





Analytical Methods

Ways testing is done

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Analytical Methods
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General Testing Methods

- All wastewater testing methods fall into four general categories
 - Titrimetric (volumetric)
 - Gravimetric
 - Colorimetric (absorption or transmittance)
 - Electrometric



Titrimetric Methods

Determining one chemical concentration by measuring the amount of another chemical required to just react with a known volume of sample.

Examples

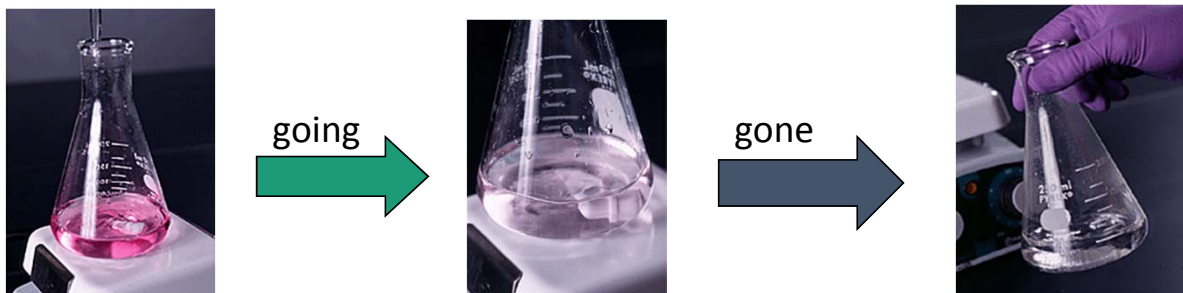
- Alkalinity
- Hardness
- Winkler Modification Dissolved Oxygen
- Iodometric TRC
- DPD TRC

Common Terms

- Aliquot
 - A precisely measured volume of sample
- Buret
 - Discussed earlier
- Normality
 - An expression of concentration
 - Example
 - 0.025N

Common Terms

- Indicator
 - A chemical that undergoes an observable change when a specific chemical reaction is complete
 - Example
 - Starch (iodometric)
 - Phenolphthalein (acid-base)
 - Methylene blue (acid-base)



Common Terms

- Titration
 - Addition of a solution of known concentration to a known volume of a second solution (sample) to determine the concentration of the second solution.
- Titrant
 - The solution of known concentration used in a titration

Preparation

- All standards to be used as titrants must be prepared/purchased
- Where necessary titrants must be standardized

Equipment

- Test will require:
 - Buret
 - Buret stand & clamp
 - Volumetric measuring devices
 - Erlenmeyer flask or beaker
 - Magnetic stirrer, stir bars and retriever



General Procedure

Previously discussed in the standardization section

Procedure

- Volumetrically measure the sample volume to be tested
 - Required accuracy determines measurement method
- Transfer sample to the flask
 - Use appropriate TD or TC procedure
- Add the indicator to the flask and mix
 - In some tests addition of the indicator is delayed until the titration is partially completed
- Add stir bar to the flask

Procedure

- Fill the buret and adjust to the 0.0 mL graduation (Follow procedure discussed earlier)
 - Rinse
 - Check for air bubbles
- Slowly add the titrant until the desired indicator change occurs
 - As reaction nears endpoint additions should be drop-wise with time for complete mixing between drops
- Record final buret volume
- Calculate test result

Avoiding Common Errors

- All chemicals must be:
 - Carefully prepared
 - Standardized as required by the test.
 - Stored as specified to maintain the shelf life
- Use lab grade water to rinse any titrant from the sides into the sample.
- All volumes must be accurately measured (bottom of the meniscus)



Gravimetric Methods

Testing by weight differences

Uses

- Solids testing
 - Suspended solids
 - Dissolved solids
 - Total solids
 - % Solids
 - Oil & Grease

