Wastewater Lab
Week 1

Course #2212

April 4-8, 2016

Fleming Training Center

Wastewater Treatment Lab - Week 1

Course #2212

Instructor: Barbara Loudermilk

Week 1

April 4 - 8, 2016

Monday, April 4:

8:30 Introductory Crossword
- Lab Basics:
  - Lab Rules
  - Safety (GHS-SDS)
  - Lab Scavenger Hunt
  - Lab Equipment
  - Sampling

Tuesday, April 5:

8:30 QA/QC Program and Method Update Rule
- Approved Methods of Analyses
  - 40CFR136 excerpts, table IA, IB, II, 136.7
  - NPDES Permit excerpts
  - Common Deficiencies in the WWTP Laboratory
- Dissolved Oxygen Analysis
- Biochemical Oxygen Demand (BOD)
- Prep Filters for TSS

Wednesday, April 6:

8:30 pH Analysis and Calibration
- Whole Effluent Toxicity Testing
- Solids Analysis: Total Suspended Solids; Settleable Solids (Imhoff)

Thursday, April 7:

8:30 Read Results of TSS
- Alkalinity
- Chemical Oxygen Demand (COD)
- Solutions Chemistry

Friday, April 8:

8:30 Exam and Course Evaluation

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Wastewater Lab Course – Week 1
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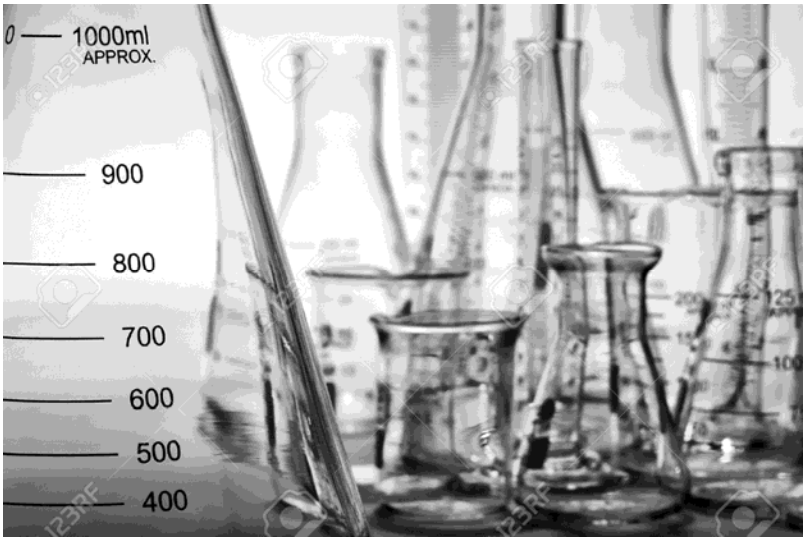
Section 1
Lab Basics



Lab Policies

1. No horse play.
2. No shorts or open-toed shoes.
3. No smoking, eating, dipping or drinking in the lab.
4. Put broken glass in broken glass container, NOT IN THE TRASH.
5. Do no pipet by mouth.
6. Each day after class:
   - All used glassware will be washed in hot soapy water, rinsed in tap water, then distilled water.
   - All counter top will be wiped clean with disinfectant.
   - Balance room must be clean.
7. Used pipets are placed in containers containing detergent immediately after use, tip up.
8. Acid spills must be cleaned up immediately.
9. Pipet bulbs must be cleaned immediately after overpipeting.
10. Wear safety glasses when performing any experiment.
11. Wear aprons in the lab at all times.
12. Wear gloves when performing any experiment or washing glassware.
13. Wash your hands before leaving the laboratory.
14. Know where the eye wash stations are located and how to use them.
15. Know where the emergency shower is and how to use it.
16. Know where each fire extinguisher is located and how to use them.
17. Read carefully the Material Safety Data Sheets for all chemicals used in the laboratory.

OSHA's Change Over to the Globally Harmonized System (GHS) of Classification

Labeling of Chemicals and SDS

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Compliance Dates

Effective Dates

The table below summarizes the phase-in dates required under the revised Hazard Communication Standard (HCS):

Effective Completion Date	Requirement(s)	Who
December 1, 2013	Train employees on the new label elements and safety data sheet (SDS) format.	Employers
June 1, 2015* December 1, 2015	Compliance with all modified provisions of this final rule, except: The Distributor shall not ship containers labeled by the chemical manufacturer or importer unless it is a GHS label	Chemical manufacturers, importers, distributors and employers
June 1, 2016	Update alternative workplace labeling and hazard communication program as necessary, and provide additional employee training for newly identified physical or health hazards.	Employers
Transition Period to the effective completion dates noted above	May comply with either 29 CFR 1910.1200 (the final standard), or the current standard, or both	Chemical manufacturers, importers, distributors, and employers

Training

- Why?
  - Some suppliers/distributors are already using the new Safety Data Sheet format and labels
  - To ensure all employees are able to interpret the new labels and Safety Data Sheets
  - Unique to each facility and is provided by the **employer**
- Who?
  - Essentially any employee *potentially exposed* to chemicals as part of their routine job. That means everyone.
    - e.g. an employee occasionally picking up a bottle of Windex to wipe down a door would not need training; however, an employee who uses Windex regularly would

WHAT IS A HAZARDOUS CHEMICAL UNDER GHS?

Hazard Classification

Hazardous Chemical

- A chemical is defined as hazardous when it is classified as one of the following:
  - Health hazard
  - Physical hazard
  - Simple asphyxiant
  - Combustible dust
  - Pyrophoric gas
  - Hazard not otherwise classified

Health Hazard Classification

- A chemical is classified as a health hazard if it poses one of the following effects:
  - Acute oral toxicity (any route)
  - Skin corrosion or irritation
  - Serious eye damage or eye irritation
  - Respiratory or skin sensitization
  - Germ cell mutagenicity
  - Carcinogenicity
  - Reproductive toxicity
  - Specific target organ toxicity
  - Aspiration hazard

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Physical Hazard Classification

- A chemical that poses one of the following hazardous effects:
  - Explosive
  - Flammable
  - Oxidizer
  - Self-reactive
  - Pyrophoric
  - Self-heating
  - Organic peroxide
  - Corrosive to metal
  - Gas under pressure
  - In contact with water emits flammable gas

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Simple Asphyxiant Classification

- A chemical is classified as such if it displaces oxygen in the ambient atmosphere and can cause oxygen deprivation leading to unconsciousness and death
  - For example:
    - Nitrogen
    - Carbon dioxide
    - Hydrogen
    - Methane

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Combustible Dust

- NFPA 654 (2006) and NEP Definitions
  - *Combustible Dust* A combustible particulate solid that presents a fire or deflagration hazard when suspended in air or some other oxidizing medium over a range of concentrations, regardless of particle size or shape
  - *Combustible Particulate Solid* Any combustible solid material, composed of distinct particles or pieces, regardless of size, shape or chemical composition

NFPA 69 (2002), and 499 (2004) Definitions

- *Combustible Dust.* Any finely divided solid material 420 microns* or less in diameter (i.e., material passing through a U.S. No 40 Standard Sieve) that presents a fire or explosion hazard when dispersed

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Combustible Dusts

Agricultural Products	Cottonseed	Soybean dust	**Chemical Dusts**	Epoxy resin
Egg white	Garlic powder	Spice dust	Adipic acid	Melamine resin
Milk, powdered	Gluten	Spice powder	Anthraquinone	Melamine, molded (phenol-cellulose)
Milk, nonfat, dry	Grass dust	Sugar (10x)	Ascorbic acid	Melamine, molded (wood flour and mineral filled phenol-formaldehyde)
Soy flour	Green coffee	Sunflower	Calcium acetate	(poly) Methyl acrylate
Starch, corn	Hops (malted)	Sunflower seed dust	Calcium stearate	(poly) Methyl acrylate, emulsion polymer
Starch, rice	Lemon peel dust	Tea	Carboxy-methylcellulose	Phenolic resin
Starch, wheat	Lemon pulp	Tobacco blend	Dextrin	(poly) Propylene
Sugar	Linseed	Tomato	Lactose	Terpene-phenol resin
Sugar, milk	Locust bean gum	Walnut dust	Lead stearate	Urea-formaldehyde/ cellulose, molded
Sugar, beet	Malt	Wheat flour	Methyl-cellulose	(poly) Vinyl acetate/ ethylene copolymer
Tapioca	Oat flour	Wheat grain dust	Paraformaldehyde	(poly) Vinyl alcohol
Whey	Oat grain dust	Wheat starch	Sodium ascorbate	(poly) Vinyl butyral
Wood flour	Olive pellets	Xanthan gum	Sodium stearate	(poly) Vinyl chloride/ ethylene/vinyl acetylene suspension copolymer
	Onion powder		Sulfur	(poly) Vinyl chloride/ vinyl acetylene emulsion copolymer
Agricultural Dusts	Parsley (dehydrated)	**Carbonaceous Dusts**		
Alfalfa	Peach	Charcoal, activated	**Metal Dusts**	
Apple	Peanut meal and skins	Charcoal, wood	Aluminum	
Beet root	Peat	Coal, bituminous	Bronze	
Carrageen	Potato	Coke, petroleum	Iron carbonyl	
Carrot	Potato flour	Lampblack	Magnesium	
Cocoa bean dust	Potato starch	Lignite	Zinc	
Cocoa powder	Raw yucca seed dust	Peat, 22%H_2O		
Coconut shell dust	Rice dust	Soot, pine	**Plastic Dusts**	
Coffee dust	Rice flour	Cellulose	(poly) Acrylamide	
Corn meal	Rice starch	Cellulose pulp	(poly) Acrylonitrile	
Cornstarch	Rye flour	Cork	(poly) Ethylene (low-pressure process)	
Cotton	Semolina	Corn		

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Pyrophoric Gas Classification

- A chemical in a gaseous state that will ignite spontaneously in air at a temperature of 130°F
  - For example:
    - Arsine
    - Silane
    - Metal carbonyls (dicobalt octacarbonyl, nickel carbonyl)
    - Diborane

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Hazard Not Otherwise Classified Classification

- A chemical is classified as such when there is an adverse physical or health effect identified through evaluation of scientific evidence that does not meet the specified criteria for the physical and health hazard classes
- Not required on the label, but should be on the MSDS
- Does not apply to adverse physical and health hazards under a GHS category that was not adopted by OSHA, such as acute toxicity Category 5

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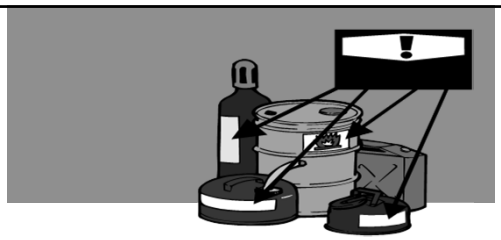
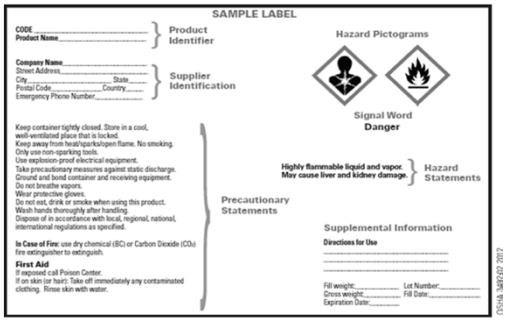


LABELING REQUIREMENTS

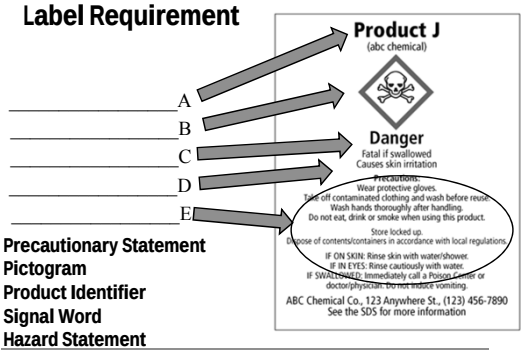
Labeling is the Law

Incoming Containers

- The requirement to have labels in unchanged
- The label content has changed
- The chemical manufacturer, distributor, or importer must label a container with
  - Product identifier
  - Signal word
  - Hazard statement(s)
  - Pictogram
  - Precautionary statement(s)
  - Name, address, telephone number of manufacturer, distributor or importer
  - Manufacturers, importers, will not ship containers without GHS labels after June 1, 2015
  - Distributors after December 1, 2015

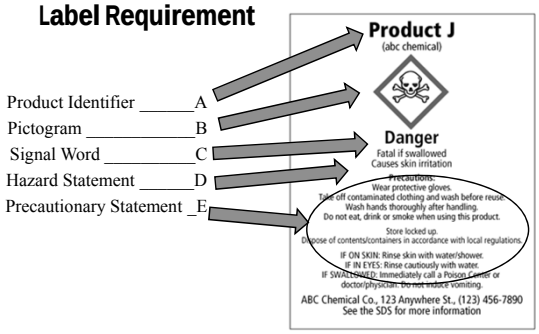


Manufacturer Container Label Requirement



Precautionary Statement
Pictogram
Product Identifier
Signal Word
Hazard Statement

Manufacturer Container Label Requirement



Product Identifier

- The name used for a hazardous chemical on the label and in the SDS
- Provides a unique means by which the user can identify the chemical
- Shall permit cross-references among the list of hazardous chemicals, the label and the SDS

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Signal Word

- Used to indicate the relative level of severity of hazard and alert the reader to a potential hazard
- One, but not both, of the following
  - Danger—more severe hazard
  - Warning—less severe hazard

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Hazard Statement

- Assigned to a hazard class and hazard category and describes the nature of the hazard
- Examples
  - Fatal if swallowed
  - May cause damage to *kidneys* through prolonged or repeated exposure
  - May cause or intensify fire
  - Extremely flammable liquid or vapor
  - Heating may cause an explosion

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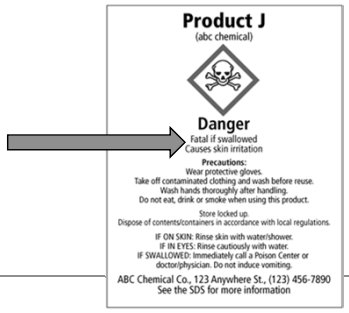
Hazard Statement



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Precautionary Statements

- A phrase that describes recommended measures that should be taken to minimize or prevent adverse effects resulting from exposure or improper storage or handling
- Prevention
- Response
- Storage
- Disposal
- They can be combined or consolidated to save space on the label

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Precautionary Statement

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Pictograms

- Nine are designated by GHS
- Eight are adopted by OSHA
- No duplicates or blank diamonds allowed on the label
- Correct name for the diamond is "squares-on-point"

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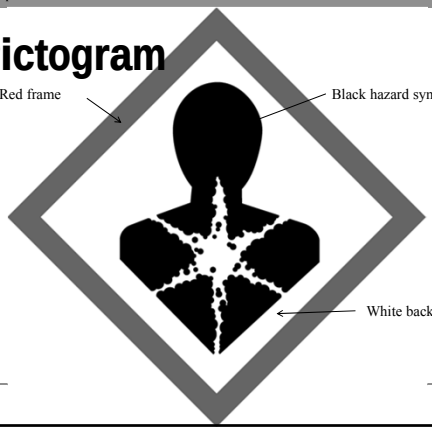
Pictogram



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Health Hazard

- Carcinogen
- Mutagenicity
- Reproductive Toxicity
- Respiratory Sensitizer
- Target Organ Toxicity
- Aspiration Toxicity

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Skull and Crossbones

- Acute Toxicity

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Flame

- Flammables
- Pyrophorics
- Self-Heating
- Emits Flammable Gas
- Self Reactives
- Organic Peroxides

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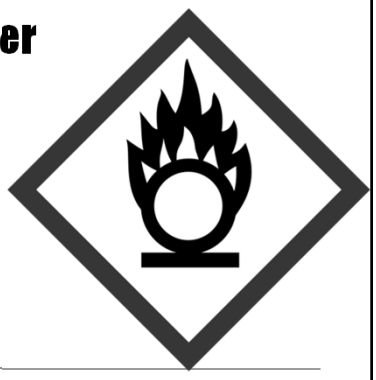
Flame Over Circle

- Oxidizers



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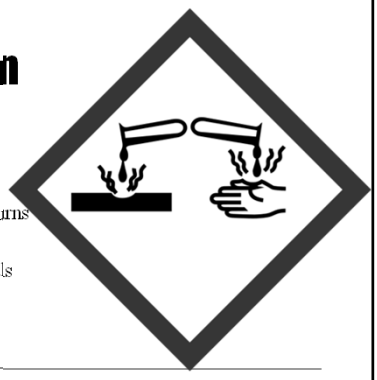
Corrosion

- Skin Corrosion/Burns
- Eye Damage
- Corrosive to Metals



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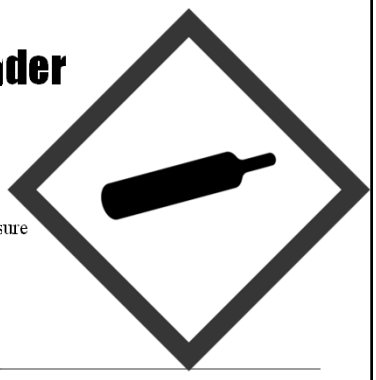
Gas Cylinder



- Gases Under Pressure

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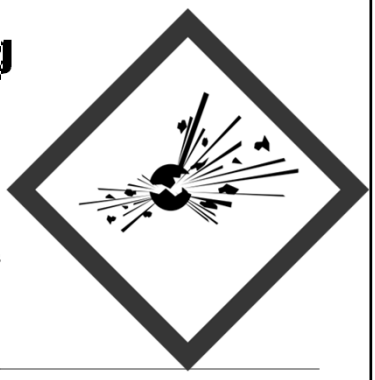
Exploding Bomb



