Reagents are chemicals of known purity that are used in analytical methods. This term does not apply to materials used to calibrate instruments or to perform quality control activities. Such materials are called standards. |
| | Significant figures | A maximum of two significant figures shall be used to report the final analytical result. Two significant figures involves two non-zero digits (e.g., 0.21, 2.1, 21, 210). |
| | SOP | Standard Operating Procedure |
| | SAP | Sample and Analysis Plan |
| | Standard | A standard is any material intended for use in instrument calibration or quality control activities. |
| | Stock Solution | A stock solution is a high-concentration standard. Stock solutions are not used to calibrate instruments or as quality control samples, but rather are diluted to produce the standards used to calibrate or prepare quality control samples. |

2. Analysis Requests and Sample Shipment

| | |
|-------------------------------|---|
| Sampling Plans | Prior to sample collection, the requestor will notify the Sampling Team, in writing, of the scheduled collection of samples. The notification shall take the form of a sample collection request order. The order will include requested analysis. Some small projects and/or rapid analysis requests may be submitted without the advance notification discussed above in order to meet project requirements. Monitoring and other routine programs such as NPDES may have a general sampling plan covering the normal requirements and objectives with individual sampling events covered using the chain of custody (COC). |
| Sample custody | Reference ENV-DO-207, <i>Handling, Packaging, and Shipping of Samples</i> . |
| Request for reanalysis | In the event that a suspected analytical error is identified by comparison with historical data, if QC data are either missing or outside the control limits, the Program Manager may request re-sampling. If re-sampling cannot be done, then data qualification or rejection may be required. |
| Time definitions | References to days, weeks, or months are defined as calendar days, weeks, and months unless otherwise specified. |

3. Quality Assurance Requirements

General data quality objectives In accordance with ENV-DO-IMP, “Integrated Management Plan for the Environmental Stewardship Division,” all effluent and environmental sampling activities are conducted in accordance with the Data Quality Objectives process. Specifically, the IMP states:

The DQO process, as described in, or similar to, EPA QA/G-4, is used for all environmental and effluent sampling programs to establish the operating parameters. The DQO process and resulting operating parameters are documented in the applicable QAPPs for the sampling program.

Internal audit requirements Periodic audits of sampling events or data acquisition may be conducted at the discretion of the ENV quality groups or at the request of program management.

Employee training and documenting employee proficiency It is the responsibility of the sampling lead to verify that all members of the sampling team meet the training requirements for a sampling event (e.g., site-specific training, radiological training, training to applicable sampling plans and procedures, etc.).
Field personnel shall demonstrate proficiency prior to conducting any field measurements and shall be periodically tested to verify continued proficiency.

3. Quality Assurance Requirements, continued

**Instrumentation,
equipment,
and reagent
maintenance**

Logbooks will be issued to personnel to document any field measurement activities not specifically covered on field worksheets. Each logbook will be uniquely identified and page numbered. The use of indelible ink to make logbook entries is required. All sampling and measurement anomalies shall be documented in the logbook and specific samples that were affected shall be identified. A cross-reference will be noted on any field worksheets that specify the logbook code and page number where the anomaly is described. Any anomaly that adversely affects the sample data quality shall be transmitted to the program immediately.

Sample weights used in calculations for a measurement will be obtained on a balance with sufficient sensitivity and which has been checked prior to and on the same day as the measurement. The balance check weights must be NIST traceable and the percent difference of the results for each weight must be within 5%. If the results are outside 5%, the balance must be recalibrated prior to use. The balance ID shall be recorded on the worksheet or in the logbook.

All reagent water used during a sampling and measurement activity shall be documented on the worksheet or in the logbook as to the quality, source, access location, date and time it was acquired. All reagent water must be EPA Quality Type I. Specific conductance must be measured and recorded on a worksheet or in a logbook daily during use.

**Analytical and
QA SOPs**

It is the responsibility of the ENV personnel to verify that they are qualified and using approved procedures. The actual procedure and revision numbers shall be documented on the worksheet or in the logbook. Any variations or modifications will be documented in the logbook.

**Holding time
requirements**

Field measurements should be made during or immediately after sampling. Whenever this is not practical, the exact date and time of sampling should be recorded and the exact date and time of the measurement should be recorded. It is crucial that ENV personnel perform measurements as soon as possible. ENV personnel shall promptly notify the sampling lead or sample requestor, if it is determined that one or more measurements cannot be performed within a reasonable amount of time(s).

NPDES field analyses for compliance are required to be made within 15 minutes of sample collection.

3. Quality Assurance Requirements, continued

**Data
verification
and review
requirements**

Field sheet review

- All analyst or field personnel worksheets describing analysis of ENV samples shall undergo supervisory and/or peer review. A field shall be provided on each field sheet for the reviewer's initials. The reviewer need not sign each page of a submittal; only one signature per data submittal is required.
- Worksheet review signatures signify that the analyst has met the requirements of the method.
- Logbooks shall be periodically reviewed by supervision or management.

Report review

All field analyses data transmitted to ENV by sampling team personnel shall undergo data verification and completeness review by appropriate QA or technical staff. Signature evidence of these reviews is required.

**Duplicate
analysis**

For quality control, field measurements should be repeated, from the beginning, on the samples that are selected for field duplicates.

4. Analytical and Quality Control Requirements

Sample analysis Field sheet requirements requirements

Analyst field sheets are used to record analytical data using specified fields. Field sheets will generally be constructed to meet specific needs for specific projects and will be named accordingly. Field sheets shall present a complete record of all information pertinent to the analysis. A completed field sheet that includes the information listed below is required for each set of analyses.

- The name of the person who performed the field analysis.
- The instrument used in the analysis. If ENV has more than one instrument of a particular model, a unique designation shall be given to each.
- The name or initials of the peer, supervisory, or QA reviewer. (See Section 2 of this document for specific review requirements.)
- Standards information, including the name, preparation date, and expiration date of calibration and calibration verification standards, as applicable.
- The analytical procedure and regulatory method used.
- The equations for calculations used to obtain results. If instrument readouts give results, without the need for further mathematical manipulation, the worksheets shall include the statement “result = instrument readout.”
- The date and time that the analysis was performed.

All fields in a field worksheet shall be completed. Fields that have no data shall be filled in with "NA".

Use of a specific field worksheet for a specific program may be mandatory. It is the sampler's responsibility to use the appropriate worksheet. When worksheets are not available or not specified, the logbook may be used but all of the required information must be included.

4. Analytical and Quality Control Requirements, continued

Sample analysis Analytical techniques and procedures

requirements (continued)

ENV personnel shall employ approved analytical techniques and documents in the analysis of samples.