Constant Weight

- The weight of an object does not change with additional drying or ignition.
 - Constant weight means that changes occurring in two successive drying-weighing cycles must be within:
 - $\pm 4\%$ or
 - ± 0.0005 grams (0.5 milligrams)

Equipment

- Depends on test being performed
 - Analytical balance
 - Filter assembly
 - Vacuum source
 - Filters
 - Drying oven
 - Muffle furnace (volatile)

Preparations

- Everything that will be weighed must be prepared:
 - In accordance with the test procedure.
 - Dried to constant weight
 - Stored in a desiccator until use

Determine Sample Volume

- Sample volume must:
 - Produce sufficient weight change
 - Specified in the test procedure
 - Allow reasonable filtration time

Sample Treatment

- Perform any pretreatment of the sample required for performing the test.
 - Chemical additions
 - pH adjustments

Test Procedure

- Perform the required procedural steps
 - Filtration
 - Drying to constant weight
 - Cooling to room temperature
 - Weighing
 - Calculating the test result

Ways to minimize errors

- Locate the balance in a proper location
- Maintain routine balance “housekeeping”
- Verify accuracy with traceable weights each day
- Service and maintain balance annually
- Maintain drying oven at specified temperature
- Maintain desiccator seal and change desiccant when needed

Handling Equipment

- Once equipment is prepared for use
 - Use forceps to move it – do not touch
 - Do not set equipment on dirty surfaces
 - Do not expose to atmosphere/allow it to absorb moisture
- Note
 - An analytical balance can weigh a fingerprint



Colorimetric Methods

Description

- When light of an appropriate wavelength is passed through a colored solution part of the light is absorbed.
- In many cases, the amount of color produced is directly related to the concentration of the chemical
- If the relationship between concentration and absorbance is linear it can form the basis of a colorimetric test procedure.

Examples

- Total chlorine residual (DPD)
- Phosphorus
- Chemical Oxygen Demand
- Nitrite Nitrogen
- Nitrate Nitrogen

Terms

- Absorbance
 - The amount of light absorbed by a sample
- Blank
 - A solution that does not contain the sample. Several different types used to:
 - zero the instrument
 - Evaluate the testing program quality assurance.

Terms

- **Background Correction**
 - A correction used to eliminate the part of the measured value caused by the instrument.
- **Colorimeter**
 - An instrument designed to produce light at a specific wavelength
- **Filter**
 - A device to allow only a specified wavelength light to pass through the measurement zone

Terms

- Filter Photometer
 - A colorimeter that uses a filter to produce the desired wavelength
- Path Length
 - The distance the light passes through the sample
 - Different path length = different absorbance
 - Usually specified in procedure

Terms

- **Photocell**
 - A light sensitive device that absorbs light and converts it to an electrical current
 - Sensing unit found in every colorimeter
- **Spectrophotometer**
 - A colorimeter that produces specified wavelength using a prism and an adjustable slot
 - Can be used for more than one test by adjusting the slot

Terms

- Transmittance
 - The amount or intensity of the light that passes through the colored solution (sample)
- Wavelength
 - All forms of light travel in waves
 - The distance between two peaks in a wave of light
 - Typically expressed as in nanometers (nm)



Colorimetric Procedures

Standard Curve

- Colorimetric test procedures require a standard curve/mathematical formula be developed that describes the relationship between the absorbance or transmittance and concentration.

Developing the Curve

- Solutions of known concentration (standards) are processed **exactly the same way** the samples will be processed.
 - At least 3 standards are required
 - Some tests may specify more
- Data generated is:
 - Evaluated to verify a linear relationship exists
 - Used to develop:
 - A mathematical relationship between colorimeter readings and concentration (line of best fit) and/or
 - A standard curve

Curve Verification

- DEQ requires that each test run include:
 - Two standards (bracketing expected test values).
 - A lab grade water blank

Procedure

- Prepare samples, blanks, standards and required QA samples
- Add required reagents
- Allow color development as specified in procedure
- Prepare the colorimeter
 - Set wavelength/insert filter
- Follow instrument procedure to set zero and maximum output
- Measure each sample & standard
- Calculate test result