- Explosives
- Self-Reactives
- Organic Peroxides

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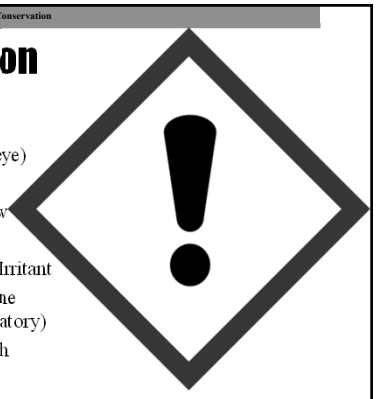
Exclamation Mark



- Irritant (skin and eye)
- Skin Sensitizer
- Acute Toxicity-low
- Narcotic Effects
- Respiratory Tract Irritant
- Hazardous to Ozone Layer (-non-mandatory)
- (Low degree health hazard)

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Environmental (non-mandatory)

OSHA Does Not Enforce This One

- Aquatic Toxicity

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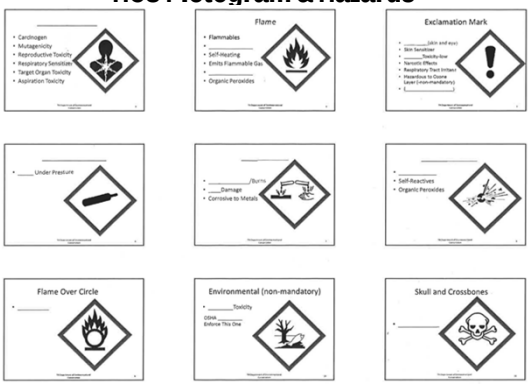
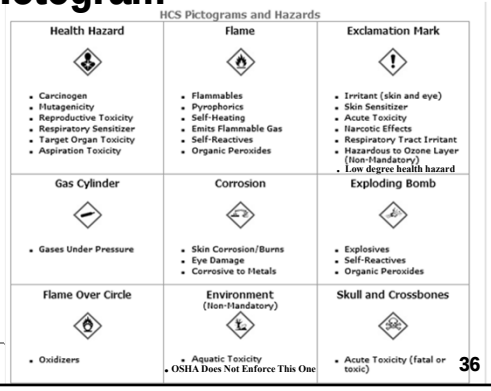
HCS Pictogram & Hazards



Pictogram



HCS Pictograms and Hazards

Health Hazard	Flame	Exclamation Mark
▪ Carcinogen ▪ Mutagenicity ▪ Reproductive Toxicity ▪ Respiratory Sensitizer ▪ Target Organ Toxicity ▪ Aspiration Toxicity	▪ Flammables ▪ Pyrophorics ▪ Self-Heating ▪ Emits Flammable Gas ▪ Self-Reactives ▪ Organic Peroxides	▪ Irritant (skin and eye) ▪ Skin Sensitizer ▪ Acute Toxicity ▪ Narcotic Effects ▪ Respiratory Tract Irritant ▪ Hazardous to Ozone Layer (Non-Mandatory) ▪ Low degree health hazard
Gas Cylinder	**Corrosion**	**Exploding Bomb**
▪ Gases Under Pressure	▪ Skin Corrosion/Burns ▪ Eye Damage ▪ Corrosive to Metals	▪ Explosives ▪ Self-Reactives ▪ Organic Peroxides
Flame Over Circle	**Environment (Non-Mandatory)**	**Skull and Crossbones**
▪ Oxidizers	▪ Aquatic Toxicity ▪ OSHA Does Not Enforce This One	▪ Acute Toxicity (fatal or toxic)

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Workplace Labels
(Transfer containers)

- The employer shall ensure that each container is labeled with either
  - Product identifier
  - Signal word
  - Hazard statement(s)
  - Pictogram

    Or
  - Product identifier and
  - Adequate information about the hazards
  - Employers must comply by June 1, 2016

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Transfer Container Labeling Exemption Continues

- Portable containers
  - Identity and hazard information (or product identifier, signal word, hazard statement, signal word, pictogram) must be transferred unless the portable container is:
    - Under the control at all times of the employee making the transfer from the labeled container <u>and</u>
    - Contents used up in one shift

Employers must comply by June 1, 2016

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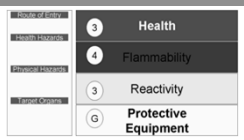
Alternative Labeling



- Permitted when employer's overall program proven effective
- Must ensure employees fully aware of hazards/use and understanding of labeling system
- Employer bears burden of establishing that employee awareness equals or exceeds conventional labeling system

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Workplace Labeling

- Can HMIS or NFPA system be used?
- While, the hazard category does not appear on the label, consider

GHS Category	GHS Hazard	HMIS/NFPA Category	HMIS/NFPA Hazard
1	highest	1	slight
2	high	2	moderate
3	medium	3	serious
4	low →	4	severe

NFPA categories were intended for emergency response, not workplace hazards; only considers acute effects, does not consider chronic effects

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Labeling Effective Dates

- Chemical manufacturers, importers, and employers
  - Will not ship containers without GHS labeling/SDS by June 1, 2015
- Employers
  - By June 1, 2016
    - Update alternative workplace labeling and hazard communication program as necessary, and provide additional employee training for newly identified physical or health hazards.

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SAFETY DATA SHEETS (SDS)

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Safety Data Sheet Info

- In English
- New 16-section format
- Compliance date for chemical manufactures, imports and distributors —June 1, 2015
- **Example pH 7 below**

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Safety Data Sheet Sections

- Section 1 Identification
- Section 2 Hazard(s) identification
- Section 3 Composition/information on ingredients
- Section 4 First-aid measures
- Section 5 Fire-fighting measures
- Section 6 Accidental release measures
- Section 7 Handling and storage
- Section 8 Exposure controls/personal protection
- Section 9 Physical and chemical properties
- Section 10 Stability and reactivity
- Section 11 Toxicological information
- Section 12 Ecological information
- Section 13 Disposal considerations
- Section 14 Transport information
- Section 15 Regulatory information
- Section 16 Other information, including date of preparation or last revision

Information in these sections will not be enforced by OSHA

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Section 1

Section 1 – Chemical Product and Company Identification

Catalog Numbers: 40475
Product Identity: Buffer Soln. pH 7.00

Manufacturer's Name: AquaPhoenix Scientific, Inc., 9 Barnhart Dr., Hanover, PA 17331
Emergency Contact Number (24hr): InfoTrac (800) 535-5053

Identification Of The Substrate Or Mixture And Of The Supplier

- GHS product identifier
- Other means of identification
- Recommended use of the chemical and restrictions on use
- Supplier's details
  - Name, address, phone #
- Emergency phone number

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Section 2

Section 2 – Composition, Information on Ingredients

Sodium Phosphate, Dibasic, CAS# 7558-79-4, <3% w/v, ACGIH TLV: NA, OSHA PEL: NA
Potassium Phosphate, Monobasic, CAS# 7778-77-0, <2% w/v, ACGIH TLV: NA, OSHA PEL: NA
Water, purified, CAS# 7732-18-5, >95% w/v, ACGIH TLV: NA, OSHA PEL: NA

Hazards Identification

- GHS classification of the substance/mixture and any national or regional information
- GHS Label elements, including precautionary statements
  - Hazard symbols may be provided as a graphical reproduction of the symbols in black and white or the name of the symbol,
    - e.g. flame, skull and crossbones
- Other hazards which do not result in classification or are not covered by the GHS

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Section 3

Section 3 – Hazard Identification

Emergency Overview: Non-flammable, non-corrosive, non-toxic. Does not present significant health hazards. Wash areas of contact with water.
Target Organs: Eyes, skin.

Potential Health Effects
Eyes: May cause slight irritation.
Skin: May cause slight irritation.
Ingestion: Large doses may cause upset stomach
Inhalation: Not likely to be a hazard
Chronic Effect / Carcinogenicity: None (IARC, NTP, OSHA)

Composition/Information Ingredients

- Substance
  - Chemical identity
  - Common name, synonyms, etc.
  - CAS number, EC number, etc.
  - Impurities and stabilizing additives which are themselves classified and which contribute to the classification of the substance
- Mixture
  - The chemical identity and concentration or concentration ranges of all ingredients which are hazardous within the meaning of the GHS and are present above their cutoff levels

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Section 4

Section 4 – First Aid

Eyes: Immediately flush eyes with water for at least 15 minutes. Immediately get medical assistance.
Skin: Flush with water for 15 minutes. Get medical assistance if irritation develops.
Ingestion: Dilute with water or milk. Get medical assistance.
Inhalation: Remove to fresh air. Give artificial respiration if necessary. If breathing is difficult, give oxygen.

First Aid Measures

- Description of necessary measures, subdivided according to the different routes of exposure
  - i.e. inhalation, skin and eye contact, and ingestion
- Most important symptoms/effects, acute and delayed
- Indication of immediate medical attention and special treatment needed, if necessary

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Section 5

Section 5 – Fire Fighting Measures

Flash Point: NA
Extinguishing Media: Use means suitable to extinguishing surrounding fire.
Fire & Explosion Hazards: Not considered to be a fire or explosion hazard.
Fire Fighting Instructions / Equipment: Use normal procedures. Poisonous gases may be produced in fire. Use protective clothing. Use NIOSH-approved breathing equipment.
NFPA Rating: (estimated) Health: 1; Flammable: 0; Reactivity: 0

Firefighting Measures

- Suitable (and unsuitable) extinguishing media
- Specific hazards arising from the chemical
  - e.g. nature of any hazardous combustion products
- Special protective equipment and precautions for firefighters

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Section 6

Section 6 – Accidental Release Measures

Absorb with suitable material. Always obey local regulations.

Accidental Release Measures

- Personal precautions, protective equipment and emergency procedures
- Environmental precautions
- Methods and materials for containment and cleaning up

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Section 7

Section 7 – Handling and Storage

Handling: Wash hands after handling. Avoid contact with skin and eyes.
Storage: Protect from freezing and physical damage.

Handling and Storage

- Precautions for safe handling
- Conditions for safe storage, including any incompatibilities

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Section 8

Section 8 – Exposure Controls, Personal Protection

Engineering Controls: Normal ventilation is adequate.

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Respiratory Controls: Normal ventilation is adequate.
Skin Protection: Chemical resistant gloves.
Eye Protection: Safety Glasses or goggles.

Exposure Controls/Personal Protection

- Control parameters
  - e.g. occupational exposure limit values or biological limit values
- Appropriate engineering controls
- Individual protection measures, such as PPE

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Section 9

Section 9 – Physical and Chemical Properties

Appearance: Clear, yellow liquid
pH: 5.8-8
Boiling Point: Approx 100C
Melting Point: Approx 0 C
Odor: Odorless
Solubility in Water: Infinite
Specific Gravity: Approx 1
Vapor Pressure: NA

Physical and Chemical Properties

- Appearance
- Odor
- Odor threshold
- pH
- Melting point/freezing point
- Initial boiling point and boiling range
- Flash point
- Flammability
- Upper/lower flammability or explosive limits
- Vapor pressure
- Vapor density
- Relative density
- Solubility(ies)
- Partition coefficient
- Autoignition temperature
- Decomposition temperature

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TN Department of Environment and Conservation

Section 10

Section 10 – Stability and Reactivity

Chemical Stability: Stable under normal conditions of use and storage.
Incompatibility: None Identified.
Hazardous Decomposition Products: Oxides of Phosphorus
Hazardous Polymerization: Does not occur

Stability and Reactivity

- Chemical stability
- Possibility of hazardous reactions
- Conditions to avoid
  - e.g. static discharge, shock or vibration
- Incompatible materials
- Hazardous decomposition products

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TN Department of Environment and Conservation

Section 11

Section 11 – Toxicological Information

LD50 orl-rat: 17 g/kg (Sodium Phosphate, Dibasic)
LC50 inhalation-rat: >4640 mg/kg (Potassium Phosphate, Monobasic)

Toxicological Information

- Concise but complete comprehensible description of the various toxicological (health) effects and the available data used to identify those effects
- Includes:
  - Information on the like routes of exposure
  - Symptoms related to the physical, chemical and toxicological characteristics
  - Delayed and immediate effects and also chronic effects from short and long term exposures
  - Numerical measures of toxicity

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TN Department of Environment and Conservation

Information in this section will not be enforced by OSHA

Section 12

Section 12 – Ecological Information

Ecotoxicity: NA

Ecological Information

- Eco-toxicity
- Persistence and degradability
- Bio-accumulative potential
- Mobility in soil
- Other adverse effects

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TN Department of Environment and Conservation

Information in this section will not be enforced by OSHA

Section 13

Section 13 – Disposal Considerations

Dilute with water.

All chemical waster generators must determine whether a discarded chemical is classified as hazardous waste.

Comply with all local, state, and federal regulations.

Disposal Considerations

- Description of waste residues and information on their safe handling and methods of disposal
  - Including the disposal of any contaminated packaging

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TN Department of Environment and Conservation

Information in this section will not be enforced by OSHA

Section 14

Section 14 – Transport Information

DOT - Not Regulated

Transport Information

- UN number
- UN proper shipping name
- Transport hazard class(es)
- Packing group, if applicable
- Marine pollutant (yes/no)
- Special precautions which a user needs to be aware of or needs to comply with in connection with transport or conveyance either within or outside their premises

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TN Department of Environment and Conservation

Information in this section will not be enforced by OSHA

Section 15

Regulatory Information

- Safety, health and environmental regulations specific for the product in question

Section 15 – Regulatory Information (not meant to be all inclusive)

OSHA Status: These chemicals are not considered hazardous by OSHA.
TSCA: The components of this solution are listed on the TSCA Inventory
SARA Title III Section 313: Not Applicable
RCRA Status: NA
CERCLA Reportable Quantity: Sodium Phosphate, Dibasic – 5,000 lbs.
WHMIS: NA

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TN Department of Environment and Conservation

Section 16

Other Information Including Information on Preparation and Revision of the SDS

Section 16 – Additional Information

Issue Date: 12/28/06
Revision Date: 6/5/08, 11/19/09

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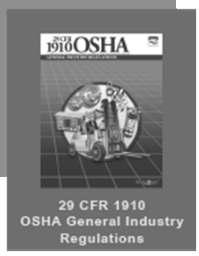

EFFECTS ON OTHER STANDARDS

TN Department of Environment and Conservation 61

TN Department of Environment and Conservation

Flammable Liquids

GHS FL Category	Flashpoint Deg F	Boiling Point Deg F	Old OSHA Class	Flashpoint Deg F	Boiling Point Deg F
1	**<73.4**	**≤95**	1A	<73	<100
2	**<73.4**	**<95**	1B	<73	≥100
3	**≥73.4 and ≤140**		1C II	≥73 and <100 ≥100 and <140	
4	**>140 and ≤199.4**		IIIA	≥140 and <200	
None			IIIB	>200	

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TN Department of Environment and Conservation

WHAT-TO-DO BOOKLET

A Template for Compliance With

(29 CFR 1910.1200 and 29 CFR 1926.59)

Hazard Communication Standard

And

(0800-1-1-.09)

The Tennessee Hazardous Chemical Right-To-Know Law

GHS

GHS

Revised November, 2012

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TN Department of Environment and Conservation

Resources

Centers for Disease Control and Prevention
CDC 24/7: Saving Lives, Protecting People™

- CDC works 24/7 to protect America from health, safety and security threats, both foreign and in the U.S. Whether diseases start at home or abroad, are chronic or acute, curable or preventable, human error or deliberate attack, CDC fights disease and supports communities and citizens to do the same. **www.cdc.gov**

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Resources

- **OSHA (www.osha.gov)**
-
  - "No one should have to sacrifice their life for their livelihood, because a nation built on the dignity of work must provide safe working conditions for its people."
    -Secretary of Labor Thomas E. Perez
  - Under federal law, you are entitled to a safe workplace. Your employer must provide a workplace free of known health and safety hazards. If you have concerns, you have the right to speak up about them **without fear of retaliation**. You also have the right to:

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TN Department of Environment and Conservation

Resources

- **OSHA (www.osha.gov)**
  - Be trained in a language you understand
  - Work on machines that are safe
  - Be provided required safety gear, such as gloves or a harness and lifeline for falls
  - Be protected from toxic chemicals
  - Request an OSHA inspection, and speak to the inspector
  - Report an injury or illness, and get copies of your medical records
  - See copies of the workplace injury and illness log
  - Review records of work-related injuries and illnesses
  - Get copies of test results done to find hazards in the workplace

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TN Department of Environment and Conservation

Resources

- **TOSHA**
  - Tennessee OSHA improves occupational safety and health through enforcement of the general industry, construction and agricultural occupational safety and health standards in workplaces. - See more at: https://www.tn.gov/workforce/section/tosha

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TN Department of Environment and Conservation

Resources

- **TOSHA**
  - TOSHA's mission is to assure the safety and health of Tennessee's working men and women
  - by promulgating and enforcing standards and regulations; providing training, outreach, and education;
  - establishing cooperative programs; and encouraging continual improvement in workplace safety and health
  - as well as the development of comprehensive safety and health management systems. Effective and
  - efficient use of resources requires careful, flexible planning. In this way, the overall goal of hazard
  - abatement and employee protection is best served.