Field analyses for temperature, specific electrical conductance, oxidation-reduction potential, turbidity, total chlorine, alkalinity, dissolved oxygen, pH, and sulfite, will be conducted in accordance with the USGS National Field Manual for the Collection of Water-Quality Data (USGS NFM), Hach methods, or EPA methods as follows:

| | |
|--|------------------|
| Temperature | USGS NFM A6.1 |
| Specific Electrical Conductance; | USGS NFM A6.3 |
| Reduction-Oxidation Potential-Electrode Method | USGS NFM A6.5 |
| Turbidity; | USGS NFM A6.7 |
| Total Residual Chlorine | Hach Method 8167 |
| Alkalinity and Acid Neutralizing Capacity | Hach Method 8203 |
| Dissolved Oxygen | Hach Method 8421 |
| pH - Electrometric | EPA Method 150.1 |
| Sulfite – Titrimetric | EPA Method 377.1 |

Analytical uncertainty

Field analytical results shall not be accompanied by estimates of uncertainty.

5. Analytical Data Deliverable Requirements

Analytical data Reporting forms for analytical results

package

Analytical results shall be reported using ENV approved forms.

contents and

format

"Less than" results

Mathematical "less than" signs shall not be used in reporting analytical results.

Completeness

Partial deliverables shall not be submitted unless specifically requested by the sampling lead or sample requestor.

Significant figures

A maximum of two significant figures shall be used to report the final analytical result. Two significant figures involves two non-zero digits (e.g., 0.21, 2.1, 21, 210). If there is any question, contact the sampling lead or sample requestor.

Uncertainty and detection limit values shall be reported to no more than two significant figures.

6. Field Measurement Methods - Electrical Conductance

Scope Electrical conductance (EC) is a measure of the capacity of water (or other media) to conduct an electrical current. Electrical conductance of water is a function of the types and quantities of dissolved substances in water, but there is no universal linear relation between total dissolved substances and conductivity. This procedure is applicable to surface water and groundwater and is the ENV standard operating procedure (SOP) for USGS NFM A6.3 for the measurement of specific electrical conductance in the field.

Equipment

- EC meter with temperature compensating capabilities
- EC sensor with thermometer or thermistor
- Deionized water
- Lint free paper tissues
- Logbook or field sheet

Reagents and standards Use conductivity standards of values that approximate the expected field values for calibration and calibration checks. Conductivity standards have a shelf life as specified by the manufacturer. Check for expiration dates prior to use.

Sample collection Samples should be analyzed as soon as possible, preferably in the field at the time of sampling.

6. Field Measurement Methods - Electrical Conductance, continued

Calibration and standardization Calibrate sensors against a standard that approximates sample conductivity and use the second standard as a calibration check. The general procedures described in steps 1–15 below apply to most instruments used for field measurements. Check the instrument manual for specific instructions.

To calibrate sensors, perform the following steps:

| Step | Action |
|------|---|
| 1 | Inspect the instrument and the conductivity sensor for damage. Make sure that all cables are clean and connected properly. |
| 2 | Turn the instrument on and allow for instrument start-up. |
| 3 | Select two conductivity standards that will bracket the expected sample conductivity. Verify that the date on the standards has not expired. |
| 4 | Follow manufacturer's instructions for calibration. |
| 5 | Rinse the sensor with deionized water and dry. |
| 6 | Pour fresh calibration standard into a clean container. Immerse the sensor in the calibration standard. |
| 7 | Agitate a submersible-type conductivity sensor up and down under the solution surface to expel air trapped in the sensor. |
| 8 | Record the instrument reading and temperature. |
| 9 | Rinse the sensor with deionized water. |
| 10 | Repeat steps 5 through 10 with the second conductivity standard. The purpose for measuring a second standard is to check instrument calibration over the range of the two standards. <ul style="list-style-type: none"> The difference from the standard value should not exceed 5 percent. If the difference is greater than 5 percent, repeat the entire calibration procedure. |
| 11 | Record the measurement for the second standard in the instrument log book or the appropriate field sheet. |

6. Field Measurement Methods - Electrical Conductance, continued

Measure the electrical conductance

Measure the conductivity of samples as soon as possible after collection. If the sample cannot be analyzed immediately, fill a bottle to the top and close it tightly. Reported conductivity values normally are determined on an unfiltered sample. Large concentrations of suspended sediment can be a source of measurement error, record such conditions in the logbook or on the field data sheet.

To measure electrical conductance of samples, perform the following steps:

| Step | Action | | | | | | | | |
|------|--|------|--------|---|---|---|--|--|--|
| 1 | Rinse sensor with deionized water and dry sensor. | | | | | | | | |
| 2 | After rinsing and drying the electrodes, immerse them into the sample beaker of sample stream. | | | | | | | | |
| 3 | To measure conductivity, perform the following steps: <table border="1" data-bbox="565 898 1386 1108"> <thead> <tr> <th>Step</th> <th>Action</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Remove any air trapped in the sensor by agitating the sensor up and down under the water surface.</td> </tr> <tr> <td>2</td> <td>Read the instrument display and allow the instrument to stabilize.</td> </tr> <tr> <td></td> <td></td> </tr> </tbody> </table> | Step | Action | 1 | Remove any air trapped in the sensor by agitating the sensor up and down under the water surface. | 2 | Read the instrument display and allow the instrument to stabilize. | | |
| Step | Action | | | | | | | | |
| 1 | Remove any air trapped in the sensor by agitating the sensor up and down under the water surface. | | | | | | | | |
| 2 | Read the instrument display and allow the instrument to stabilize. | | | | | | | | |
| | | | | | | | | | |
| 4 | Record the conductivity. <ul style="list-style-type: none"> If the instrument is not temperature compensating, record the raw data and convert the values to conductivity at 25°C using temperature-correction factors provided by the manufacturer. | | | | | | | | |
| 5 | <ul style="list-style-type: none"> Rinse the sensor with deionized water. | | | | | | | | |

Quality control Using an aliquot of the standard solution, calibration verification should be checked every 10 sample locations or a minimum of once per day. This check should occur following the last EC measurement performed during that day and should employ the use of a high and low standard. Reading should be within 5 percent of the standard solution value. If it is not, then recalibrate the instrument before continued use. A duplicate measurement should be made using a new sample aliquot every 10 samples.

6. Field Measurement Methods - Electrical Conductance, continued

Calculations ENV reports conductivity in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).e. If instrument does not read in microsiemens per centimeter or the instrument does not correct to 25 degrees Celsius, the actual reading is to be recorded and a separate entry made for the converted result. The conversion formula shall be documented on the worksheet.

Data reporting Report routine conductivity measurements in microsiemens per centimeter ($\mu\text{S}/\text{cm}$) at 25°C .

7. Field Measurement Methods - Reduction-Oxidation Potential

Scope

Measurement of redox potential, described here as Eh measurement, is not recommended in general because of the difficulties inherent in its theoretical concept and its practical measurement. Reduction-oxidation potential (reported as Eh) is a measure of the equilibrium potential, relative to the standard hydrogen electrode, developed at the interface between a noble metal electrode and an aqueous solution containing electroactive redox species.

- Eh measurement may show qualitative trends but generally cannot be interpreted as equilibrium values.
- Determinations of redox using the platinum (or other noble metal) electrode method (Eh) are valid only when redox species are (a) electroactive, and (b) present in the solution at concentrations of about 10^{-5} molal and higher. Redox species in natural waters generally do not reach equilibrium with metal electrodes.