Potential sources of error

- Small errors in standard preparations or treatment can generate large errors in measurement
- Not treating standards exactly as samples are treated
- Not verifying procedure by running standards with test runs
- Failing to prepare a new curve when standards are outside of specs
- Attempting to use the curve outside the linear portion
- Using colorimetric methods for highly colored or turbid samples

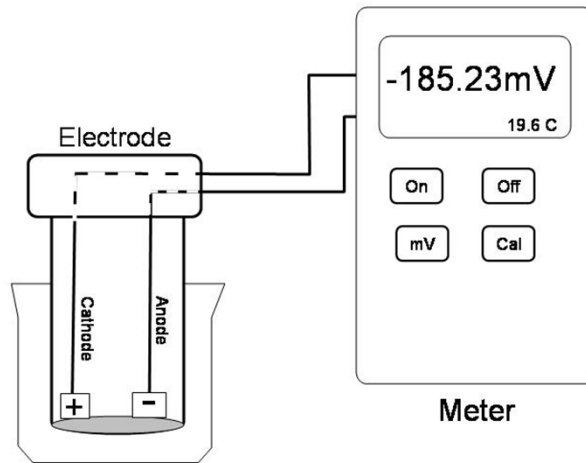


Electrometric Methods

Electrometric Methods

- Electrometric methods
 - Measure electrical current produced by chemical reactions
 - Examples
 - pH meter
 - Dissolved Oxygen (polarographic or luminescent electrode method)
 - Total residual chlorine (amperometric & electrode methods)
 - Ammonia & TKN (ISE method)
 - Nitrate (ISE method)

Description



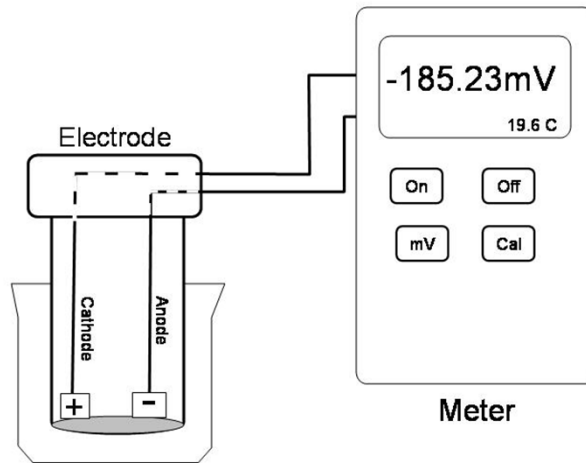
- Electrodes

- Devices to sense electrical current.
- Two electrodes required to complete circuit
 - Cathode (+)
 - Anode (-)
 - May be combined into a single unit (combined electrode)

Electronics

- Internal circuitry that allows the meter to:
 - Read current generated across electrodes
 - Be adjusted to calibrate or match meter output to specific concentrations

Meter



- Displays the output
- Sometimes readout is in millivolts or milliamps, etc
- Typically meter electronics can convert readout to display result in concentration (direct readout)

Standards

- Solutions of accurately known concentration used to calibrate the meter or provide data to:
 - Verify linearity
 - Calculate line of best fit
 - Develop standard curve

General Procedure

- Prepare standards or reference solutions
- Inspect meter and probe, perform any required maintenance
- Turn meter on and allow to warm-up.
- Starting with “cleanest” sample test all blanks, standards and samples
- Verify curve accuracy or perform calculations to verify linearity and develop line of best fit
- Calculate/record test data

Considerations

- Confirm meter accuracy by running at least (2) standards and a blank with each test run.
- Use duplicate samples at least 10% of the time
- Have instrument serviced in accordance with manufacturer's recommended schedule.
- Calibrate/verify calibration as required by DEQ, manufacturer and/or test procedure.

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