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TN Department of Environment and Conservation

Resources

- **OSHA www.osha.gov**
- **CDC www.cdc.gov**
- **TOSHA https://www.tn.gov/workforce/article/standards-and-rules**
  - **Memphis Office 901-543-7259**
  - **Jackson Office 731-423-5641**
  - **Nashville Office 615-741-2793**
    1-800-249-8510
  - **Knoxville Office 865-594-6180**
  - **Kingsport Office 423-224-2042**
  - **Chattanooga 423-634-6424**

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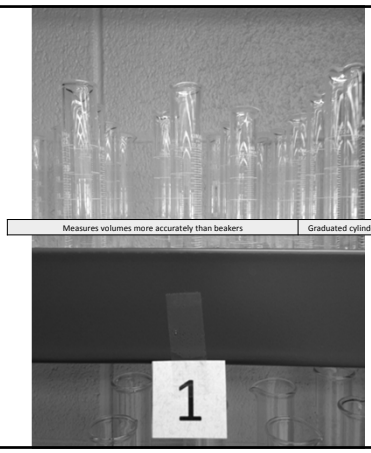
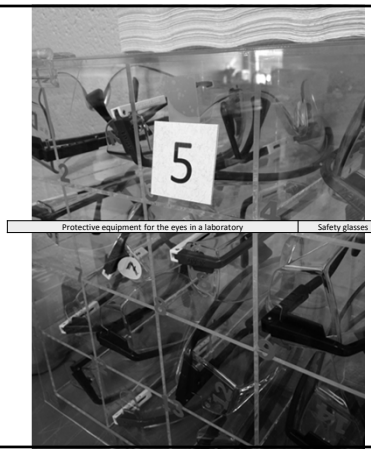
Lab Exercise
Fleming Training Center
1-25-16


Measures volumes more accurately than beakers
Graduated cylinder
1

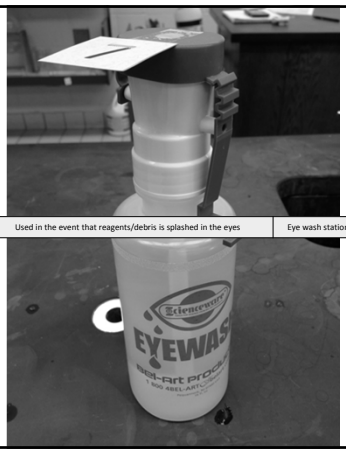
Used mainly for mixing chemicals and to measure approximate volumes
Beaker
2

Used in the event of a laboratory spill on person's body
Safety shower

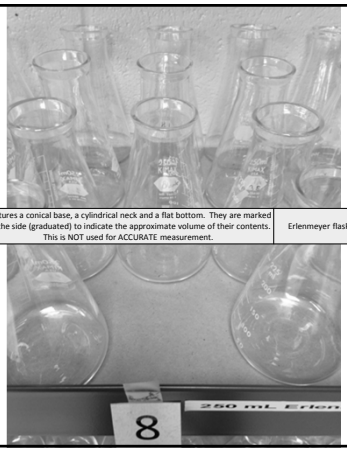
FIRE
4
Location of equipment used to extinguish a fire
Fire extinguisher


5
Protective equipment for the eyes in a laboratory
Safety glasses

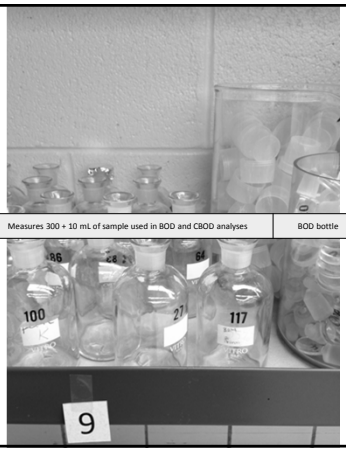
Protective equipment for hands	gloves



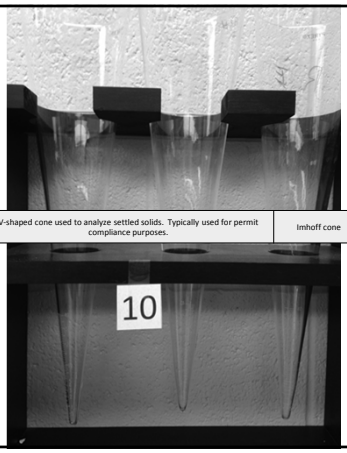
Used in the event that reagents/debris is splashed in the eyes	Eye wash station



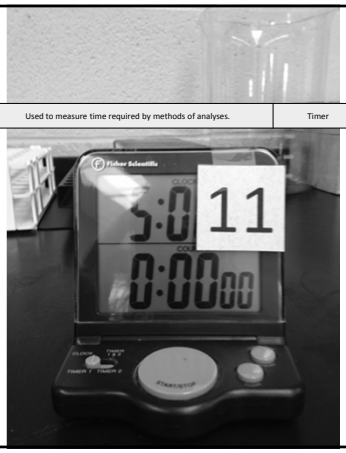
Features a conical base, a cylindrical neck and a flat bottom. They are marked on the side (graduated) to indicate the approximate volume of their contents. This is NOT used for ACCURATE measurement.	Erlenmeyer flask



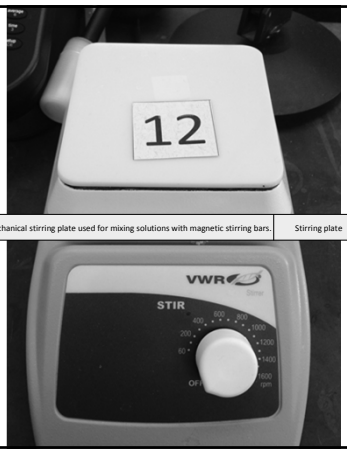
Measures 300 + 10 mL of sample used in BOD and CBOD analyses	BOD bottle



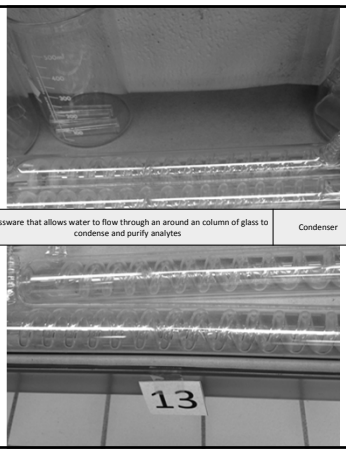
V-shaped cone used to analyze settled solids. Typically used for permit compliance purposes.	Imhoff cone



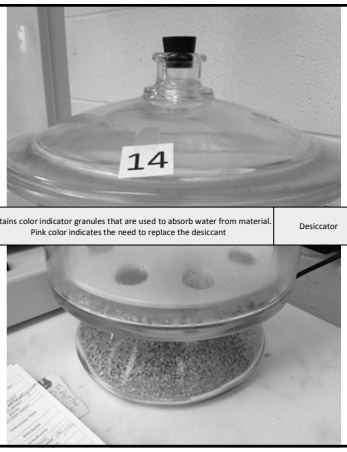
Used to measure time required by methods of analyses.	Timer



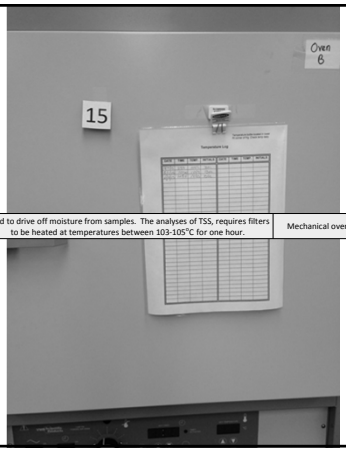
Mechanical stirring plate used for mixing solutions with magnetic stirring bars. | Stirring plate



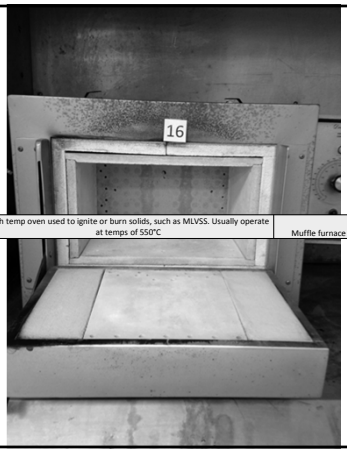
Glassware that allows water to flow through an around an column of glass to condense and purify analytes | Condenser



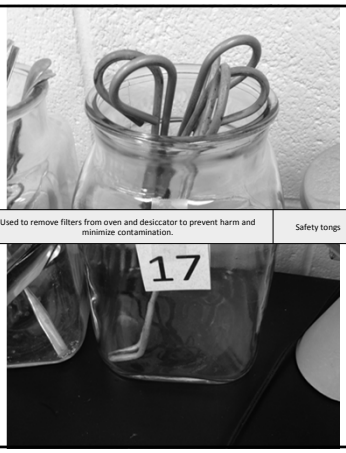
Contains color indicator granules that are used to absorb water from material. Pink color indicates the need to replace the desiccant | Desiccator



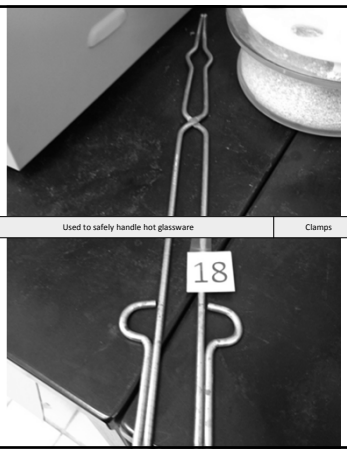
Used to drive off moisture from samples. The analyses of TSS, requires filters to be heated at temperatures between 103-105°C for one hour. | Mechanical oven



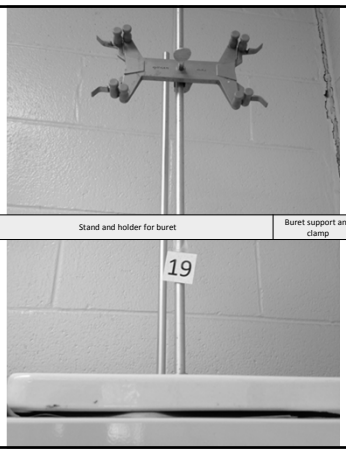
High temp oven used to ignite or burn solids, such as MLVSS. Usually operate at temps of 550°C | Muffle furnace



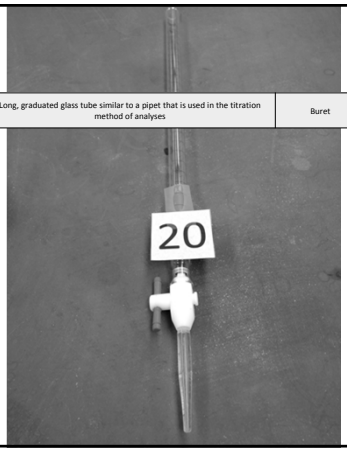
Used to remove filters from oven and desiccator to prevent harm and minimize contamination. | Safety tongs



Used to safely handle hot glassware	Clamps

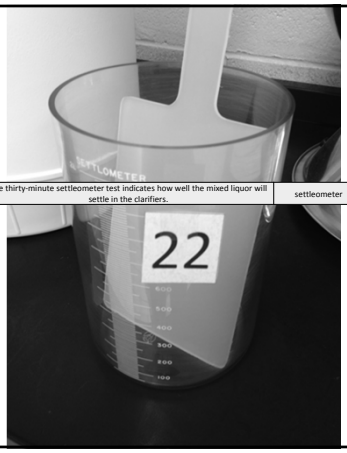


Stand and holder for buret	Buret support and clamp

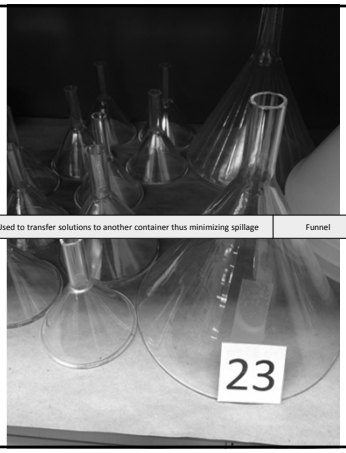


Long, graduated glass tube similar to a pipet that is used in the titration method of analyses	Buret

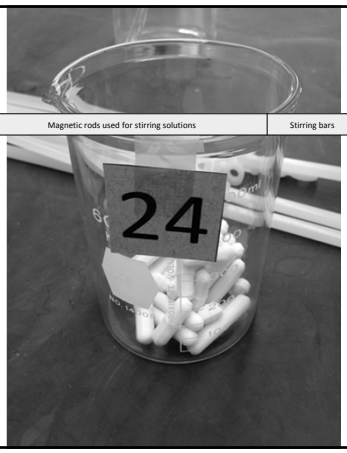
beads used to minimize the solution boiling up during distillation	Glass beads



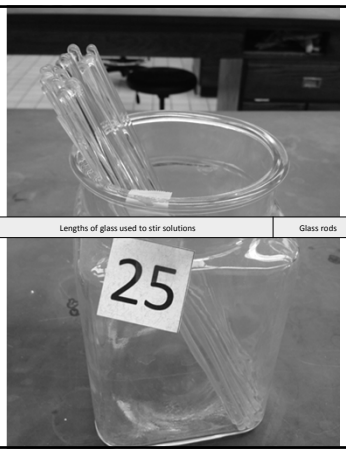
The thirty-minute settleometer test indicates how well the mixed liquor will settle in the clarifiers.	settleometer



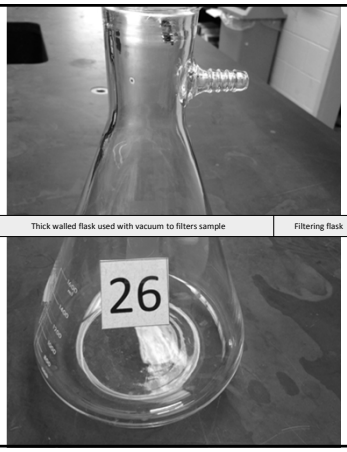
Used to transfer solutions to another container thus minimizing spillage	Funnel



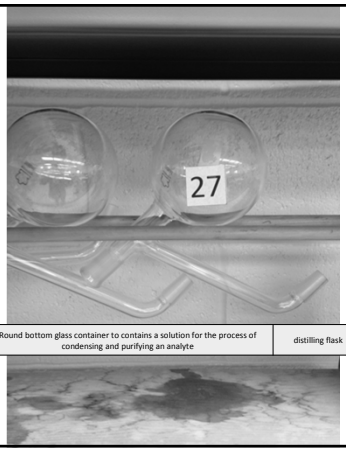
Magnetic rods used for stirring solutions	Stirring bars



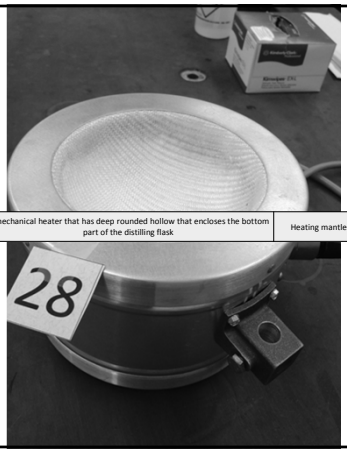
Lengths of glass used to stir solutions	Glass rods



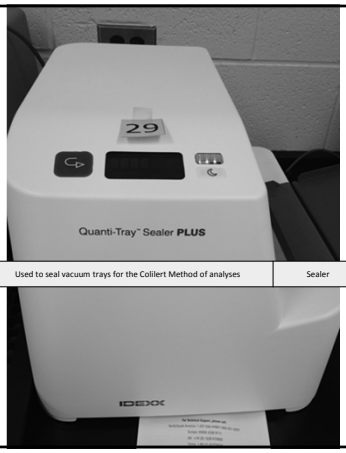
Thick walled flask used with vacuum to filters sample	Filtering flask



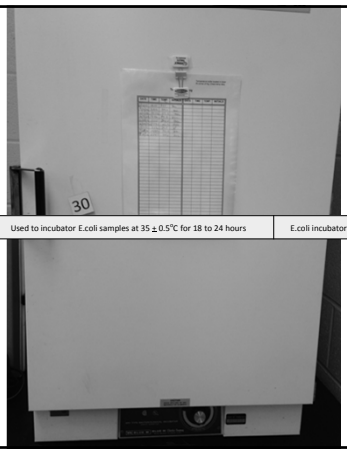
Round bottom glass container to contains a solution for the process of condensing and purifying an analyte	distilling flask



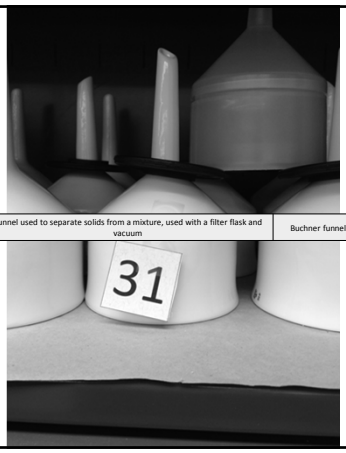
A mechanical heater that has deep rounded hollow that encloses the bottom part of the distilling flask	Heating mantle



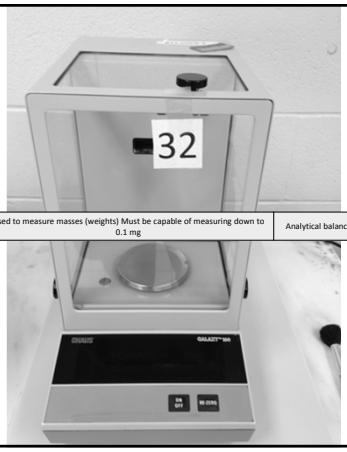
Used to seal vacuum trays for the Colilert Method of analyses	Sealer



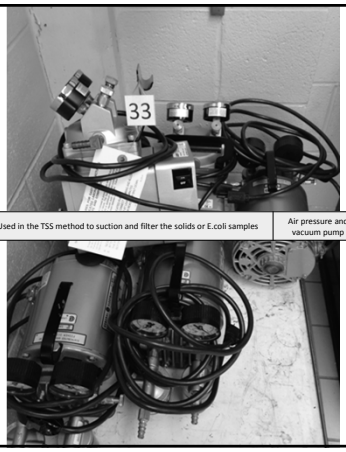
Used to incubator E.coli samples at 35 ± 0.5°C for 18 to 24 hours	E.coli incubator