This procedure is applicable to surface water and ground water. This is the ENV SOP for USGS NFM A6.5 for the measurement of oxidation-reduction in the field.

Equipment

- Millivolt meter or pH meter with millivolt reading capability, preferably with automatic temperature compensator; 0.1-mV sensitivity; scale to at least $\pm 1,400$ mV; BNC connector (see instrument specifications for pH meters)
- Redox electrodes, either (a) platinum and reference electrode (calomel or silver:silverchloride) or (b) combination electrode
- Electrode filling solutions (refer to manufacturer's specifications)
- Thermometer (liquid-in-glass or thermistor type), calibrated for use with millivolt meters without temperature compensator
- Flowthrough cell with valves, tubing, and accessories impermeable to air (for use with pump system)
- Manufacturer's recommended electrode-cleaning solution
- Liquid nonphosphate laboratory-grade detergent (Alconox)
- Deionized water (maximum conductivity of $1.0 \mu\text{S/cm}$)
- Bottle, squeeze dispenser for deionized water
- Paper tissues, disposable, lint free
- Waste-disposal container
- Instrument log book for recording calibrations, maintenance, and repairs

7. Field Measurement Methods - Reduction-Oxidation Potential, continued

Reagents and standards

ZoBell's is the standard solution for testing redox instruments. ZoBell's solution consists of a 0.1 molal KCl solution containing equimolar amounts of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$. ZoBell's is reported stable for at least 90 days if kept chilled at 4°C.

An Orion ORP Standard may be used to calibrate the offset of samples using Orion Models 91-79 and 91-80 electrodes. Refer to manufacturer's instructions for standards and calibrations.

CAUTION: ZoBell's solution is toxic—handle with care.

Calibration and standardization Eh measuring systems can be tested for accuracy but they cannot be adjusted. Eh equipment must be tested, either in the laboratory or in the field, against a ZoBell, or pre-prepared, standard solution before making field measurements. In general, field testing with ZoBell's is not required, but the protocol used will depend on study needs.

Before using, check that the standard solution has not exceeded its shelf life.

Test the Eh equipment using the standard solution before and after field use.

Be aware if using a ZoBell's solution that:

- ZoBell's is toxic and needs to be handled with care.
- ZoBell's reacts readily with minute particles of iron, dust, and other substances, making field use potentially difficult and messy.

The Eh measurements are made by inserting a platinum electrode coupled with a reference electrode into the solution to be measured. The resulting potential, read directly in millivolts from a potentiometer (such as a pH meter), is corrected for the difference between the standard potential of the reference electrode being used at the solution temperature and the potential of the standard hydrogen electrode (reference Attachment 1, Standard Half-cell Potentials).

TECHNICAL NOTE: E_{ref} is the whole-cell potential of the reference electrode in ZoBell's solution.

- $E_{ref} = 238$ mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the silver:silver-chloride (Ag:AgCl) electrode;
- $E_{ref} = 185.5$ mV (saturated KCl, immersed with the platinum electrode in ZoBell's at 25°C) is the measured potential of the calomel (Hg:HgCl₂) electrode;
- $E^\circ = 430$ mV is the standard electrode potential of ZoBell's solution measured against the hydrogen electrode at 25°C.

7. Field Measurement Methods - Reduction-Oxidation Potential, continued

Calibration and standardization (continued) Half-cell potentials for the calomel, silver:silver chloride, and combination electrodes are shown in Attachment 1, Standard Half-cell Potentials. Attachment 1, Eh of ZoBells Solution, provides the theoretical Eh of ZoBell's solution as a function of temperature. For those temperatures not shown on the tables, interpolate the values. Add the value corresponding to the solution temperature to the measured potential electromotive force (emf measurement).

To test Eh equipment, follow manufacturer's instructions and record the results in a logbook, or on a field sheet.

Measure Eh To obtain accurate results, it is necessary to prevent losses and gains of dissolved gases in solution.

- Chemical, physical, and biological reactions can cause the Eh of water to change significantly within minutes or even seconds after the collection of a sample.
- Water samples cannot be preserved and stored for the Eh measurement.
- Use equipment that eliminates sample aeration and operate the equipment to meet this goal. If using a flowthrough chamber or cell:
 - Use tubing that is impermeable (relatively) to oxygen.
 - Channel the sample flow through an airtight cell (closed system) constructed specifically to accommodate redox or ion-specific electrodes, temperature, and other sensors.
 - Connections and fittings must be airtight.
 - Purge atmospheric oxygen from the sample tubing and associated flow channels before measuring Eh.

Measure Eh in situ with a submersible instrument or use an airtight flowthrough system.

7. Field Measurement Methods - Reduction-Oxidation Potential, continued

**Measure Eh,
(continued)**

To measure Eh of sample, perform the following steps:

| Step | Action |
|------|--|
| 1 | Record the type of reference-electrode system being used. |
| 2 | Check for the correct electrode filling solution. If working in very hot or boiling waters, change the reference electrode filling solution daily. |
| 3 | Keep the electrode surface brightly polished. Follow manufacturer's instructions. TECHNICAL NOTE: Temperature determines the Eh reference potential for a particular solution and electrode pair, and may affect the reversibility of the redox reactions, the magnitude of the exchange current, and the stability of the apparent redox potential reading. The observed potential of the system will drift until thermal equilibrium is established. Thermal equilibrium can take longer than 30 minutes but it is essential before beginning the measurements. |
| 4 | Select an in situ or closed-system sampling method. Immerse the electrodes and temperature sensors in the sample water. <ul style="list-style-type: none"> In situ (or downhole)—Lower the sensors to the depth desired and follow the manufacturer's recommendations. Closed-system flow cell—Check that the connections and sensor grommets do not leak, and that the water being pumped fills the flowthrough cell. |
| 5 | Allow the sensors to reach thermal equilibrium with the aqueous system being measured and record the time lapsed. <ul style="list-style-type: none"> It is essential that platinum electrodes be flushed with large volumes of sample water to obtain reproducible values. Record the pH and temperature of the sample water. |
| 6 | Switch the meter to the millivolt function. <ul style="list-style-type: none"> Allow the reading to stabilize (± 5 mV). Record the value and temperature (see the TECHNICAL NOTE below). Stabilization should occur within 30 minutes. |
| 7 | Take readings of the sample temperature and potential (in millivolts). It is best to stop the flow of the sample while the reading is being taken to prevent streaming-potential effects. |
| 8 | Switch the meter to the Eh function. Record Eh value and temperature. |
| 9 | After the measurements have been completed for the day, rinse the electrode(s) thoroughly with deionized water. |
| 10 | Record all data and mV and Eh values. |

7. Field Measurement Methods - Reduction-Oxidation Potential, continued

Quality control Calibration Verification: Measure an aliquot of standard solution after every 10 samples, or at the end of the day.

Duplicates: Precision should be determined about every tenth sample or more frequently, depending on study objectives. Successive measurements should be repeated until they agree within 5 percent.