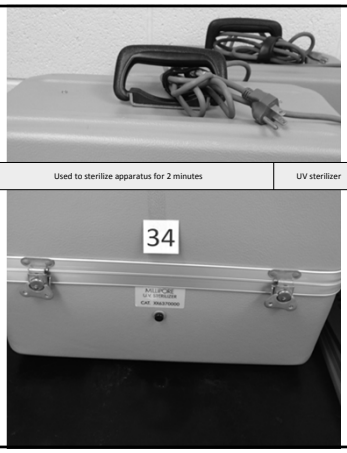
Funnel used to separate solids from a mixture, used with a filter flask and vacuum	Buchner funnel



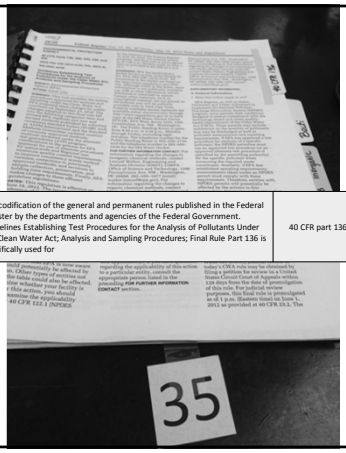
Used to measure masses (weights) Must be capable of measuring down to 0.1 mg	Analytical balance



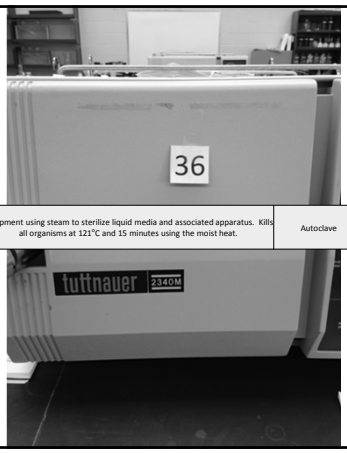
Used in the TSS method to suction and filter the solids or E.coli samples	Air pressure and vacuum pump



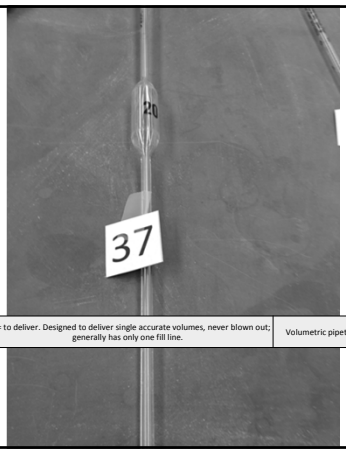
Used to sterilize apparatus for 2 minutes	UV sterilizer



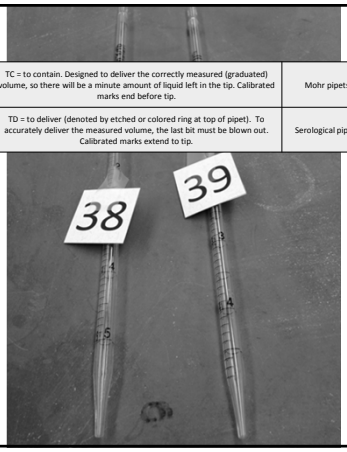
The codification of the general and permanent rules published in the Federal Register by the departments and agencies of the Federal Government. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; Final Rule Part 136 is specifically used for	40 CFR part 136



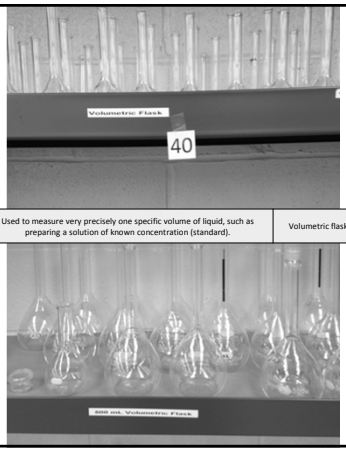
Equipment using steam to sterilize liquid media and associated apparatus. Kills all organisms at 121°C and 15 minutes using the moist heat.	Autoclave



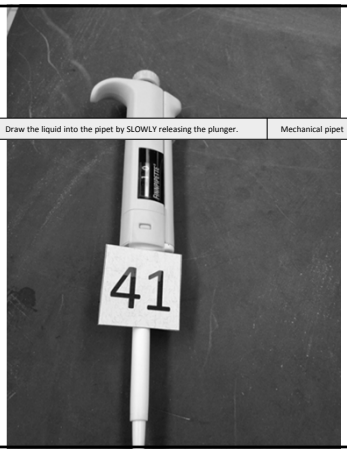
TD = to deliver. Designed to deliver single accurate volumes, never blown out; generally has only one fill line.	Volumetric pipets



38	TC = to contain. Designed to deliver the correctly measured (graduated) volume, so there will be a minute amount of liquid left in the tip. Calibrated marks end before tip.	Mohr pipets
39	TD = to deliver (denoted by etched or colored ring at top of pipet). To accurately deliver the measured volume, the last bit must be blown out. Calibrated marks extend to tip.	Serological pipets



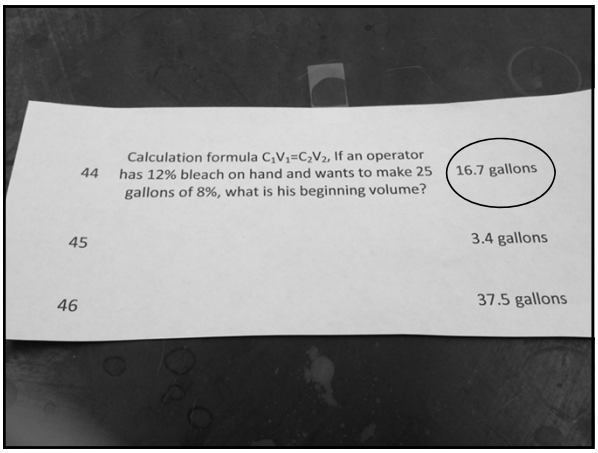
Used to measure very precisely one specific volume of liquid, such as preparing a solution of known concentration (standard).	Volumetric flask

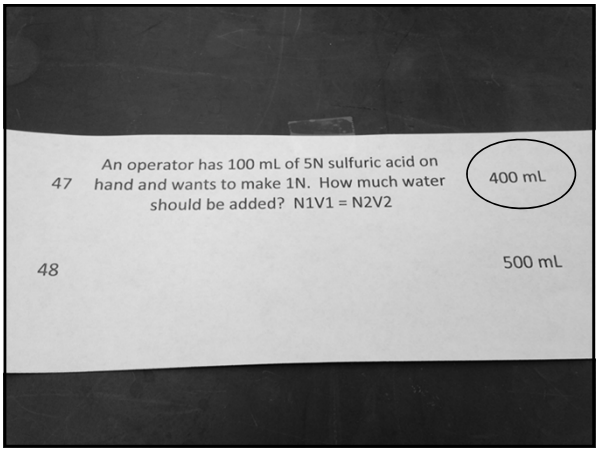


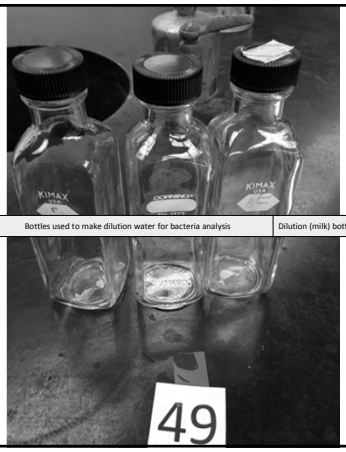
Draw the liquid into the pipet by SLOWLY releasing the plunger.	Mechanical pipet

Used in analyzing dissolved oxygen in the field.	DO meter

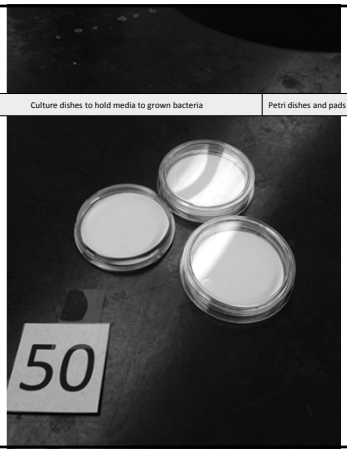
instrument which measures the amount of light of a specificed wavelength which passes through a medium. According to Beer's law, the amount of light absorbed by a medium is proportional to the concentration of the absorbing material or solute present.	Spectrophotometer



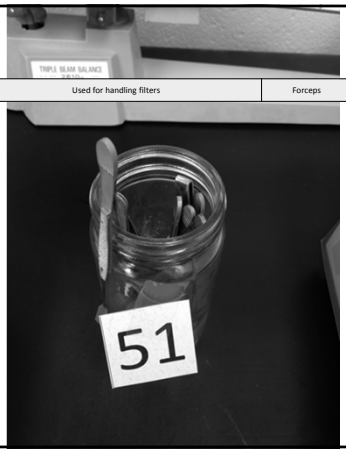




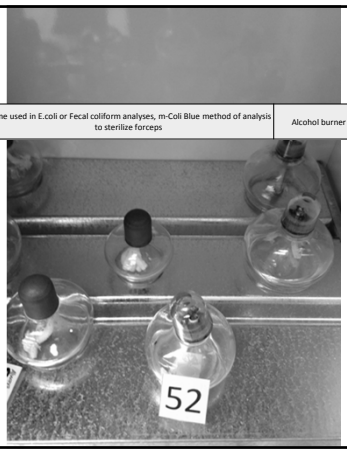
Bottles used to make dilution water for bacteria analysis	Dilution (milk) bottles



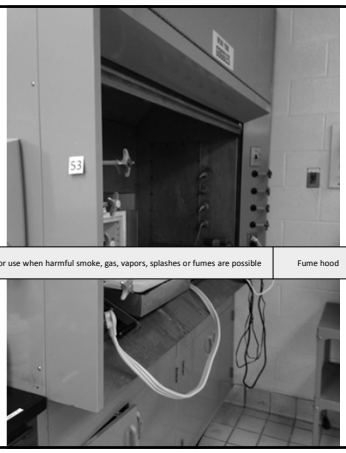
Culture dishes to hold media to grown bacteria	Petri dishes and pads



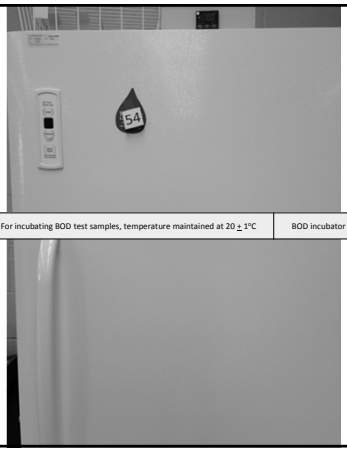
Used for handling filters	Forceps



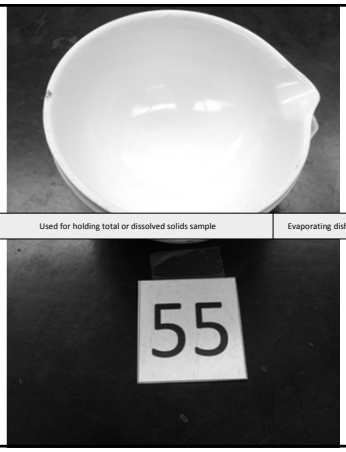
Flame used in E.coli or Fecal coliform analyses, m-Coli Blue method of analysis to sterilize forceps	Alcohol burner



For use when harmful smoke, gas, vapors, splashes or fumes are possible	Fume hood

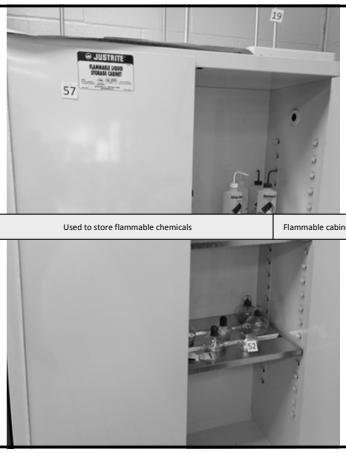


For incubating BOD test samples, temperature maintained at 20 ± 1ºC	BOD incubator



Used for holding total or dissolved solids sample	Evaporating dish

Used to store chemicals, acid and bases stored separately	Chemical storage cabinet



Used to store flammable chemicals	Flammable cabinet

HACH
2100N Turbidimeter
NTU
EBC
NEPH
Manual Range
Auto Range
CAL?
CALIBRATE
EDIT
ENTER
RANGE
UNITS
SIGNAL AVG
RATIO
PRINT
58

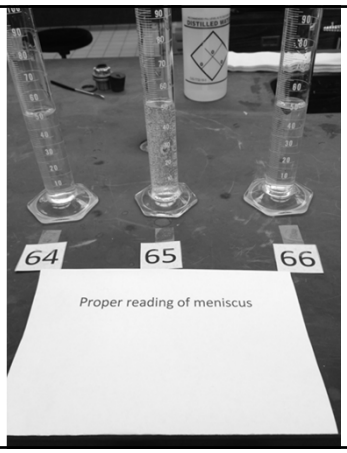
59

0.01 g
On
Menu
Re-Zero
60

61

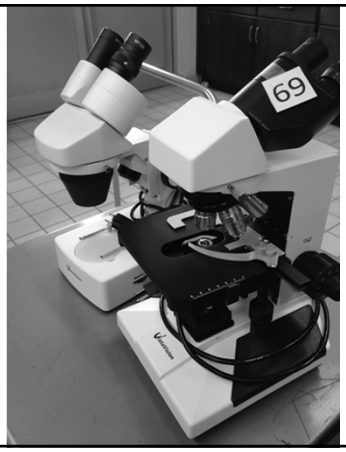
62

Fisher Scientific
63


64
65
66
Proper reading of meniscus

HACH
67

HACH
DRB 200
68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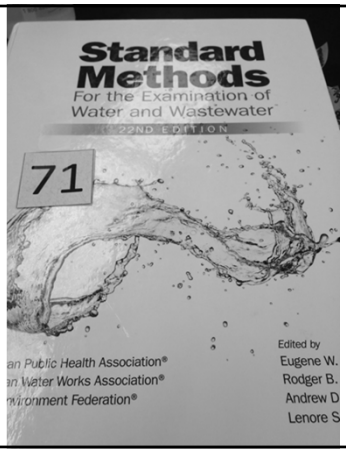
70
IDEXX


Standard Methods
For the Examination of Water and Wastewater
22ND EDITION
71
Edited by

72

pH-indicator strips non bleeding
colorpHast®
pH 0 - 14
EMD
Dip in - read while still moist.
73

74
SIEMENS
SIEMENS

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Laboratory Equipment

Identification, Handling, Cleaning and Safety

TENNESSEE DEPARTMENT OF ENVIRONMENT AND CONSERVATION

TDEC - Fleming Training Center 1

Objectives

- Identify equipment commonly used in water treatment and wastewater laboratory
- Discuss accuracy and use of glassware
- Discuss how to maintain analytical equipment

TDEC - Fleming Training Center 2

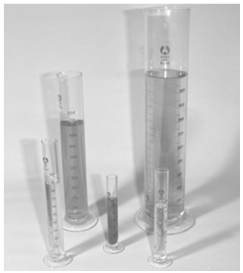
Beakers

- Used for:
  - Mixing
  - Measuring approximate volumes
  - ~10% accuracy

TDEC - Fleming Training Center 3

Graduated Cylinders

- Accurate to ~1%
- Measures liquid volumes more accurately than beakers, but still not the most accurate
- Measure quicker



TDEC - Fleming Training Center 4

Volumetric Flasks

- Most accurate way to measure volume
- Disadvantage:
  - Only can measure one volume
  - Not used for storing or heating solutions

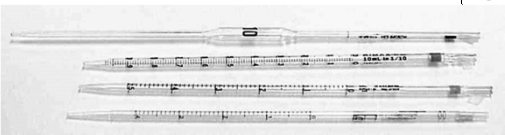
TDEC - Fleming Training Center 5

What Are Pipets?

- Pipets are glass or plastic tubes, usually open at both ends,which are used to transfer specific amounts of liquid from one container to another.
- They are usually used for volumes between 1 and 100 milliliters.

TDEC - Fleming Training Center 6

Types of Pipets



- Volumetric
- Measuring
  - Mohr
  - Serological

Volumetric Pipets

- Used to deliver a single specific volume of liquid, usually between 1 and 100 ml.
- Shaped like rolling pins with a large belly, one blunt end, the neck, and one tapering end, the tip.

Volumetric Pipets

- Used for accurate measurements, since it is designed to deliver only one volume and is calibrated at that volume.
- Should be used when accuracy and reproducibility are crucial, because these can achieve accuracy to four significant figures.

Specifications on a Volumetric Pipet

- When emptying a volumetric pipet, the liquid is allowed to drain out
  - It is NOT forced out.
- After it is emptied, the small amount of liquid which remains in the tip should not be blown out.
- Volumetric pipets are NOT blow-out pipets

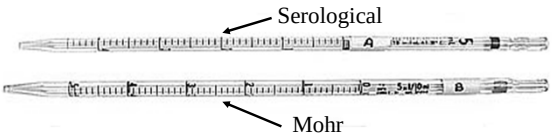
Measuring Pipets

- They are straight glass or plastic tubes with one tapering end.
- Calibrated into small divisions so that various amounts of liquid can be measured with the same pipet.
- Usually used to measure any amount between 0.1ml and 25.0ml.
- They are not as accurate due to the fact that any imperfection in their internal diameter will have a greater effect on the volume delivered.

Mohr and Serological Pipets

- Measuring pipets are divided into:
  - Mohr Pipets
    - Graduations on these always end before the tip
  - Serological Pipets
    - Graduation marks continue to the tip

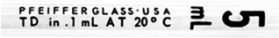
Examine pipets A and B.
Which is the serological and which is the Mohr?



Specifications on a Measuring Pipet

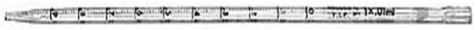
- Maximum volume of liquid that can be transferred
- Size of the divisions on the pipet
- Temperature at which calibrations were made
- If the pipet is a “to deliver”(TD) or “to contain”(TC) pipet.

5 in 1/10 ml
TD 20oC



- Specifications on a pipet as shown above indicate that the pipet is calibrated in 1/10ml divisions and will deliver up to 5.0 ml within published tolerance levels at 20°C.

1 ml in1/100
TD 20oC



- These specifications indicate that the pipet is calibrated in 1/100 ml divisions and it will deliver up to 1.00 ml within published tolerance levels at 20°C.

Handling and Disposing of Pipets

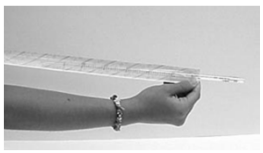
- Chipped and cracked pipets should be replaced as they are unsafe and may affect the accuracy of measurements.
- NEVER mouth pipet.
- Hold the pipet by the upper third of the tube and keep the tip from touching anything.

Handling and Disposing of Pipets

- Dispose dirty pipets by placing in soapy water solution in a tray or pipet washer.
- Place disposable pipets in a cardboard holder.
- Do not leave pipets on counters or sinks.

Handling Sterile Pipets

- When using sterile pipets, be sure to use proper sanitary techniques.
- If you have a sterile package of disposable pipets, tear only a small corner of the package open and push one pipet out of this opening, then immediately close the package to prevent contamination.



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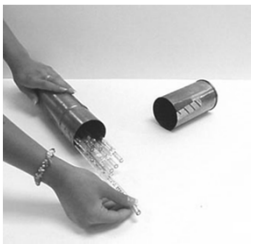
Handling Sterile Pipets

- If you are using sterile pipets in a pipet canister, place the canister on its side, slide off the cover, pull out one pipet and replace the cover immediately.



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Transferring a Precise Volume of Liquid

- A pipet bulb is used to draw liquid up into the pipet.
- There are many types of pipet bulbs.

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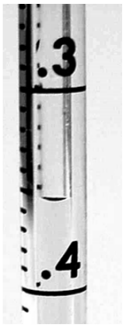
Transferring a Precise Volume of Liquid

- You should observe the meniscus at eye-level
- Touch the tip of the pipet to the inside of the container when the meniscus is at the desired level



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Transferring a Precise Volume of Liquid

- Squeeze bulb and touch it to the mouth of the pipet.
- Place other end of the pipet in liquid to be transferred and slowly release pressure on bulb.
- Draw liquid up past desired level, quickly replacing bulb with index finger.

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Transferring a Precise Volume of Liquid

- Let liquid drain until bottom of meniscus lines up with desired level on pipet.
- Touch tip of pipet to inside of beaker to remove any adhering drops.
- Transfer liquid to second beaker and touch tip to inside of beaker and let liquid drain out of pipet.

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Other Pipet Bulbs

- Other pipet bulbs that are often used include the Vadosa pipet filler, seen on the left, and the pipet Pumper, on the right.

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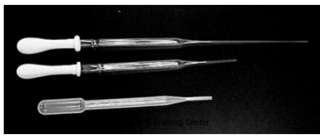
Other Pipet Types

- Transfer of uncalibrated volumes up to 2.5 ml can be accomplished using glass “transfer” or “Pasteur” pipets shown below. These may be sterilized before use.
- Roughly calibrated volumes of 1 and 2 ml can be transferred with the one piece plastic transfer pipets which may be purchased as sterile or non-sterile units.



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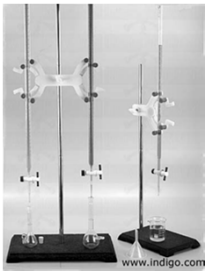
Burettes and Titrations



- Burettes
  - Used for titrations
  - Treat like a Mohr pipet, do not let liquid completely drain out
  - Also, make sure to remove air bubble in tip before titrating

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Flasks

- Distilling Flask

- Florence (Flat Bottom) Flask

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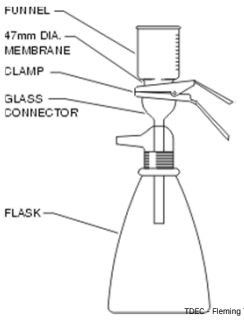
Flasks

- Erlenmeyer Flasks

- Filter Flask

TDEC - Fleming Training Center 29

Filter Apparatus



- Vacuum Pump

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Bottles

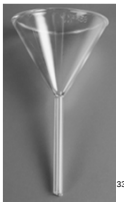
- Dilution Bottle
- Sample Bottles

Bottles

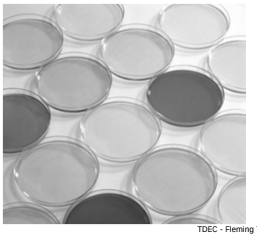
- Reagent Bottle
- Weighing Bottles

Funnels

- Separatory
- Buchner
- General



- Petri Dish
  - Culturing container
- Desiccators
  - Dust and moisture free



- Evaporating Dish
- Crucible

Centrifuge

- Used to separate materials of different density

Autoclave

- Pressure cooker used to sterilize glassware, bottles, membrane filter equip, culture media and contaminated material to be discarded.
- Standard temperature is set at121°C and 15 PSI

TDEC - Fleming Training Center 37

Refrigerators

Explosion proof

Walk-in cooler

- Sample storage should maintain between 1-5 °C
- Never store samples and chemicals together

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Incubators

- Artificially heated container used for growing bacteria cultures
- Dry-Heat types hold temperatures to ± 0.5°C
- For E. coli and Total coliform = 35 ± 0.5°C
- Water Bath for fecals = 44.5 ± 0.2°C

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Incubators

- For BOD incubation at 20 ± 1 °C
- Do not store chemical solutions and samples in same refrigerator

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UV Sterilizer

- Use in Bac'T Lab to sterilize test equipment

TDEC - Fleming Training Center 41

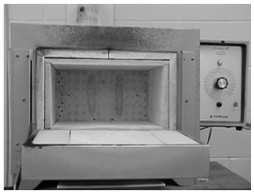
Drying Oven

Used more often in wastewater labs

For solids testing set oven at 103-105°C

TDEC - Fleming Training Center 42

Muffle Furnace



- High temp oven used to ignite or burn solids.
- Usually operate at temps of 550°C.
- More often used in Wastewater lab work.

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Fume Hood

- Can prevent serious accidents
- Use whenever heat is used in a test procedure
- Fumes vented out of lab
- Use when harmful smoke, gas, vapors, splashes or fumes are possible

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Water Still

- Produces distilled water for lab tests and rinsing washed glassware
- Removes dissolved minerals, organic and inorganic nonvolatile compounds
- Does not sterilize

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Heating and Stirring Samples

- Combo Heat/Stir Plate
  - Can be used to stir or heat and stir samples
  - Safer than heating with an open flame
- Gas Burner
  - Uses natural gas

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Balances

- Top Loading
  - Weighs to the nearest 0.01 g
- Analytical
  - Precise to 0.0001 g

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pH Meter

- Use buffer solutions to calibrate
- Store electrodes properly
- Calibrate daily
- Maintain records on daily calibrations

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Spectrophotometer

- HACH DR 4000
  - Factory pre-set programs for lab chemical analysis
- Very versatile

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Colorimeters

- Determine the concentration of many chemicals
- Most commonly used is chlorine type colorimeter
- Portable and battery powered

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Amperometric Titrator

- Chlorine analysis
- Accurate and unaffected by sample color or turbidity
- Takes greater skill to use than DPD method with colorimetric devices

TDEC - Fleming Training Center 51

Turbidimeter

- Desk top and continuous on-line monitoring
- Position away from direct sunlight and have extra light bulb on hand
- Ensure sample bottles maintained; no scratches; acid clean if necessary

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Chemical Storage

- Do not store volatile chemicals together
- Have separate storage cabinets for acids and bases/caustics

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Flammable Cabinet

- Flammable chemicals should be kept in a flammable cabinet.

TDEC - Fleming Training Center 54

Safety Equipment

PPE (Personal Protective Equipment):

Goggles

Gloves

Aprons

Wear safety clothing.

Eye Wash and Shower

Cleaning Glassware

- Just because it looks clean does not mean residues are not left behind
- Results need to be accurate to use data for process control and/or reporting to the State
- Detergents, such as Alconox, may be sufficient
  - Should be phosphate-free

- Residues of minerals and other substances can build up on glassware, causing erroneous test results

Steps for Washing

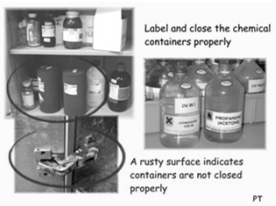
- Clean glassware using laboratory detergent (phosphate-free)
- Rinse with tap water
- Rinse at least three times with distilled water
- Let air dry

Steps for Acid-Washing

- Clean glassware using laboratory detergent (phosphate-free)
- Rinse with tap water
- Rinse with 1:1 hydrochloric acid or nitric acid
  - 1:1 means equal parts distilled water and acid
- Rinse well with distilled water
- Let air dry

Note: always use gloves and goggles when handling acids

Chemical Safety - Storage

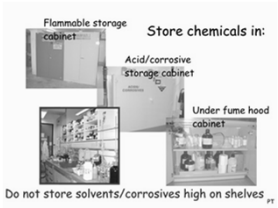


- Current chemical inventory available
- No expired chemicals.
  - Disposed of out-dated chemicals
- Chemical containers properly labeled, in good condition and closed properly
- Only compatible chemicals are stored together
  - Everything *not* stored in alphabetical order

TDEC - Fleming Training Center 61

Chemical Safety - Storage

- Secondary containment for stored chemicals as necessary.
  - Polyethylene trays for separate storage of acids and bases
- Chemicals stored at safe levels, in cabinets or on stable shelving (but not on high levels)



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Chemical Safety - Flammables

- Stored in flammable cabinet and/or explosion-proof or flammable storage refrigerator
- Stored away from sources of heat and ignition
- Not stored along path of egress or in aisle space

TDEC - Fleming Training Center 63

Autoclave Safety

- To prevent bottles from shattering during pressurization, the caps of containers with liquids must be loosened before loading
- Before removing autoclaved items, wait 5 minutes for loads containing only dry glassware, and 10 minutes for autoclaved liquid loads
- Remember: these are not used to steam your lunch!!

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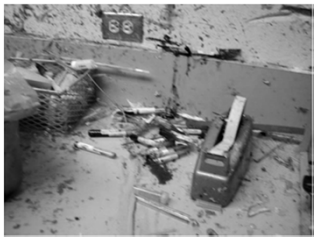
Autoclave Safety



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TDEC - Fleming Training Center 66

Lab Hygiene

- Food and drink are not to be stored or prepared in laboratories or chemical storerooms
- Use appropriate personal protective equipment and wash your hands regularly when working with chemical reagents, especially before meals or snacks.
- Smoking in laboratories is prohibited.

TDEC - Fleming Training Center 67

Lab Hygiene

- Loose sleeves are a hazard and should not be worn in the lab.
- If you have long hair, ensure that it is properly tied back.
- Wearing of contact lenses in the lab is strongly discouraged.
  - If it is unavoidable, advise your supervisor and co-workers so that this information is known in the event of a chemical splash in the eyes.

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Personal Practices

- No inappropriate clothing and shoes (shorts, sandals, slippers, etc.)
- Gloves removed before handling telephone, door handle or leaving laboratory
- No pipeting by mouth

TDEC - Fleming Training Center 69

Personal Practices

- Lab coats and safety glasses/ goggles worn by all where necessary
- Proper gloves are used as needed
- Other personal protective equipment used properly as needed

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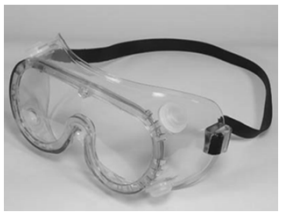
Safety Glasses

- Unbreakable lenses of plastic or tempered glass
- For light-to-moderate work
- Can be prescription glasses
- Do not interfere with contact lenses

TDEC - Fleming Training Center 71

Goggles

- Work with significant risk of splash of chemicals or projectiles
- Can be worn over prescription glasses



TDEC - Fleming Training Center 72

Face Shield

- Work with significant risk of splash on face or possible explosion
- Face shield protects face adequately but not eyes
  - Should be worn with safety glasses and/or goggles to protect eyes

TDEC - Fleming Training Center 73

Pregnancy

- Women who are pregnant should discuss their work assignments with their supervisors to seek alternate work assignments if the potential for exposure to teratogens exist
  - Teratogens are reproductive toxins that may cause damage to the fetus
  - THM Plus method by Hach for determining Trihalomethanes deals with chloroform, a teratogen

TDEC - Fleming Training Center 74

Fume Hood

- All work generating toxic/hazardous vapor, fume, or aerosol performed in hood
- Front sash at appropriate level when hood is in use/ not in use
- Storage within the hood minimized and containers kept sealed

TDEC - Fleming Training Center 75

Fume Hood

- Verify that the fume cupboard is working properly.
- Locate work at least 6 inches inside the hood.
- Do not block the face of the hood, e.g. with shielding or large equipment.
- Do not block the space between tapered metal front lip and the work surface.
- Do not block rear exhaust slot. Place bulky items to rear and sides.
- Secure papers and other light weight materials to prevent their entrainment in the exhaust.

TDEC - Fleming Training Center 76

Lab Work Area

- The work bench is to be kept clean at all times, and free from chemicals and apparatus which are not required.
- Before starting an experiment, make sure you are familiar with all the procedures and the potential hazards of the starting materials and products.
  - Determine the appropriate safeguards and remedies.
  - Know the procedures for emergency shut off as well as the person and phone numbers to contact in case of emergency.
  - If anything unexpected occurs during your experiment, or if you are in any doubt, consult your supervisor immediately.

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Handling Glassware

- Examine all glassware before use.
  - Discard any broken glass apparatus in the appropriate sharps container.
- Never store damaged glassware in cupboards.
  - Damaged glassware should either be sent for repair properly or disposed in a separate labeled container for sharps disposal.
- Use gloves when sweeping up broken glass, do not use bare hands.
  - Pick up fine glass particles with wet paper toweling.

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Handling Glassware

- Cut ends of glass rods and tubing should always be fire-polished before use.
- Use a cloth for protection when inserting glass tubing, rods or thermometers into bungs or tubing
  - Use a lubricant or water where necessary.

Chemical Spills

- Small spills (generally less than 100 mL) can usually be cleaned up safely by the employees involved.
- The hazardous properties of the material must be considered when deciding whether it is a “small” spill or not, and therefore whether unassisted clean-up should be attempted.
- Employees must be trained in advance to handle cleanup of even small spills

TENNESSEE DEPARTMENT OF ENVIRONMENT AND CONSERVATION

SAMPLING

TDEC - Fleming Training Center 1

Why Sample?

- Meet compliance requirements
- Process control
- Ensure public safety / protect the environment

TDEC - Fleming Training Center 2

Considerations

- The way the sample is collected
- The sample volume required
- The way the sample is stored
- The selection of sample points
- The sampling frequency

TDEC - Fleming Training Center 3

Grab Samples

- Single volume of water
- Representative of water quality at exact time and place of sampling
- Grab samples are used to test for unstable parameters that could change if the sample were allowed to stand for any length of time
  - DO
  - pH
  - Chlorine residual
  - Temperature
  - E. coli and / or fecal coliform

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Composite Sample

- Collected at regular intervals
- In proportion to existing flow
- Combined to form sample representative of entire flow for period

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Composite Sample

- Refrigerated; thoroughly mixed
- Measure flow and sample volume
- Examples:
  - BOD
  - Total N
  - Settleable solids

TDEC - Fleming Training Center 6

Sampling Guidelines

- Representative
- Proper container
- Do not contaminate the lid
- Preservative / dechlorinating agent

Sampling Guidelines

- Hold by base
- Turn into current
- Avoid air bubbles
- Label containers with sampler name; date and time; method; test to run; preservatives.

Sample Volume

- Depends on test procedure
- Headspace for mixing
- Preservative
- QA / QC comparisons

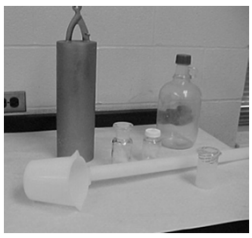
Sampling Point Selection

- Flow well mixed
- Exclude large particles (>1 / 4 inch)
- Exclude floating matter
- Readily accessible & in safe area

Sampling Devices

- Automatic:
  - Timesavers
  - Clean intake line regularly to prevent growth of bacteria

Sampling Devices



- Manual:
  - Dippers
  - Weighted bottle sampler
  - Whirl-pak® bags
  - Jugs

Sources of Error

- Improper sampling
- Poor or improper sample preservation
- Lack of sufficient mixing during compositing and testing

Preservation Techniques

- Refrigeration at 6°C
- pH<2:
  - Using HCl
  - Using H_2SO_4
  - Using HNO_3
- pH>9 using NaOH
- pH>12 using NaOH

Section 2
QA/QC & Method Update Rule

QA/QC

2014 Updates for 40CFR136

Method Update Rule
February 5, 2014
Fleming Training Center

TDEC - Fleming Training Center 1

NPDES Permit

- Section 1.2.3 Test Procedures
  - b. Unless otherwise noted in the permit, all pollutant parameters shall be determined according to methods prescribed in Title 40, Code of Federal Regulations, Part 136, as amended, promulgated pursuant to Section 304 (h) of the Act.
- Section 2.1.4 Proper O&M
  - a. ….proper O&M also includes …. appropriate quality assurance procedures.

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You Have Heard it All Before

- More Rules
- More Testing
- More Paperwork
- More Cost
- But everything we do is regulated.

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2012 Update of 136

- Standard Methods approved by date not Edition
- Section 136.7 Quality Assurance and Quality Control.