- Repeat procedure with at least two fresh sub-samples, rinsing the instrument between samples.
 - Sub-sample values should be within ± 5 percent.
-

Data reporting Report the calculated Eh in mV to two significant figures.

Potentials are reported to the nearest 10 mV, along with the temperature at which the measurement was made, the electrode system employed, and the pH at time of measurement.

8. Field Measurement Methods - Turbidity

Scope Turbidity measures the scattering effect that suspended solids have on light: the higher the intensity of scattered light, the higher the turbidity. Primary contributors to turbidity include clay, silt, finely divided organic and inorganic matter, soluble colored organic compounds, plankton, and microscopic organisms. In surface water, the clarity of a natural body of water is used routinely as an indicator of the condition and productivity of the aqueous system. In ground water, turbidity commonly is measured during well development and well purging to indicate the extent to which particulates occurring as a result of well installation and sampling activities have been removed. This is the ENV SOP for USGS NFM A6.7 for the measurement of turbidity in the field.

Equipment

- Turbidimeter
- Turbidity stock solutions and standards:
- Manufacturer-provided secondary standards.
- Sample cells (cuvettes), clear colorless glass (supplied from instrument manufacturer)
- Silicon oil, optical grade (with same index of refraction as sample cells; supplied by instrument manufacturer)

Reagents and standards Use commercially prepared turbidity standards.

Sample collection Surface Water –
Collect samples for turbidity measurement or make in situ measurements using either discharge-weighted, pumped-sample, or grab-sample procedures, as appropriate for site characteristics and for study objectives.

Verify the turbidity determination by measuring turbidity on two or more samples until readings stabilize to within $\pm 10\%$. Collect turbidity sample directly into the sample cell for immediate measurement or into a clean amber glass bottle for short-term storage.

8. Field Measurement Methods – Turbidity, continued

Sample collection (continued)

Groundwater –

Turbidity in ground water generally is less than 5 NTU. Natural ground-water turbidity of up to 19 NTU has been reported for some environmental settings. Some groundwater, however, can have considerably higher turbidity.

For discrete-sample measurement using a turbidimeter or spectrophotometer:

- Pump the ground-water sample directly from the sample discharge line into a precleaned glass, polyethylene sample collection bottle, or directly into a sample cell.
 - Bailers are not recommended for collecting turbidity samples, as bailer deployment can cause turbidity.
 - Do not collect the discharge passing through the flowthrough chamber in which pH, conductivity, or other field-measurement sensors are installed.
-

Calibration and standardization

The calibration steps that follow are general and should be modified to apply to the instrument being used—check manufacturer’s instructions. To calibrate the turbidimeter, follow the manufacturer’s instructions for instrument calibration. Record calibration data in the instrument calibration log book.

Measure turbidity

Turbidity is time sensitive—Measure sample turbidity on site to avoid biased values that can result from (1) biodegradation, settling, or sorption of particulates in the sample; or (2) precipitation of humic acids and minerals (carbonates and hydroxides, for example) caused by changes in sample pH during transport and holding.

- Biased or erroneous readings can result from unmatched cell orientation, colored sample solutions, gas bubbles, condensation, and scratched or dirty sample cells.
- Condensation on the sample cell commonly occurs on hot days when humidity is high.

TECHNICAL NOTE: Causes of low-biased readings include particulate settling or sorption on container surfaces, biodegradation, and sample solutions with true color (color from dissolved substances that absorb light—some instruments are designed with optics to eliminate bias from color). High-biased or false turbidity readings can be caused by the presence of condensation and finely-divided air or other gas bubbles in the sample or on the cell or probe surface, and scratches, fingerprints, or dirt on the surface of the sample cell or turbidity probe.

8. Field Measurement Methods – Turbidity, continued

Measure turbidity (continued)

To measure turbidity, perform the following steps:

| Step | Action | | | | | | | | | | |
|------|--|------|--------|---|--|---|--|---|--|---|--|
| 1 | Turn on the turbidimeter according to the manufacturer's instructions. TECHNICAL NOTE: Turbidity should be measured immediately. However, if temporary storage of samples becomes necessary, collect samples in clean amber glass bottles, keep out of sunlight, and keep chilled at or below 4°C to prevent biodegradation of solids. The holding time must not exceed 24 hours. | | | | | | | | | | |
| 2 | Measure the discrete sample by performing the following steps: <table border="1" style="margin-left: 20px;"> <thead> <tr> <th>Step</th> <th>Action</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Shake the sample vigorously to completely disperse the solids. Allow air bubbles to disappear before filling sample cell</td> </tr> <tr> <td>2</td> <td>Pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers.</td> </tr> <tr> <td>3</td> <td>Remove condensation from the cell with a clean, soft, lint free cloth or tissue. If condensation continues, apply a thin coating of silicon oil on the outside of the cell about every third time the cell is wiped dry of moisture.</td> </tr> <tr> <td>4</td> <td>Orient the cell with standard in the turbidimeter.</td> </tr> </tbody> </table> | Step | Action | 1 | Shake the sample vigorously to completely disperse the solids. Allow air bubbles to disappear before filling sample cell | 2 | Pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers. | 3 | Remove condensation from the cell with a clean, soft, lint free cloth or tissue. If condensation continues, apply a thin coating of silicon oil on the outside of the cell about every third time the cell is wiped dry of moisture. | 4 | Orient the cell with standard in the turbidimeter. |
| Step | Action | | | | | | | | | | |
| 1 | Shake the sample vigorously to completely disperse the solids. Allow air bubbles to disappear before filling sample cell | | | | | | | | | | |
| 2 | Pour the sample into a sample cell to the line marked (to the neck if there is no line). Do not touch cell walls with fingers. | | | | | | | | | | |
| 3 | Remove condensation from the cell with a clean, soft, lint free cloth or tissue. If condensation continues, apply a thin coating of silicon oil on the outside of the cell about every third time the cell is wiped dry of moisture. | | | | | | | | | | |
| 4 | Orient the cell with standard in the turbidimeter. | | | | | | | | | | |
| 3 | Determine the measured NTU value of the sample either by reading turbidity directly from the instrument. | | | | | | | | | | |
| 4 | Record measurement on field data sheet. | | | | | | | | | | |

Quality control Calibration Verification: The calibration should be checked daily prior to use with secondary standards. The measured value of the standard should be within 10% of the expected value. Failure requires re-calibration.

Duplicate: Perform a duplicate measurement every 10 samples. Repeat discrete sample measurement on two additional samples and check that they fall within the ± 10-percent criterion. Report the value of the first if two samples are measured, or report the median if three or more samples are measured.

Calculations The instrument is a direct read-out instrument.

Data reporting Turbidity is measured in nephelometric turbidity units (NTU). Turbidity values are entered into the ENV database only as NTU.

9. Field Measurement Methods - pH

Scope This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition). This is the ENV SOP for EPA method 150.1 for the measurement of pH in the field.

Equipment

- pH Meter and electrode - laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment. NOTE: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available.
- Thermometer or temperature sensor for automatic compensation

Reagents and standards

- Standard buffers should be used for calibration
- Standard buffers should be traceable to NIST, and are available for purchase from commercial vendors.