Federal Register May 18, 2012

TDEC - Fleming Training Center 4

Routinely run parameter	New approval year for parameter method in Std Methods	Method #	Associated methods	Found in 20th Ed. Std Methods
Oxygen	2001	4500-O	B,C,D, E, F	No
Phenols	2005	5530-phenols	B, D	No
Oil & Grease	2001	5520-Oil and Grease	B, F	No
Total Phosphorus	1999	4500-P	E,F, G, H	No
Nitrate	2000	4500-NO3	D	No
TSS	1997	2540-TSS	B,C,D,E,F	Yes
Ammonia as N	1997	4500-NH_3	B,C,D,E,F,G,H	Yes
Cyanide	1999	4500-CN	G	No
Hydronium ion, pH	2000	4500-H	B	No
CBOD, BOD	2001	5210	B	No
Total residual Chlorine	2000	4500-Cl	D,E,B,C,F,G	No

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40 CFR 136 03-12-2007

TABLE IB.—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology[58]	Reference (method number or page)				
		EPA [56, 57]	Standard methods (18th, 19th)	Standard methods (20th)	Standard methods online	ASTM
1. Acidity, as $CaCO_3$, mg/L	Electrometric endpoint or phenolphthalein endpoint.		2310 B(4a)	2310 B(4a)	2310 B(4a)–97	D1067–92, 02
2. Alkalinity, as $CaCO_3$, mg/L	Electrometric or Colorimetric titration to pH 4.5, manual, or automatic	310.2 (Rev. 1974) [1].	2320 B	2320 B	2320 B–97	D1067–92, 02
3. Aluminum—Total,[4] mg/L	Digestion[4] followed by:					
	AA direct aspiration [36]		3111 D		3111 D–99	
	AA furnace		3113 B		3113 B–99.	
	STGFAA	200.9, Rev. 2.2 (1994).				
	ICP/AES [30]	200.7, Rev. 4.4 (1994).	3120 B	3120 B	3120 B–99	
	ICP/MS	200.8, Rev. 5.4 (1994).				D5673–03
	Direct Current Plasma (DCP) [30]					D4190–94, 99
	Colorimetric (Eriochrome cyanine R)		3500–Al D	3500–Al B	3500–Al B–01.	
	Manual, distillation (at pH 9.5)[4] followed by:	350.1, Rev. 2.0 (1993).	4500–NH B_5	4500–NH_3 B	4500–NH_3 B–97	
	Nesslerization		4500–NH_3 C (18th only).			D1426–98, 03 (A)
	Titration		4500–NH_3 C (19th) and 4500–NH_3 E (18th).	4500–NH_3 C	4500–NH_3 C–97.	
	Electrode		4500–NH_3 D or E (19th) and 4500–NH_3 F or G (18th).	4500–NH_3 D or E	4500–NH_3 D or E–97.	D1426–98, 03 (B).
	Automated phenate, or	350.1 [40], Rev. 2.0 (1993).	4500–NH_3 G (19th) and 4500–NH_3 H (18th).	4500–NH_3 G	4500–NH_3 G–97	
	Automated electrode					
	Ion Chromatography					D6919–03.

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40 CFR 136 05-21-2012

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology[16]	EPA[13]	Standard methods	ASTM	USGS/AOAC/Other
1. Acidity, as $CaCO_3$, mg/L.	Electrometric endpoint or phenolphthalein end-point.		2310 B–1997	D1067–06	I–1020–85.[7]
2. Alkalinity, as $CaCO_3$, mg/L.	Electrometric or Colorimetric titration to pH 4.5, Manual.		2320 B–1997	D1067–06	973.43[7], I–1030–85.[7]
	Automatic	310.2 (Rev. 1974)[1]			I–2030–85.[7]
3. Aluminum—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration[36]		3111 D–1999 or 3111 E–1999. 3113 B–2004.		I–3051–85.[7]
	AA furnace	200.9, Rev. 2.2 (1994).			
	ICP/AES[34]	200.7, Rev 4.2 (2003)[38]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[33]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[1] I–4471–97.[33]
	Direct Current Plasma (DCP)[34].			D4190–08	See footnote.[34]
	Colorimetric (Eriochrome cyanine R).		3500–Al B–2001.		
4. Ammonia (as N), mg/L.	Manual distillation[4] or gas diffusion (pH > 11), followed by any of the following:	350.1, Rev. 2.0 (1993).	4500–NH_3 B–1997		973.49I.
	Nesslerization		4500–NH_3 C–1997	D1426–08 (A)	973.49I, I–3520–85.[7]
	Titration		4500–NH_3 D–1997	D1426–08 (B).	
	Electrode		4500–NH_3 E–1997 or E–1997.		
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.		4500–NH_3 F–1997		See footnote.[60]
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	350.1[10], Rev. 2.0 (1993).	4500–NH_3 G–1997 4500–NH_3 H–1997.		I–4523–85.[7]

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"Standard Methods" Changes

- Most recent revision of a Standard Method
- Noted in "On-Line" version
- Located at the end of the "A" version of each Standard Method in hard copy
- Many new revisions of Standard Methods added

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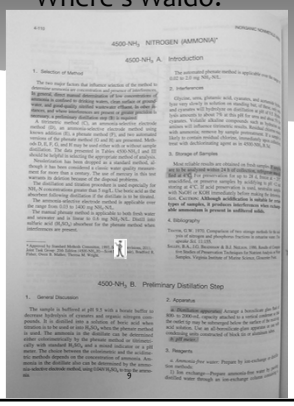
Where's Waldo?


4500-NH_3 NITROGEN (AMMONIA)*

4500-NH_3 A. Introduction

4500-NH_3 B. Preliminary Distillation Step

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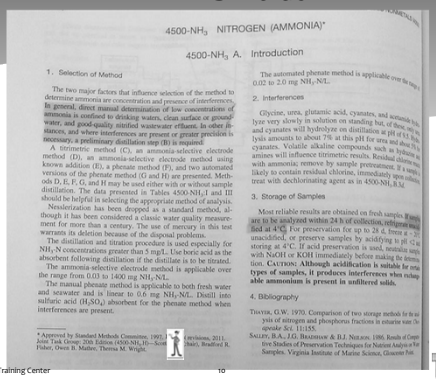
THERE'S Waldo!


4500-NH_3 NITROGEN (AMMONIA)*

4500-NH_3 A. Introduction

1. Selection of Method

2. Interferences

3. Storage of Samples

4. Bibliography

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Section 136.7 Lab QA

- …suitable QA/QC procedures…
- …QA/QC procedures are generally included in the method or may be found in the methods compendium… (Standard Methods)
- "The permittee/lab shall follow these QA/QC procedures, as described in the method or methods compendium. (Standard Methods)
- If the method lacks QA/QC…

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Three QA Options

- A. …follow equivalent EPA procedures
- B. Refer to QA/QC in consensus organization compendium. (Follow Standard Methods) didn't we have that on the previous slide?
- **C. Follow the 12 Steps where applicable.**

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12 Quality Control Elements

1. DOC – demonstration of capability
2. MDL – method detection level
3. LRB/MB – method blank
4. LFB – laboratory fortified blank (standard)
5. LFM/LFMD – laboratory fortified matrix/duplicate (spike)
6. Internal standards, surrogate standards or tracer – ***only applies to organic analysis and radiochemistry***
7. Calibration- initial and continuing
8. Control charts or other trend analysis
9. Corrective action – root cause analysis
10. QC acceptance criteria
11. Definition of a batch (preparation and analytical)
12. Minimum frequency for conducting all QC elements
13. Unwritten 13th Step – SOP – Standard Operating Procedures need to be written and followed for all lab sampling and analyses

Not all of these items apply to all tests, there are many exceptions!

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Can you defend what you do?

- How do you interpret your Permit language or the Rule?
- Can you defend that interpretation, will a judge or jury support you?
- What do Regulators say and what is written?
  - Is it clear?
  - Don't be afraid to ask Why?
  - Don't be afraid to ask for directives in writing.

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What You Are Already Doing

- Most Labs are doing lots of QA/QC stuff
- Write down what you do….SOP
- Summarize QC Data
  - Table Form
  - Average, Max, Min.
  - Control Charts

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Demonstration of Capability

- DOC
- Standard Methods 1020.B.1
  - As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 10 times the MDL and the midpoint of a calibration curve.
- Standard Methods 2020B.1.a, 4020B.1.a. & 5020.B.1.a
  - Run a laboratory-fortified blank (LFB) at least four times and compare to the limits listed in the method
  - LFB initial recovery limits = Mean ± (5.84xStandard Deviation)

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Demonstration of Capability

- What tests does this apply to?
  - Ammonia, BOD/CBOD, Chlorine, pH, DO, Total Phosphorus, TSS
  - Analyst needs to make up this standard, cannot be bought premade
  - Example: for ammonia, the analyst needs to make up 1.0 mg/L, not purchase pre-made 1.0 mg/L
    - Analyst can make 1 L of 1.0 mg/L by diluting down from 100 mg/L or 1000 mg/L and then pour up 4-100 mL aliquots

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Demonstration of Capability

- How often?
  - Once for each analyst.
    - Recommended yearly for backup analyst who does not perform tests frequently
    - EPA highly recommends running every 2-3 years for every analyst
  - Each analyst should have a file kept on their training within and for the lab.
  - Something to keep along with these records is a signed form (documentation) that analyst has read and understands all appropriate SOPs and Methods.

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Demonstration of Capability

- **2014 Update**
  - **DMRQA's were removed as acceptable DOC**
    - **Analyst have had a year, there should be at least 4 standards that have been analyzed and within limits to demonstrate capability.**

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Method Detection Level

- MDL
- Standard Methods 1020.B.4
  - As a starting point for selecting the concentration to use when determining the MDL, us an estimate of five times the estimated true detection level
  - Ideally, prepare and analyze at least seven portions of this solution over a 3-day period to ensure the MDL determination is more representative of routine measurements as performed in the laboratory

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Method Detection Level

- Standard Methods 1020.B.4 - continued
  - Recommended that the replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50-150% , with RSD (relative standard deviation) values ≤ 20%
- Standard Methods 4020.B.1.b
  - Ideally use pooled data from several analysts rather than data from one analyst

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Method Detection Level

- What tests does this apply to?
  - Ammonia, Chlorine, Total Phosphorus
- How often?
  - Annually

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What the heck IS an MDL study?

- It is a calculation that statistically gives the lowest concentration that a lab/facility can "see", that is detect an analyte
- Not practical for many analyses
- It is a bit tricky the first time, but KEEP RECORDS so next year it will be a breeze.
- Fresh samples prepared daily are preferred and it is recommended that samples are run over 3 days to give a more accurate account of how samples are run.

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How MDL Studies are Performed

- Make seven very low level blank spikes (can be lower than the lowest point on your curve)
- Analyze all seven over several days and calculate the standard deviation
- Multiply the standard deviation by the "student t" for 7 values (3.14)
- You cannot "cherry pick" your results, they must be 7 samples in a row

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MDL Calculations

- The result is the MDL (method detection level)
- The MDL must be greater than 1/10 the concentration of each spike
  - Example: if the spike was 3, the MDL cannot be lower than 0.3 (3 divided by 10)
- Keep up with the best spike value used for your MDL study so you don't have to go through several attempts each year
- **2014 Update – this is your reporting limit**

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Good MDL Values for Cl_2

Date	Analyst	Number	True Value	Value Read	% Recovery (50-150%)
1/28/2013	SEP	1	0.05	0.09	180.00
1/28/2013	SEP	2	0.05	0.07	140.00
1/28/2013	SEP	3	0.05	0.07	140.00
1/30/2013	SEP	4	0.05	0.08	160.00
1/30/2013	SEP	5	0.05	0.08	160.00
2/1/2013	SEP	6	0.05	0.07	140.00
2/1/2013	SEP	7	0.05	0.08	160.00
			Standard Deviation	**0.007559289**	
	Relative Standard Deviation (RSD)			9.7990789	(Needs to be ≤ 20%)
			MDL	**0.0237362**	

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MDL is NOT good because it is < 1/10th of the spike of 1.00. 1/10th of the spike is 0.10 mg/L and the calculated MDL is less than this and therefore unacceptable.

NOT Good MDL Values for Cl_2

Date	Analyst	Number	True Value	Value Read	% Recovery (50-150%)
1/28/2013	SEP	1	1.00	1.00	100.00
1/28/2013	SEP	2	1.00	0.99	99.00
1/28/2013	SEP	3	1.00	1.00	100.00
1/30/2013	SEP	4	1.00	1.00	100.00
1/30/2013	SEP	5	1.00	0.98	98.00
2/1/2013	SEP	6	1.00	1.01	101.00
2/1/2013	SEP	7	1.00	1.00	100.00
			Standard Deviation	**0.009511897**	
	Relative Standard Deviation (RSD)			0.9539152	(Needs to be ≤ 20%)
			MDL	**0.0298674**	

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Laboratory Reagent Blank

- LRB
- Also known as Method Blank
- Standard Methods 1020.B.5
  - A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure (distillation, incubation, etc.)
- What tests does this apply to?
  - Ammonia, BOD/CBOD, Chlorine, Total Phosphorus, TSS
- How often?
  - Depends on method QA/QC

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Laboratory Fortified Blank

- LFB
- Standard Methods 1020.B.6
  - A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added
  - Sample batch = 5% basis (see batch size for more information)
  - Use an added concentration of at least 10 times the MDL, or less than or equal to the midpoint of the calibration curve

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Laboratory Fortified Blank

- Standard Methods 2020.B.2.e – TSS
  - Using stock solutions, prepare fortified concentrations so they are within the calibration curve
- Standard Methods 4020.B.2.e – Ammonia, BOD/CBOD, Chlorine, Phosphorus
  - Calculate percent recovery, plot control charts and determine control limits
  - **More control chart info later**
- What tests does this apply to?
  - Ammonia, BOD/CBOD, Chlorine, Total Phosphorus, TSS

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Laboratory Fortified Blank

- How often?
- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
  - *Influent and Effluent are 2 different samples*
  - If a permit stated that 3 analyses per week, we would allow for a LFB to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Laboratory Fortified Matrix and Duplicate

- LFM/LFMD
- Also known as a spike and spike dup
- Standard Methods 1020.B.7
  - A laboratory matrix (LFM) is an additional portion of a sample to which a known amount of the analyte of interest is added before sample preparation
  - The LFM is used to evaluate analyte recovery in a sample
  - Sample batch = 5% basis
  - Add a concentration less than or equal to the midpoint of the calibration curve
  - Preferably the same concentration as the LFB (laboratory fortified blank)

Laboratory Fortified Matrix and Duplicate

- Standard Methods 4020.B.2.g
  - When appropriate for the analyte, include at least one LFM/LFMD … with each batch of 20 samples
  - Add a known concentration of analyte (ideally from a second source) to a randomly selected routine sample Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations
- What tests does this apply to?
  - Ammonia and Total Phosphorus

Laboratory Fortified Matrix and Duplicate

- How often?
- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
  - *Influent and Effluent are 2 different samples*
  - If a permit stated that 3 analyses per week, we would allow for a spike to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Laboratory Fortified Matrix and Duplicate

- Also called a Matrix Spike/Matrix Spike Duplicate (MS/MSD)
  - Calculate RPD between Spike and Spike Dup
- Shows if there are interferences in the effluent matrix
- **2014 Update – Spike volume should be less than 1% of the volume.**
  - **Example: spike with 1 mL of 1000 mg/L into 100 mL sample will equal a 10 mg/L increase in ammonia concentration.**

Duplicate

- Dup
- Not a part of the 12 Steps of QA, an addition from the State of TN
- Standard Methods 1020.B.8
  - As a minimum, include one duplicate sample with each sample set or on a 5% basis
- Standard Methods 1020.B.12
  - Calculate the RPD (relative percent difference)
  - Equal to or less than 20% RPD

Duplicate – TSS & Sett. Solids

- Standard Methods 2020.B.2.f
  - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples
- Standard Methods 2540.A.2
  - To aid in quality assurance, analyze samples in duplicate.
  - Dry samples to constant weight if possible.
  - This entails multiple drying-cooling-weighing cycles for each determination… more info later in presentation.
- Standard Methods 2540.D.3.c
  - Analyze at least 10% of all samples in duplicate

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Duplicate – Cl_2, pH and DO

- Standard Methods 4020.B.2.f
  - Randomly select routine samples to be analyzed twice
  - Process duplicate sample independently through the entire sample preparation and analysis
  - Include at least one duplicate for each matrix type daily or with each batch of 20

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Duplicate – BOD/CBOD

- Standard Methods 5020.B.2.f
  - Randomly select routine samples to be analyzed twice
  - Process duplicate sample independently through the entire sample preparation and analysis
  - Include at least one duplicate for each matrix type daily or with each batch of 20

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Duplicate

- What tests does this apply to?
  - BOD/CBOD, Chlorine, pH, DO, TSS and Settleable Solids
- How often?
- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria: (10% would be once every 10 samples for TSS)
  - If a permit stated that 3 analyses per week, we would allow for a dup to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

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Initial Calibration Verification & Continuing Calibration Verification

- ICV
  - Standard Methods 1020.B.11.b
    - Perform initial calibration using at least three concentrations of standards for linear curves
  - Calibrate meter (DO, pH or ISE) or verify balance, thermometer and colorimeter/spectrophotometer

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Initial Calibration Verification & Continuing Calibration Verification

- CCV
  - Standard Methods 1020.B.11.c
    - Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
  - Verify the calibration (especially if preset by manufacturer) at beginning of day, after every 10 readings and at the end of the batch
  - Daily (day of)

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ICV - TSS

- Standard Methods 2020.B.2.a
  - Check instrument balances daily
- Standard Methods 9020.B.4.b
  - Service balances annually or more often as conditions change or problems occur
    - Check balances routinely, preferably daily before use, with at least two working weights that bracket the normal usage range (e.g. ANSI/ASTM Class 1 or NIST Class S accompanied by appropriate certificate) for accuracy, precision and linearity.
    - Record results along with date and technicians initials
    - Recertify reference weights as specified in the certificate of calibration or at least every 5 years.

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ICV – Temperature

- Standard Methods 9020.B.4.a
  - Annually, or preferably, semiannually check accuracy of all working temperature sensing devices, such as liquid-in-glass thermometers, thermocouples and temperature-recording instruments at the use temperature against a certified National Institute of Standards and Technology (NIST) thermometer or one traceable to NIST and conforming to NIST specifications.
  - Record calibration results, along with the date and the technician's signature, in a quality control logbook.
  - Mark the necessary calibration correction factor on each temperature measuring device so that only calibrated-corrected temperature values are recorded.
  - Verify accuracy of the reference certified thermometer as specified on the certificate of calibration or at least every 5 years.

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ICV –Ammonia, BOD/CBOD, Chlorine, pH, DO, Phosphorus

- Standard Methods 4020.B.2.a
  - Calibrate initially with at least one blank and three calibration standards
  - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
  - The back-calculated and true concentrations should agree within ± 10%.

TDEC - Fleming Training Center 45

CCV –Ammonia, BOD/CBOD, Chlorine, pH, DO, Phosphorus

- Standard Methods 4020.B.2.b
  - Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
  - For the calibration verification to be valid, check standards must be within 10% of its true value

TDEC - Fleming Training Center 46

ICV –Probes for Ammonia

- Standard Methods 4500-NH_3 D.4.a.
  - Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1 and 0.1 mg NH_3-N/L
- Standard Methods 4500-NH_3 D.4.b.
  - Calibrate from lowest to highest concentration.
  - Wait until the reading has stabilized (at least 2-3 min) before recording millivolts for standards and samples containing ≤ 1 mg NH_3-N/L.
- Standard Methods 4500-NH_3 D.4.c.
  - If the electrode is functioning properly a tenfold change of NH_3-N concentration produces a potential change of about 59 mV.

TDEC - Fleming Training Center 47

ICV/CCV –Chlorine

- Prepare a set of Chlorine Standards or Potassium Permanganate ($KMnO_4$) standards in accordance with "Guidance for Secondary Standards use in Calibration" monthly.
- Initial – Chlorine Standards or Potassium Permanganate ($KMnO_4$) standards monthly.
- Continuing – Chlorine Standards, Potassium Permanganate ($KMnO_4$) standards or gel standards daily (day of).

TDEC - Fleming Training Center 48

ICV/CCV –Chlorine

- Secondary standards (gel standards) are specifically designed to verify the instrument's calibration and to check the instrument's performance.
- They are not intended to be used to create calibration curves or to calibrate the instrument.
- Because the DPD reagent cannot be mixed with the gel standards, the quality and the reaction time of the reagent cannot be assessed.
- For these reasons gel standards cannot take the place of primary standards.

TDEC - Fleming Training Center 49

ICV/CCV – Phosphorus

- ICV/CCV – does not go through digestion
- LFM and LFB – does go through digestion

TDEC - Fleming Training Center 50

Accuracy Control Charts

- Standard Methods 1020 B.13.a
  - The accuracy chart for QC samples (e.g., reagent blanks, LFBs, calibration check standards and LFMs) is constructed from the average and standard deviation of a specified number of measurements of the analyte of interest.
  - The accuracy chart includes upper and lower warning levels (WL) and upper and lower control levels (CL).
  - Common practice is to use ±2s and ±3s limits for the WL and CL, respectively, where *s* represents standard deviation.

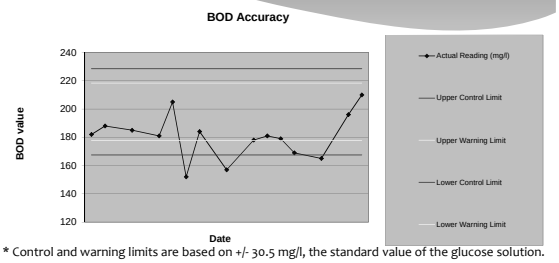
TDEC - Fleming Training Center 51

BOD Accuracy Control Charts

Date	Reading (mg/l)	Standard Value	Difference	*Upper Limit	*Lower Limit	*2/3 Upper	*2/3 Lower
8/22	182	198	-16	228.5	167.5	218.33	177.67
8/23	188	198	-10	228.5	167.5	218.33	177.67
8/25	185	198	-13	228.5	167.5	218.33	177.67
8/27	181	198	-17	228.5	167.5	218.33	177.67
8/28	205	198	7	228.5	167.5	218.33	177.67
8/29	152	198	-46	228.5	167.5	218.33	177.67
8/30	184	198	-14	228.5	167.5	218.33	177.67
9/1	157	198	-41	228.5	167.5	218.33	177.67
9/3	178	198	-20	228.5	167.5	218.33	177.67
9/4	181	198	-17	228.5	167.5	218.33	177.67
9/5	179	198	-19	228.5	167.5	218.33	177.67
9/6	169	198	-29	228.5	167.5	218.33	177.67
9/8	165	198	-33	228.5	167.5	218.33	177.67
9/10	196	198	-2	228.5	167.5	218.33	177.67
9/11	210	198	12	228.5	167.5	218.33	177.67

TDEC - Fleming Training Center 52

BOD Accuracy Control Charts



* Control and warning limits are based on +/- 30.5 mg/l, the standard value of the glucose solution.

TDEC - Fleming Training Center 53

Precision Control Charts

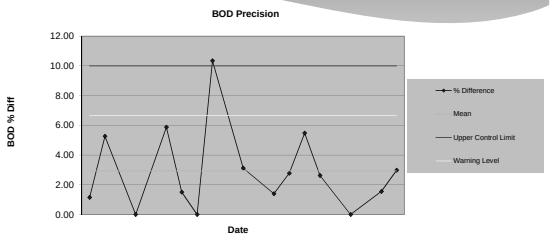
- Standard Methods 1020 B.13.b
  - The precision chart also is constructed on the average and standard deviation of a specified number of measurements (e.g., %RSD [relative standard deviation] or RPD) for a replicate or duplicate analyses of the analyte of interest.

TDEC - Fleming Training Center 54

BOD Precision Control Charts

Date	#1 (mg/l)	#2 (mg/l)	Avg.	Diff. (Range)	% Diff.	2 X SD	3 X SD	Mean	Max Variat.	2/3 Max Var.
8/22	87	86	86.5	1.0	1.16	5.63	8.45	2.94	10.00	6.67
8/23	78	74	76.0	4.0	5.26	5.63	8.45	2.94	10.00	6.67
8/25	62	62	62.0	0.0	0.00	5.63	8.45	2.94	10.00	6.67
8/27	70	66	68.0	4.0	5.88	5.63	8.45	2.94	10.00	6.67
8/28	67	66	66.5	1.0	1.50	5.63	8.45	2.94	10.00	6.67
8/29	76	76	76.0	0.0	0.00	5.63	8.45	2.94	10.00	6.67
8/30	61	55	58.0	6.0	10.34	5.63	8.45	2.94	10.00	6.67
9/1	65	63	64.0	2.0	3.13	5.63	8.45	2.94	10.00	6.67
9/3	72	71	71.5	1.0	1.40	5.63	8.45	2.94	10.00	6.67
9/4	73	71	72.0	2.0	2.78	5.63	8.45	2.94	10.00	6.67
9/5	75	71	73.0	4.0	5.48	5.63	8.45	2.94	10.00	6.67
9/6	77	75	76.0	2.0	2.63	5.63	8.45	2.94	10.00	6.67
9/8	83	83	83.0	0.0	0.00	5.63	8.45	2.94	10.00	6.67
9/10	65	64	64.5	1.0	1.55	5.63	8.45	2.94	10.00	6.67
9/11	66	68	67.0	2.0	2.99	5.63	8.45	2.94	10.00	6.67
TDEC - Fleming Training Center					2.94	mean				
					2.82	St.Dev.				

BOD Precision Control Charts



TDEC - Fleming Training Center 56

Control Charts

- **2014 Update** - Create and maintain control charts if you have 20-30 data points within 90 days.
  - If you do not meet the above criteria, follow QC Acceptance Criteria below.
    - Blanks < MDL
    - LFB ± 15%
    - ICV/CCV ± 10%
    - LFM/LFMD ± 20%
    - RPD < 20%
    - Reporting limit = MDL

TDEC - Fleming Training Center 57

Corrective Action

- Standard Methods 1020 B.15
  - QC data that are outside the acceptance limits or exhibit a trend are evidence of unacceptable error in the analytical process.
  - Take corrective action promptly to determine and eliminate the source of error.
  - Do not report data until the cause of the problem is identified and either corrected or qualified (see Table 1020:II)

TDEC - Fleming Training Center 58

Corrective Action

- The corrective action plan needs to be in your SOP for each method on what to do if your QC tests fail or are out of range
- If you have a "boo boo", write down how you fixed it
- Any issues should be recorded and a sentence on how it can be prevented, if possible, in the future
- Common problems and their corrections should be covered in your Standard Operating Procedures (SOP)
  - If you see things frequently, you can give them qualifiers that are noted in your SOP;
    - R = rain event
    - D = bad dilution, etc.

TDEC - Fleming Training Center 59

QC Acceptance

- Have in SOP for each method the acceptance ranges for standards, duplicates, spikes, etc. and make sure they match the method requirements.
- If not mentioned in method, these are the accepted criteria for QC:
  - Blank < reporting limit
  - LFB ± 15%
  - MS/MSD ± 20%
  - ICV/CCV ± 10%
  - RPD < 20%
  - Reporting limit = MDL

TDEC - Fleming Training Center 60

Batch Size

- Each "Batch" could be daily (day of), every 10 samples or every 20 samples.
- Check method
- *Influent and Effluent are 2 different samples*
- If you sample only once a month, need to run QC each time.
  - Once per month is minimum requirement

TDEC - Fleming Training Center 61

Batch Size

- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
  - If a permit stated that 3 analyses per week, how many samples would that be a week?
    - TSS and BOD would be 6, Cl_2 would be 3
  - If a permit stated 5 analyses per week, how many samples would that be a week?
    - TSS and BOD would be 10, Cl_2 would be 5

TDEC - Fleming Training Center 62

QC Frequency

- Usually lumped in with the definition of a "batch" and should be in the SOP of some kind

TDEC - Fleming Training Center 63

Standard Operating Procedure

- Here's that "13th Step", your SOP
- All procedures must be documented in some type of SOP
- It can be very simple but must provide the information necessary for someone who is not familiar with the test to perform it
  - Step by step instructions on how and where to collect the samples, how to run the test and how to report values.
- It must include the QC Acceptance Criteria, the definition of a "Batch" and the minimum frequency of QC checks

TDEC - Fleming Training Center 64

Total Suspended Solids, SM 2540 D, 22nd edition (1997)

Initial Demonstration of Capability (DOC)

- 2020 B.1 - each analyst must run a known standard concentration at least four times and compare limits listed in the method (under Precision). Table 2020:II lists duplicates and MB for QC only.
- Recommend running replicates and compare results and calculate the standard deviation to compare with that reported in 2540 D.5.
- **Real people language - *each* operator running this test needs to analyze 4 samples of a TSS Standard**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 2020 B.2.a.– check instrument balance daily as stated below.
- 9020.B.4.b. Service balances annually or more often as conditions change or problems occur…

  Check balance routinely, preferably daily before use, with at least two working weights that bracket the normal usage range. (e.g., ANSI/ASTM Class 1 or NIST Class S accompanied by appropriate certificate) for accuracy, precision, and linearity. Record results along with date and technician's initials.

  Recertify reference weights as specified in the certificate of calibration or at least every 5 years.
- 2540 B.2. analytical balance, with a sensitivity of 0.1 mg
- **Real people language – check balance *daily* *(day of)* with at least 2 working weights that bracket the normal usage range and record results on bench sheet or separate log book.**

Method Blank

- 2020 B.2.d.– include at least 1 method blank (MB) daily or with each batch of 20 or fewer samples, whichever is more frequent.
- **Real people language – on a 5% basis (see batch size for more information) filter 100 mL of distilled water.**
    - **Should be less than 2.5 mg/L.**

Laboratory Fortified Blank (LFB)

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis

12 Steps of Lab Quality Assurance

Parameter	Method	DOC	MDL	Method Blank	LFB	LFM / LFMD	Dup	ICAL / CCV	Control Charts	Corrective Action	QC Acceptance	Batch Size	*QC Frequency
Ammonia	SM4500-NH3 D - 1997	X	X	X	X	X		X, Calibrate meter daily	X	X	X	20	Depends on Permit
BOD_5 / $CBOD_5$	SM5210 B - 2001	X		X	X		X	X, Calibrate meter daily	X	X	X	20	Depends on Permit
Chlorine, TR	SM4500-Cl G - 2000	X	X	X	X		X	X, verify meter daily w Secondary Gel Standards	X	X	X	20	Depends on Permit
pH	SM4500-H+ B - 2000	X					X	X, Calibrate meter daily		X	X	20	Depends on Permit
Oxygen, dissolved	SM4500-O G - 2001	X					X	X, Calibrate meter daily & verify with air-saturated water		X	X	20	Depends on Permit
	Hach Method 10360 Luminescence Oct. 2011	X					X	X, Calibrate meter daily & verify with air-saturated water		X	X	20	Depends on Permit
Phosphorus, total	SM4500-P B and E - 1999	X	X	X	X	X		X, verify meter	X	X	X	20	Depends on Permit
TSS	SM2540 D - 1997	X		X	X		X	X, verify scale daily		X	X	20	Depends on Permit
Sett. Solids	SM2540 F - 1997						X			X		20	Depends on Permit
Temperature	SM2550 B - 2000							X, verify against NIST thermometer		X			Annually

DOC – Demonstration of Capability

- Each analyst should have a file kept from where they have calibrated and analyzed 4 standards to demonstrate they can accurately run this test
- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods
- Recommend backup analyst do this once a year

MDL – Method Detection Limit

- Annually run at least 7 samples at low levels

Method Blank – aka Laboratory Reagent Blank (LRB)

- Analyze distilled/deionized water as a sample

LFB – Laboratory Fortified Blank

- Analyze a known standard

LFM/LFMD – Laboratory Fortified Matrix/Laboratory Fortified Matrix Duplicate

- Analyze a sample with a known amount of standard added (spike)

Dup – Duplicate

- Analyze the same sample twice

ICAL/CCV – Initial Calibration/Continuing Calibration Verification

- Calibrate meter (DO, pH, ISE) or verify balance, thermometer and colorimeter/spectrophotometer
- Verify the calibration (especially if preset by manufacturer) at beginning of day and/or after every 10 readings, whichever comes first.

Control Charts

- Create and maintain control charts if you have 20-30 data points within 90 days.
- If you do not meet the above criteria, follow QC Acceptance Criteria below.

Corrective Action

- Have corrective action plan in SOP for each method on what to do if QC tests fail or are out of range.
- For example, if standards fail, re-calibrate and run test again.

QC Acceptance

- Have in SOP for each method the acceptance ranges for standards, duplicates, spikes, etc. and make sure they match the method requirements.

Batch Size

- Each batch could be daily, every 10 samples or every 20 samples. Check method.

*QC Frequency (depends on permit) – at least once a month

- For samples that need to be analyzed on a 5% basis or once for every 20 samples, follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - **Please note that influent and effluent samples count as two separate samples. For example, if you are supposed to run 3 BODs a week, that should be counted as running 6 samples for that week.**
- For samples that need to be analyzed on a 10% basis or once for 10 samples, follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least twice per month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow a duplicate to be analyzed once per week.
    - Pick a date and be consistent, every Monday or Wednesday. Mark your calendar!!
  - **Please note that influent and effluent samples count as two separate samples. For example, if you are supposed to run 5 TSSs a week, that should be counted as running 10 samples for that week and you should run your duplicates once a week.**

Standard Operating Procedure

- Here's that "13th Step", your SOP
- All procedures must be documented in some type of SOP
- It can be very simple but must provide the information necessary for someone who is not familiar with the test to perform it
  - Step by step instructions on how and where to collect the samples, how to run the test and how to report the values.
- It must include the QC Acceptance Criteria, the definition of a "Batch" and the minimum frequency of QC checks

- 2020 B.2.e. – Using stock solutions, prepare fortified concentrations so they are within the calibration curve.
- **Real people language – analyze TSS Standard sample that can be prepared from recipe below or bought premade.**
    - **Run on a 5% basis (see batch size for more information).**

TSS Standard Samples

To prepare TSS check samples from dry reference material:

1. Dry the reference material* in the desiccator
2. On an analytical balance, weigh 0.1000 gram of the dry powder, put it in a 1000 mL volumetric flask, bring it to the mark with distilled or deionized water and shake well until well suspended.
3. Measure 100 mL and process as usual for environmental samples.
4. A difference of 10 mg should be obtained.
5. Calculation:

$$\frac{(A - B)\ (1000)}{\text{Vol. used}} = \frac{(10\ \text{mg})\ (1000)}{100\ \text{mL}} = 100\ \text{mg/L}$$

*Example of material available from Fisher

- Celite 545 Fitler Aid (Powder), Fisher Chemical, 500 gram bottle – Cat#C212-500

Procedure to Omit Re-drying/Re-cooling/Re-weighing Cycle

How to acquire acceptable results for the total suspended solids comparability data:

- The maximum holding time for a total suspended solids sample prior to analysis is 7 days if stored at temperatures of 6°C and below (not 0°C). (*40CFR part 136, Table II*)
- EPA recommends that 4-7 different samples, in duplicate, be collected and analyzed for this procedure in order to prove that the step for "reheating, recooling, and reweighing" is unnecessary. "Different" could mean samples collected 4-7 consecutive days or 4-7 samples run in one day. These 4-7 samples are dried ***overnight*** at 103-105°C.
- The next morning, the filters are removed from the oven, allowed to cool in the desiccator and weighed.
- The samples are then returned to the drying oven for one hour, recooled and reweighed.
- The resulting data should be examined to determine if the difference between the overnight values and the redried values are less than 4% or 0.5 mg, whichever is less. If so, the redrying step may be omitted for a normal set of samples.
- This procedure excludes atypical samples. (i.e. high fat, oil and grease samples).
- The operator may choose not to perform this study and continue to follow the procedure for redrying/recooling/reweighing cycle as stated the method (SM 2540 D.3.c.).