Sample collection Samples should be analyzed as soon as possible preferably in the field at the time of sampling.

Calibration and standardization

- Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.
- Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart.
- Standard buffers used for calibration must be traceable to NIST.
- Document calibration in the sampler's log book.

9. Field Measurement Methods – pH, continued

Measure pH To measure pH for water samples, perform the following steps:

| Step | Action |
|------|---|
| 1 | Standardize the meter and electrode system as outlined above. |
| 2 | Place the sample or buffer solution in a clean container using a sufficient volume to cover the sensing elements of the electrodes. If field measurements are being made, the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to insure sufficient sample movement across the electrode sensing element. |
| 3 | Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions. |
| 4 | After rinsing and drying the electrodes, immerse them into the sample beaker of sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. Note and record sample pH and temperature. |
| 5 | For acid rain samples, swirl the sample gently for a few seconds after the introduction of the electrode(s). Allow the instrument to equilibrate. The air-water interface should not be disturbed while measurement is being made. If the sample is not in equilibrium with the atmosphere, pH values will change as the dissolved gases are either absorbed or desorbed. Record sample pH and temperature. |

- Quality control**
- Using an aliquot of the buffer solution, calibration verification should be checked every 10 sample locations or a minimum of once per day. This check should occur following the last pH measurement performed during that day and should employ the use of a high and low buffer.. Alternate between the high and low buffers. Reading should within 0.1 pH units of the buffer solution value. If it is not, then recalibrate the instrument before continued use.
 - A duplicate measurement should be made using a new sample aliquot every 10 samples.

Calculations pH meters read directly in pH units.

Data reporting Report pH to the nearest 0.01 unit and temperature to the nearest 0.1°C.

10. Field Measurement Methods - Titrimetric Sulfite

Scope This method is applicable to drinking and surface waters, sewage and industrial wastes. The primary application has been to cooling, process and distribution water systems and boiler feedwaters to which sulfide is added in order to reduce dissolved oxygen and eliminate corrosion. This is the ENV SOP for EPA method 377.1 for the measurement of sulfite in the field.

Reagents and standards Standardized per Std. Method, 19th Ed.

- Sulfuric acid, H₂SO₄
- Starch indicator: Amylose, Mallinckrodt Chemical Works; Thyodene, Magnus Chemical Co. or equivalent.
- Dual-Purpose Sulfite Indicator Powder: a proprietary formulation containing sulfamic acid to destroy nitrite.
- Standard potassium iodide-iodate titrant, 0.0125N: Dissolve 445.8 mg anhydrous potassium iodate, KIO (primary standard grade dried for several hours at 120°C), 4.25 g KI and 310 mg NaHCO in distilled water and dilute to 1 liter.
- Sulfamic Acid: Crystalline
- EDTA Reagent Dissolve 2.5 g EDTA in 100 mL distilled water.

Sample collection Collect a fresh sample, taking care to minimize contact with air. Fix cooled samples (<50°C) immediately by adding 1 mL EDTA solution/100 mL sample. Cool hot samples to 50°C or below. Do not filter.

Measure titrimetric sulfate To measure titrimetric sulfate in water samples, perform the following steps:

| Step | Action | | | | | | | | | | | | | | |
|------|---|------|--------|---|--|---|-----------------------------------|---|------------------|---|---|---|---|---|--|
| 1 | Sampling Contact with air must be minimized. If the sample temperature is greater than 50°C, it must be cooled in a special apparatus described elsewhere. Immediately add 1 mL of EDTA Solution per 100 mL of sample. | | | | | | | | | | | | | | |
| 2 | Starch Indicator: <table border="1" style="width: 100%;"> <thead> <tr> <th>Step</th> <th>Action</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Place 1 mL H₂SO₄ in titration vessel.</td> </tr> <tr> <td>2</td> <td>Add 0.1 g sulfamic acid crystals.</td> </tr> <tr> <td>3</td> <td>Add 50 mL sample</td> </tr> <tr> <td>4</td> <td>Add approximately 1 ml starch indicator</td> </tr> <tr> <td>5</td> <td>Titrate with potassium iodide-iodate titrant until a faint permanent blue color develops. Keep the pipet tip below the surface of the sample. View the color change against a white background. Record the titrant in mL.</td> </tr> <tr> <td>6</td> <td>Run a reagent blank using distilled water instead of sample.</td> </tr> </tbody> </table> | Step | Action | 1 | Place 1 mL H ₂ SO ₄ in titration vessel. | 2 | Add 0.1 g sulfamic acid crystals. | 3 | Add 50 mL sample | 4 | Add approximately 1 ml starch indicator | 5 | Titrate with potassium iodide-iodate titrant until a faint permanent blue color develops. Keep the pipet tip below the surface of the sample. View the color change against a white background. Record the titrant in mL. | 6 | Run a reagent blank using distilled water instead of sample. |
| Step | Action | | | | | | | | | | | | | | |
| 1 | Place 1 mL H ₂ SO ₄ in titration vessel. | | | | | | | | | | | | | | |
| 2 | Add 0.1 g sulfamic acid crystals. | | | | | | | | | | | | | | |
| 3 | Add 50 mL sample | | | | | | | | | | | | | | |
| 4 | Add approximately 1 ml starch indicator | | | | | | | | | | | | | | |
| 5 | Titrate with potassium iodide-iodate titrant until a faint permanent blue color develops. Keep the pipet tip below the surface of the sample. View the color change against a white background. Record the titrant in mL. | | | | | | | | | | | | | | |
| 6 | Run a reagent blank using distilled water instead of sample. | | | | | | | | | | | | | | |

Table continued on next page.

10. Field Measurement Methods - Titrimetric Sulfite, continued

Measure
titrimetric
sulfate
(continued)

| Step | Action | | | | | | | | | | |
|------|---|------|--------|---|---|---|------------------------|---|---|---|---|
| 3 | Dual Purpose Sulfite Indicator Powder. | | | | | | | | | | |
| | <table border="1"> <thead> <tr> <th>Step</th> <th>Action</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Place 50 mL sample in a titration vessel.</td> </tr> <tr> <td>2</td> <td>Add 1 ml of indicator.</td> </tr> <tr> <td>3</td> <td>Titrate with potassium iodide-iodate titrant until a faint permanent blue color develops. View the color change against a white background. Record the volume of titrant in mL.</td> </tr> <tr> <td>4</td> <td>Run a reagent blank using distilled water instead of sample</td> </tr> </tbody> </table> | Step | Action | 1 | Place 50 mL sample in a titration vessel. | 2 | Add 1 ml of indicator. | 3 | Titrate with potassium iodide-iodate titrant until a faint permanent blue color develops. View the color change against a white background. Record the volume of titrant in mL. | 4 | Run a reagent blank using distilled water instead of sample |
| Step | Action | | | | | | | | | | |
| 1 | Place 50 mL sample in a titration vessel. | | | | | | | | | | |
| 2 | Add 1 ml of indicator. | | | | | | | | | | |
| 3 | Titrate with potassium iodide-iodate titrant until a faint permanent blue color develops. View the color change against a white background. Record the volume of titrant in mL. | | | | | | | | | | |
| 4 | Run a reagent blank using distilled water instead of sample | | | | | | | | | | |

- Quality control**
- Calibration Verification: The calibration should be checked prior to use. Calculated recovery shall be between 85% and 115% following measurement of a sample. Failure requires re-standardization.
 - Duplicate: Repeat discrete sample measurement on two additional samples and check that they fall within ± 10 -percent. Report the value of the first if two samples are measured, or report the median if three or more samples are measured.

11. Field Measurement Method - Total Residual Chlorine

Scope Chlorine can be present in water as free chlorine and as combined chlorine. Both forms can exist in the same water and be determined together as the total chlorine. Free chlorine is present as hypochlorous acid or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine and free chlorine reacts with DPD (N,N-diethyl-p-phenylenediamine) to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run a free chlorine test. Subtract the results of the free chlorine test from the total chlorine test to obtain the combined chlorine concentration. Test results are measured at 530 nm. This is the ENV SOP for HACH Method 8167 (EPA 330.5) for the measurement of total chlorine using the HACH CL17 Chlorine Analyzer.

Equipment

- HACH CL17 Chlorine Analyzer
- A 50ml beaker
- Sample cells

Calibration and standardization Calibrate instrument daily, before sampling activity, and only in the WQH Lab, per the manufacturer's instructions and document in the sampler's NPDES log book.

Reagents and standards

- Total Chlorine Reagent AccuVac® Ampuls or DPD Total Chlorine Reagent Powder Pillows
- Water, deionized
- Chlorine Standard Solution, 2-mL Voluette® Ampule, 20–30 mg/L

Sample collection Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and more slowly oxidizes organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of free chlorine in water.

Avoid plastic containers since these may have a large chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

11. Field Measurement Method - Total Residual Chlorine, continued

Sample collection, continued

A common error in testing for chlorine is not obtaining a representative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine analysis immediately.

Measure total residual chlorine

To measure total residual chlorine, perform the following steps:

| Step | Action |
|------|--|
| 1 | Touch Start. |
| 2 | Fill a round sample cell with 10 mL of sample. |
| 3 | Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell. (This is the prepared sample). Swirl the sample cell for 20 seconds to mix. |
| 4 | Touch the timer icon. Touch OK. A three-minute reaction period will begin. Perform steps 5 and 6 during this time period. |
| 5 | Fill another round sample cell with 10-mL of sample (This is the blank.). Wipe the sample cell and place it into the cell holder. |
| 6 | Touch Zero. The display will show:0.00 mg/L Cl ₂ . |
| 7 | Within three minutes after the timer beep, wipe the prepared sample and place it into the cell holder. Results will appear in mg/L Cl ₂ . |

- Quality control**
- **Calibration Verification:** The calibration and intercept should be checked prior to use, every 10 samples, and at the end of the day or sampling event sample measurements. Measure a mid-level calibration standard and a blank every 10 samples. The measured value of the standard should be within 10% of the expected value and the blank should be less than the reporting limit. Failure to be within 10% requires re-calibration.
 - **Duplicate:** Repeat discrete sample measurement on two additional samples and check that they fall within the ± 10 -percent criterion. Report the value of the first if two samples are measured, or report the median if three or more samples are measured.

11. Field Measurement Method - Total Residual Chlorine, continued

Quality control, • Standard Additions Method:
continued

| Step | Action |
|------|--|
| 1 | After reading test results, leave the sample cell (unspiked sample) in the instrument . |
| 2 | Touch Options. Touch Standard Additions. A keypad will appear. Enter the average chlorine concentration shown on the certificate enclosed with the Chlorine Voluette® Ampules. Touch OK. |
| 3 | A summary of the Standard Additions procedure will appear. Touch OK to accept the values for standard concentration, sample volume, and spike volumes as shown. Touch Edit to change these values. After values are accepted, the unspiked sample reading will appear in the top row. See Standard Additions in the instrument manual for more information. |
| 4 | Snap the neck off a LR Chlorine Voluette® Ampule Standard, 25–30 mg/L Cl ₂ . |
| 5 | Prepare three sample spikes. Fill three mixing cylinders (Cat. No. 1896-40) with 10 mL of sample. Use the TenSette® Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 10-mL samples and mix each thoroughly. Note: For AccuVac® Ampuls, fill three mixing cylinders (Cat. No. 1896-41) with 50-mL of sample and spike with 0.4 mL, 0.8 mL, and 1.2 mL of standard. Transfer 40 mL from each of the three mixing cylinders to three 50-mL beakers (Cat. No. 500-41H). Analyze each standard addition sample as described in the procedure above. Accept each standard additions reading by touching Read. Each addition should reflect approximately 100% recovery. |
| 6 | Analyze each sample spike as described in the procedure above, starting with the 0.1 mL sample spike. Accept each standard additions reading by touching Read. Each addition should reflect approximately 100% recovery. |
| 7 | After completing the sequence, touch Graph to view the best-fit line through the standard additions data points, accounting for matrix interferences. Touch View: Fit, then select Ideal Line and touch OK to view the relationship between the sample spikes and the “Ideal Line” of 100% recovery. |

Calculations Direct instrument readout.

12. Field Measurement Methods - Alkalinity

Scope The sample is titrated with sulfuric acid to a colorimetric end point corresponding to a specific pH. Phenolphthalein alkalinity is determined by titration to a pH of 8.3, as evidenced by the color change of phenolphthalein indicator, and indicates the total hydroxide and one half the carbonate present. M (methyl orange) or T (total) alkalinity is determined by titration to a pH between 3.7 and 5.1, and includes all carbonate, bicarbonate and hydroxide. Alternatively, total alkalinity end points may be determined by using a pH meter and titrating to the specific pH required for the sample composition. This is the ENV SOP for HACH Method 8203 (EPA 310.1) for the measurement of alkalinity in the field.

Equipment

- Cylinders, graduated,
 - 10mL
 - 25mL
 - 50mL
 - 100mL.
- Digital Titrator
- Flask, Erlenmeyer, 250-mL

Reagents and standards

- Alkalinity Reagent Set
 - Bromcresol Green-Methyl Red Powder Pillows
 - Phenolphthalein Powder Pillows
 - Sulfuric Acid Titration Cartridge, 1.600 N
 - Sulfuric Acid Titration Cartridge, 0.1600 N
 - Water, demineralized

Sample collection Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation or prolonged exposure to air. Samples should be analyzed as soon as possible after collection but can be stored at least 24 hours by cooling to 4 °C or below.

12. Field Measurement Methods – Alkalinity, continued

Measure alkalinity

To measure alkalinity, perform the following steps:

| Step | Action | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------------------------------|--|---|--------------------|---|------------------|-------|-----|--------|-----|--------|----|--------|-----|---------|-----|-------|-----|---------|----|-------|-----|----------|----|-------|-----|-----------|----|-------|------|
| 1 | Select the sample volume and Sulfuric Acid (H ₂ SO ₄) Titration Cartridge that correspond to the expected alkalinity concentration as mg/L calcium carbonate (CaCO ₃). | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | Use a graduated cylinder or pipet to measure the sample volume from Table 1. Transfer the sample into a clean, 250-mL Erlenmeyer flask. Dilute to the 100-mL mark with deionized water, if necessary. Table 1: | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | <table border="1"> <thead> <tr> <th>Range (mg/L as CaCO₃)</th> <th>Sample Volume (mL)</th> <th>Titration Cartridge (H₂SO₄)</th> <th>Digit Multiplier</th> </tr> </thead> <tbody> <tr> <td>10-40</td> <td>100</td> <td>0.1600</td> <td>0.1</td> </tr> <tr> <td>40-160</td> <td>25</td> <td>0.1600</td> <td>0.4</td> </tr> <tr> <td>100-400</td> <td>100</td> <td>1.600</td> <td>1.0</td> </tr> <tr> <td>200-800</td> <td>50</td> <td>1.600</td> <td>2.0</td> </tr> <tr> <td>500-2000</td> <td>20</td> <td>1.600</td> <td>5.0</td> </tr> <tr> <td>1000-4000</td> <td>10</td> <td>1.600</td> <td>10.0</td> </tr> </tbody> </table> | Range (mg/L as CaCO ₃) | Sample Volume (mL) | Titration Cartridge (H ₂ SO ₄) | Digit Multiplier | 10-40 | 100 | 0.1600 | 0.1 | 40-160 | 25 | 0.1600 | 0.4 | 100-400 | 100 | 1.600 | 1.0 | 200-800 | 50 | 1.600 | 2.0 | 500-2000 | 20 | 1.600 | 5.0 | 1000-4000 | 10 | 1.600 | 10.0 |
| Range (mg/L as CaCO ₃) | Sample Volume (mL) | Titration Cartridge (H ₂ SO ₄) | Digit Multiplier | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10-40 | 100 | 0.1600 | 0.1 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 40-160 | 25 | 0.1600 | 0.4 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 100-400 | 100 | 1.600 | 1.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 200-800 | 50 | 1.600 | 2.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 500-2000 | 20 | 1.600 | 5.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1000-4000 | 10 | 1.600 | 10.0 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | Add the contents of one Phenolphthalein Indicator Powder Pillow and swirl to mix. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | If the solution turns pink, titrate to a colorless end point. Place the delivery tube tip into the solution and swirl the flask while titrating with sulfuric acid. Record the number of digits required. If the solution is colorless before titrating with sulfuric acid, the Phenolphthalein (P) alkalinity is zero. Proceed to step 8. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7 | Calculate: (Digits Required) * (Digit Multiplier) = mg/L as CaCO ₃ P Alkalinity. See Table 1 in Step 4 above. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 8 | Add the contents of one Bromocresol Green-Methyl Red Indicator Powder Pillow to the flask. Swirl to mix. | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

Table continued on next page.

12. Field Measurement Methods – Alkalinity, continued

Measure alkalinity (continued)

| Step | Action | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|------------------------------------|--|------------------------|------------------------|--------------------------|------------------------|---------------------------|--------|---------------------------|--------|---------------------------------|--------|------------------------------------|--------|----|---|---|---|---------------|---|--------|---------------|---|---------------|---|----|---|---|---------------|---------------|-------------|---|------|--------|---|--|---|--|---|-----------------------|---|--|---|---|---|--|
| 9 | <p>Titrate with sulfuric acid to a light pink (pH 4.5) color as required by sample composition. Record the number of digits required. Note: A pH meter may be used to titrate to a specific pH as required by sample composition. Reference Table 2.</p> <p>Table 2:</p> <table border="1"> <thead> <tr> <th>Sample Composition</th> <th>End Point</th> </tr> </thead> <tbody> <tr> <td>Alkalinity about 30 mg/L</td> <td>pH 4.9</td> </tr> <tr> <td>Alkalinity about 150 mg/L</td> <td>pH 4.6</td> </tr> <tr> <td>Alkalinity about 500 mg/L</td> <td>pH 4.3</td> </tr> <tr> <td>Silicates or phosphates present</td> <td>pH 4.5</td> </tr> <tr> <td>Industrial waste or complex system</td> <td>pH 4.5</td> </tr> </tbody> </table> | Sample Composition | End Point | Alkalinity about 30 mg/L | pH 4.9 | Alkalinity about 150 mg/L | pH 4.6 | Alkalinity about 500 mg/L | pH 4.3 | Silicates or phosphates present | pH 4.5 | Industrial waste or complex system | pH 4.5 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Sample Composition | End Point | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Alkalinity about 30 mg/L | pH 4.9 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Alkalinity about 150 mg/L | pH 4.6 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Alkalinity about 500 mg/L | pH 4.3 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Silicates or phosphates present | pH 4.5 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Industrial waste or complex system | pH 4.5 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10 | <p>Calculate: (Digits Required) * (Digit Multiplier) = mg/L as CaCO₃ Total (T or M) Alkalinity Carbonate, bicarbonate, and hydroxide concentrations may be expressed individually using the relationships shown in Table 3.</p> <p>Table 3: (PA=Phenolphthalein Alkalinity; TA=Total Alkalinity)</p> <table border="1"> <thead> <tr> <th>Row</th> <th>Result of Titration</th> <th>Hydroxide Alkalinity =</th> <th>Carbonate Alkalinity =</th> <th>Bicarbonate Alkalinity =</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>PA=0</td> <td>0</td> <td>0</td> <td>TA</td> </tr> <tr> <td>2</td> <td>PA=TA</td> <td>TA</td> <td>0</td> <td>0</td> </tr> <tr> <td>3</td> <td>PA < 0.5 * TA</td> <td>0</td> <td>2 x PA</td> <td>TA - (2 * PA)</td> </tr> <tr> <td>4</td> <td>PA = 0.5 * TA</td> <td>0</td> <td>TA</td> <td>0</td> </tr> <tr> <td>5</td> <td>PA > 0.5 * TA</td> <td>(2 * PA) - TA</td> <td>2 * (TA-PA)</td> <td>0</td> </tr> </tbody> </table> <p>To use Table 3, perform the following steps:</p> <table border="1"> <thead> <tr> <th>Step</th> <th>Action</th> </tr> </thead> <tbody> <tr> <td>1</td> <td>Does the PA equal zero? If yes, use Row 1.</td> </tr> <tr> <td>2</td> <td>Does the PA equal TA? If yes, use Row 2.</td> </tr> <tr> <td>3</td> <td>Multiply the PA by 2.</td> </tr> <tr> <td>4</td> <td>Select Row 3, 4, or 5 based on comparing the result of Step 3 of this table with the TA.</td> </tr> <tr> <td>5</td> <td>Perform the required calculations in the appropriate row, if any.</td> </tr> <tr> <td>6</td> <td>Check your results. The sum of the three alkalinity types will equal the TA.</td> </tr> </tbody> </table> | Row | Result of Titration | Hydroxide Alkalinity = | Carbonate Alkalinity = | Bicarbonate Alkalinity = | 1 | PA=0 | 0 | 0 | TA | 2 | PA=TA | TA | 0 | 0 | 3 | PA < 0.5 * TA | 0 | 2 x PA | TA - (2 * PA) | 4 | PA = 0.5 * TA | 0 | TA | 0 | 5 | PA > 0.5 * TA | (2 * PA) - TA | 2 * (TA-PA) | 0 | Step | Action | 1 | Does the PA equal zero? If yes, use Row 1. | 2 | Does the PA equal TA? If yes, use Row 2. | 3 | Multiply the PA by 2. | 4 | Select Row 3, 4, or 5 based on comparing the result of Step 3 of this table with the TA. | 5 | Perform the required calculations in the appropriate row, if any. | 6 | Check your results. The sum of the three alkalinity types will equal the TA. |
| Row | Result of Titration | Hydroxide Alkalinity = | Carbonate Alkalinity = | Bicarbonate Alkalinity = | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 | PA=0 | 0 | 0 | TA | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | PA=TA | TA | 0 | 0 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | PA < 0.5 * TA | 0 | 2 x PA | TA - (2 * PA) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | PA = 0.5 * TA | 0 | TA | 0 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | PA > 0.5 * TA | (2 * PA) - TA | 2 * (TA-PA) | 0 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Step | Action | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 | Does the PA equal zero? If yes, use Row 1. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2 | Does the PA equal TA? If yes, use Row 2. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 | Multiply the PA by 2. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4 | Select Row 3, 4, or 5 based on comparing the result of Step 3 of this table with the TA. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5 | Perform the required calculations in the appropriate row, if any. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6 | Check your results. The sum of the three alkalinity types will equal the TA. | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

12. Field Measurement Methods – Alkalinity, continued

Quality control

Duplicates: Repeat discrete sample measurement or two additional samples every 10 measurements, and check that they fall within $5.1 > \text{pH} > 3.7$ criterion. Report the value of the first if two samples are measured, or report the median if 3 or more samples are measured.

End Point Confirmation: Confirm proper end point color with a pH meter ($5.1 > \text{pH} > 3.7$).

Data reporting

Report total alkalinity.

13. Field Measurement Method - Dissolved Oxygen

Scope The High Range Dissolved Oxygen AccuVac Ampul contains reagent vacuum sealed in a 14-mL ampule. When the AccuVac Ampul is opened in a sample containing dissolved oxygen, it forms a yellow color which turns purple. The purple color development is proportional to the concentration of dissolved oxygen. Test results are measured at 535 nm. This is the ENV SOP for HACH Method 8166 (EPA 360.1) for the measurement of dissolved oxygen in the field. Dissolved oxygen probes provide an alternative to the HACH Method.

Equipment

- Polypropylene Beaker, 50-mL, Low Form, with pour spout
- Sample Cells, 10-mL, w/cap
- HACH Spectrophotometer

OR

- Flow through DO probe meters

Reagents and standards using HACH For HACH spectrophotometer:

- High Range Dissolved Oxygen AccuVac® Ampuls
- reusable ampule caps.

Sample collection The main consideration in sampling with the High Range Dissolved Oxygen Ampul is to prevent the sample from becoming contaminated with atmospheric oxygen between breaking open the ampule and reading the absorbance. This is accomplished by capping the ampule with an ampule cap. If the ampule is securely capped, the ampule should be safe from contamination for several hours. The absorbance will decrease by approximately 3% during the first hour and will not change significantly afterwards.

Sampling and sample handling are important considerations in obtaining meaningful results. The dissolved oxygen content of the water being tested may change with depth, turbulence, temperature, sludge deposits, light, microbial action, mixing, travel time, and other factors. A single dissolved oxygen test rarely reflects the accurate overall condition of a body of water. Several samples taken at different times, locations, and depths are recommended for most reliable results. Samples must be tested immediately upon collection, although only a small error results if the absorbance reading is taken several hours later.

Measure dissolved oxygen Follow manufacturer's instructions for measurement of dissolved oxygen.

13. Field Measurement Method – Dissolved Oxygen, continued

**Quality
control**

Duplicate: Repeat discrete sample measurement on two additional samples every 10 measurements and check that they fall within a ± 10 -percent criterion. Report the value of the first if two samples are measured, or report the median if three or more samples are measured.

**Data
reporting**

Report dissolved oxygen in mg/L of O₂ .

14. Lessons Learned

Review lessons learned Before performing work described in this SOP, **participants** shall go to the Department of Energy Lessons Learned Information Services home page, located at <http://www.tis.eh.doe.gov/ll/ll.html>, and/or to the LANL Lessons Learned Resources web page, located at http://www.lanl.gov/projects/lessons_learned/, and search for applicable lessons.

Provide lessons learned During work performance and/or after the completion of work activities, **participants**, as appropriate, shall identify, document, and submit lessons learned in accordance with the LANL, Lessons Learned System located at http://www.lanl.gov/projects/lessons_learned/.

15. Records resulting from this procedure

Records

The following records generated as a result of this procedure are to be submitted to the generating group's records coordinator as applicable:

- Log book entries
- Field sheets

[Click here to record "self-study" training to this procedure.](#)

Standard Half-cell Potentials

| Temp °C | Silver:silver chloride | | | Calomel | | | | Orion 96-78 |
|------------|------------------------|-------------|------------------|-----------|-------------|-----------|------------------|--------------------------|
| | 3M KCl | 3.5M KCl | Saturated KCl | 3M KCl | 3.5M KCl | 4M KCl | Saturated KCl | Combination electrode |
| 10 | 0.220 | 0.215 | 0.214 | 0.260 | 0.256 | | 0.254 | 0.256 |
| 15 | 0.216 | 0.212 | 0.209 | | | | 0.251 | 0.253 |
| 20 | 0.213 | 0.208 | 0.204 | 0.257 | 0.252 | | 0.248 | 0.249 |
| 25 | 0.209 | 0.205 | 0.199 | 0.255 | 0.250 | 0.246 | 0.244 | 0.246 |
| 30 | 0.205 | 0.201 | 0.194 | 0.253 | 0.248 | 0.244 | 0.241 | 0.242 |
| 35 | 0.202 | 0.197 | 0.189 | | | | 0.238 | 0.238 |
| 40 | 0.198 | 0.193 | 0.184 | 0.249 | 0.244 | 0.239 | 0.234 | 0.234 |

Eh of ZoBells Solution

| Temperature °C | Eh (mv) | Temperature °C | Eh (mv) |
|-------------------|------------|-------------------|------------|
| 10 | 467 | 26 | 428 |
| 12 | 462 | 28 | 423 |
| 14 | 457 | 30 | 418 |
| 16 | 453 | 32 | 416 |
| 18 | 448 | 34 | 407 |
| 20 | 443 | 36 | 402 |
| 22 | 438 | 38 | 397 |
| 24 | 433 | 40 | 393 |
| 25 | 430 | | |