  The study should be re-evaluated at least once per year or whenever a change in sample characteristics occurs and kept on file at the treatment plant.

Duplicate

- 1020 B.8. states as a minimum to include one duplicate sample with each sample set or on a 5% basis whichever is more frequent.
- 2020 B.2.f. states to include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- 2540 A.2. "*To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This entails multiple drying-cooling-weighing cycles for each determination.*"
- 2540 D.3.c. Analyze at least 10% of all samples in duplicate.
- **Real people language – analyze 2 samples for TSS.**

- **For example, filter 100 mL of effluent through filter pad A then filter another 100 mL of effluent through filter pad B. Dry, cool and weigh. Figure RPD for both samples.**
    - **Target value should be close to the first value and have a small RPD (less than 15%)**
    - **Analyze a duplicate at a 10% rate (see batch size for more information).**
- **For reporting purposes, average sample and duplicate.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Blanks < 2.5 mg/L
- LFB ± 15%
- RPD± 15%

Batch Size

- *Influent and Effluent are 2 different samples*
- For samples that need to be analyzed on a 5% basis or once for every 20 samples follow these criteria:
    - If a permit stated that 3 analyses per week, that would be 6 samples per week, we would allow for a blank and LFB to be analyzed at least twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, that would be 10 samples per week, we would allow once a week.
        - Pick a date and be consistent, every Monday. Mark your calendar!!
- For samples that need to be analyzed on a 10% basis or once for every 10 samples follow these criteria:
    - If a permit stated that 3 analyses per week, that would be 6 samples per week, we would allow for a duplicate to be analyzed at least twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, that would be 10 samples per week, we would allow once a week.
        - Pick a date and be consistent, every Monday. Mark your calendar!!

Calculations

- % Recovery for LFB
  - $= \frac{\text{LFB concentration}}{\text{Expected concentration}} \times 100\%$
- RPD – relative percent differences for duplicates and LFM/LFMD
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

Settleable Solids, SM 2540 F, 22nd edition (1997)

Initial Demonstration of Capability (DOC)

- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- NONE

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate –

- 2540 A.2. "*To aid in quality assurance, analyze samples in duplicate.*
- **Real people language – analyze 2 samples for Sett. Solids.**
    - **For example, pour up 1000 mL of effluent into Imhoff then pour up another 1000 mL of effluent in another Imhoff. Wait 45 min, stir, wait 15 min, read. Figure RPD for both samples.**
    - **Target value should be close to the first value and have a small RPD (less than 20%)**
    - **Run on a 5% basis (see batch size for more information).**
    - **For reporting purposes, average sample and duplicate.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- RPD < 20%
- Reporting Limit = lowest graduation makr on Imhoff cone

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:

- If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
- If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations

- RPD – relative percent differences for duplicates
    - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

Temperature, SM 2550 B, 22nd edition (2000)

Initial Demonstration of Capability (DOC)

- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 2020 B.2.a.– Verify calibration ***annually***
- 9020.B.4.a. – Annually or, preferably, semiannually check accuracy of all working temperature-sensing devices, such as liquid-in-glass thermometers, thermocouples, and temperature-recording instruments at the use temperature against a certified National Institute of Standards and Technology (NIST) thermometer or one traceable to NIST and conforming to NIST specifications.
    - Record calibration results, along with the date and the technician's signature, in a quality control logbook.
    - Mark the necessary calibration correction factor on each temperature measuring device so that only calibrated-corrected temperature values are recorded.
    - Verify accuracy of the reference certified thermometer as specified on the certificate of calibration or at least every 5 years.
- **Real people language – have thermometers verified annually by a NIST thermometer.**

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate

- NONE

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

Batch Size

- NONE

Total Residual Chlorine, SM 4500-Cl G, 22nd edition (2000) – DPD Colorimetric Method

Minimum Detectable Concentration – 4500-Cl G.1.c. – approximately 10 μg/L (0.010 mg/L)

Initial Demonstration of Capability (DOC)

- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to analyze 4 samples of a chlorine or potassium permanganate ($KMnO_4$) standard at a concentration of 0.5 mg/L**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**
    - **Only good for that type of instrument you are using at that plant. If you have a backup instrument made by a different manufacturer or you work at another plant with a different make/model, you would need another DOC.**
        - **DOCs demonstrate you are proficient with that one instrument.**

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, use an estimate of five times the estimated true detection level (5 x 0.010 mg/L = 0.050 mg/L).
    - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
    - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.
- 4020 B.1.b. – Verify MDL at least ***annually***.
    - Ideally use pooled data from several analysts rather than data from one analyst.
- **Real people language – have several operators, who run this test, analyze chlorine or Potassium Permanganate ($KMnO_4$) standards at a concentration of 0.05 mg/L over several days with a total of at least 7 samples**
    - **Joe analyzes 3 samples on Monday**
    - **Bob analyzes 3 samples on Tuesday**
    - **Mary analyzes 3 samples on Wednesday**
- **Run this once a year**

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- 4020.B.2.a. – Calibrate initially with at least one blank and three calibration standards.
    - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
    - The back-calculated and true concentrations should agree within ± 10%.

- **Real people language – prepare a set of chlorine or potassium permanganate ($KMnO_4$) standards in accordance with Guidance for Secondary Standards Use in Calibration 12-19-2013 monthly.**

Method Blank

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 4020 B.2.d. – Include at least one method blank *daily* or with each batch of 20 or fewer samples, whichever is more frequent.
    - If any method blanks measurements are at or above the reporting level, take immediate corrective action.
- **Real people language – analyze distilled water as a sample by adding a DPD powder pillow and waiting the 3-6 minutes before reading**
    - **Target value is less than reporting limit**
        - **Reporting limit will be equal to your Method Detection Limit (MDL)**
    - **Run on a 5% basis (see batch size for more information).**

Laboratory Fortified Blank (LFB)

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis = 1 every 20 samples
    - Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.
- 4020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits
- **Real people language – analyze chlorine or potassium permanganate standard at a concentration of 0.5 mg/L**
    - **Run on a 5% basis (see batch size for more information).**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 4020 B.2.f. – Randomly select routine samples to be analyzed twice.
    - Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – on a 5% basis (see batch size for more information) analyze 2 samples for chlorine, after reading one, pour out sample and start with a fresh sample**
    - **For reporting purposes, average sample and duplicate.**
    - **Target value should be close to the first value and have a small RPD (less than 20%)**

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
  - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
  - For the calibration verification to be valid, check standards must not exceed 10% of its true value
- **Real people language**
  - **Read Secondary Standards in accordance with Guidance for Secondary Standards Use in Calibration 12-19-2013 daily (day of).**
  - **OR run a chlorine or potassium permanganate standard daily.**

Control Charts – 1020 B.13.

- **Real people language**
  - **Create and maintain control charts if you have 20-30 data points within 90 days.**
  - **If you do not meet the above criteria, follow QC Acceptance Criteria below.**

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Blanks < Method Detection Limit (MDL)
- LFB ± 15%
- ICV/CCV ± 10%
- RPD < 20%
- Reporting Limit = MDL

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
  - If a permit stated 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - If sampling only once a month, need to run QC once a month (when samples are analyzed).

Calculations

- % Recovery for LFB
  - $= \frac{\text{LFB concentration}}{\text{Expected concentration}} \times 100\%$

- RPD – relative percent differences for duplicates
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$

The Use of Secondary Standards for Spectrophotometer/Colorimeter Calibration

Secondary standards (gel standards) are specifically designed to verify the instrument's calibration and to check the instrument's performance. They are not intended to be used to create calibration curves or to calibrate the instrument. Because the DPD reagent cannot be mixed with the gel standards, the quality and the reaction time of the reagent cannot be assessed. For these reasons gel standards cannot take the place of primary standards.

The analyst is responsible for the following:

- Preparing the calibration curve for each instrument ***once per month*** at a minimum with chlorine standards or potassium permanganate (see instructions below for $KMnO_4$), before the use of new DPD reagents, or the use of new gel standards
- Recording reagent lot #'s for reagents and standards
- Recording calibration concentrations
- Verifying the calibration curve using a minimum of one blank and two gel standards that bracket the expected sample concentration
- Recording all verification data

POTASSIUM PERMANGANATE ($KMnO_4$) STOCK STANDARD SOLUTION

0.891 grams of reagent grade $KMnO_4$ in 1000 mL vol. flask made to mark with deionized water. Deionized water must never be stored in plastic containers or exposed to airborne contamination. Store the stock solution in an amber bottle in a cool area. The typical shelf life of the stock solution is six (6) months. If solids appear in the solution, **do not use.**

*****Avoid leaving the cap off for extended periods of time and avoid contamination.*****

INTERMEDIATE (WORKING) STANDARD SOLUTION (10 mg/L)

10 mL of *STOCK* made in *1000* mL vol. flask made to mark with deionized water. The flask should be labeled with the name, $KMnO_4$, date of preparation, and initials of who made it.
This information should also be entered into a logbook.
The intermediate stock solution should be stable for approximately 5 days if kept cool and away from light.

Care should be taken that the pipette and glassware are clean and thoroughly rinsed with deionized water to avoid contamination. Store only in a glass container (preferably amber glass) never in plastic containers. The working solution should be remade if solids appear in the bottom of the container.

CALIBRATION STANDARD SOLUTIONS

If using $KMnO_4$, four to five calibration standard solutions should be made according to the table below with the addition of DPD to create a calibration curve ***once per month*** at a minimum. The correlation coefficient of the curve should correlate to 0.995 or better. This curve is then used to check instrument calibration. Gel standards are run against the curve and must agree to within $\pm$ 10%.
The working solution should be stable for approximately 2 hours and will fade rapidly (within 15 minutes) if chlorine demand-free water is not used.

A target value (e.g. permit value for a facility) should be known, and three gel standards, 0.00 mg/L (blank) and two other standards (a low and a high standard) that bracket the target value should be chosen. Gel standards are run against the curve and must agree to within $\pm$ 10%.

mL Working Standard Diluted w/Deionized water	Chlorine Equivalent mg/L
20 mL (vol. Pipette) to **100** mL (vol. flask)	**2.0** mg/L
10 mL (vol. Pipette) to **100** mL (vol. flask)	**1.0** mg/L
5 mL (vol. Pipette) to **100** mL (vol. flask)	**0.5** mg/L
1 mL (vol. Pipette) to **100** mL (vol. flask)	**0.1** mg/L
1 mL (vol. Pipette) to **200** mL (vol. flask)	**0.05** mg/L
1 mL (vol. Pipette) to **500** mL (vol. flask)	**0.02** mg/L
100 mL of deionized water	**0.00** mg/L

pH, SM 4500-H+ B, 22nd edition (2000) – Electrometric Method

Initial Demonstration of Capability (DOC)

- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to calibrate instrument and analyze 4 buffers at a pH of 7**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**
    - **Only good for that type of instrument you are using at that plant. If you have a backup instrument made by a different manufacturer or you work at another plant with a different make/model, you would need another DOC.**
        - **DOCs demonstrate you are proficient with that one instrument.**

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration
- **Real people language – calibrate daily (day of) with fresh buffers by following manufacturer's instructions.**
- **Analyze 7 buffer solution as a sample after calibration and before samples to verify initial calibration (ICV), should be within ± 0.2 s.u.**

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 4020 B.2.f. – Randomly select routine samples to be analyzed twice.
    - Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – on a 5% basis (see batch size for more information) analyze 2 samples for pH, after reading one, pour out sample and start with a fresh sample**
    - **Example, grab sample in bucket and dip pH probe in twice to get a duplicate reading**
    - **Target value should be close to the first value (within ± 0.2 s.u.)**

- **For reporting purposes, all duplicates should be reported according to your permit limits. If your permit sets a minimum or maximum limit such as pH, then the minimum or maximum value should be reported even if falls outside your permit limit.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard during a run – typically after each batch of 10 samples and at the end of the run.
- **Real people language – read 7 Buffer after analyzing samples daily (day of and within ± 0.2 pH units).**

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- ICV/CCV within ± 0.2 s.u.
- Duplicates within ± 0.2 s.u.

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would allow twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations

- NONE

Ammonia, SM 4500-NH_3 D, 22nd edition (1997) – Ammonia-Selective Electrode Method

40 CFR 136 Table 1B says the approved methodology is manual distillation[6] or gas diffusion (pH>11) followed by any of the following: Nesslerization, titration, electrode, manual phenate or automated phenate. Footnote 6 states: "Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. **In general, the analytical method should be consulted regarding the need for distillation**. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as < 20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test."

Standard Methods

- 4500-NH_3 A.1 – In general, direct manual determination of low concentrations of ammonia is confined to drinking waters, clean surface or groundwater and good-quality nitrified wastewater effluent.
- 4500-NH_3 D.1.b. – Sample distillation is unnecessary.

Tennessee recommends that one sample is run yearly to compare the distilled and undistilled results and that the results are within 20% of each other.

- Note – if distilled sample and undistilled sample are below detection limit, you cannot calculate the percent difference.

Initial Demonstration of Capability (DOC)

- 1020 B. 1 – As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 10 times the MDL and the midpoint of a calibration curve.
- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to calibrate the probe and analyze 4 samples of an NH_3 Standard at a concentration around 1.0 mg/L**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, use an estimate of five times the estimated true detection level (5 x 0.03 mg/L = 0.15 mg/L).
    - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
    - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.

- 4020 B.1.b. – Verify MDL at least ***annually***.
    - Ideally use pooled data from several analysts rather than data from one analyst.
- **Real people language – have several operators, who run this test, analyze an NH3 Standard at a concentration of 0.15 mg/L over several days with a total of at least 7 samples**
    - **Joe analyzes 3 samples on Monday**
    - **Bob analyzes 3 samples on Tuesday**
    - **Mary analyzes 3 samples on Wednesday**
- **Run this once a year**

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- 4020 B.2.a. – Calibrate initially with at least one blank and three calibration standards.
    - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
    - The back-calculated and true concentrations should agree within ± 10%.
- 4500-NH_3 D.4.a. – Prepare a series of standard solutions covering the concentrations of 1000, 100, 10, 1 and 0.1 mg NH_3-N/L
- 4500-NH_3 D.4.b. – calibrate from lowest to highest concentration. Wait until the reading has stabilized (at least 2-3 min) before recording millivolts for standards and samples containing ≤ 1 mg NH_3-N/L.
- 4500-NH_3 D.4.c. – If the electrode is functioning properly, a tenfold change of NH_3-N concentration produces a potential change of about 59 mV.
- **Real people language – calibrate according to manufacturer's instructions with at least 3 standards that will bracket your sample range *daily* (day of).**
- **Analyze a 10 mg/L standard as a sample after calibration and before samples to verify initial calibration (ICV)**

Method Blank – goes through distillation if you distill

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 4020 B.2.d. – Include at least one method blank daily or with each ***batch of 20*** or fewer samples, whichever is more frequent.
    - If any method blank measurements are at or above the reporting level, take immediate corrective action.
- **Real people language – analyze distilled water as a sample by going through distillation (if you still distill samples) and using ISA (ion strength adjuster).**
    - **Target value is less than reporting limit**
        - **Reporting limit will be equal to your Method Detection Limit (MDL)**
    - **Run on a 5% basis (see batch size for more information).**

Laboratory Fortified Blank (LFB) – goes through distillation if you distill

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.

- Sample batch = 5% basis = 1 every 20 samples
    - Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.
- 4020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits (see Control Charts below)
- **Real people language – analyze an NH_3 standard at a concentration of 5.0 mg/L**
    - **Run on a 5% basis (see batch size for more information).**

Duplicate

- NONE

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD) – goes through distillation if you distill

- 1020 B.7.– A laboratory fortified matrix (LFM) is an additional portion of a sample to which a known amount of the analyte of interest is added before sample preparation
    - The LFM is used to evaluate analyte recovery in a sample
    - Sample batch = 5% basis
    - Add a concentration that is at least 10 times the MRL (minimum reporting level), less than or equal to the midpoint of the calibration curve.
    - Preferably use the same concentration as the LFB
- 4020 B.2.g. – When appropriate for the analyte, include at least one LFM/LFMD daily or with each batch of 20 or fewer samples
    - Add a known concentration of analyte to a randomly selected routine sample
    - Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations (see Control Charts below)
- **Real people language – add a known amount of ammonia to a sample and expect that amount to be added to your sample concentration and repeat process for LFMD.**
    - **Run on a 5% basis (see batch size for more information).**
    - **Calculate RPD between spiked sample and spiked duplicate, target value should be close to the first value and have a small RPD (less than 20%).**
    - **Spike volume should be less than 1% of the volume.**
        - **Example: spike with 1 mL of 1000 mg/L into 100 mL sample will equal a 10 mg/L increase in ammonia concentration.**

Continuing Calibration Verification (CCV)

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
    - For the calibration verification to be valid, check standards must be within 10% of its true value
- **Real people language – analyze 10 mg/L at the end of all samples daily (day of).**

Control Charts – 1020 B.13.

- **Real people language**
  - **Create and maintain control charts if you have 20-30 data points within 90 days.**
  - **If you do not meet the above criteria, follow QC Acceptance Criteria below.**

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Blanks < MDL
- LFB ± 15%
- ICV/CCV ± 10%
- LFM/LFMD ± 20%
- RPD < 20%
- Reporting limit = MDL

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
  - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
    - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
  - If a permit stated 5 analyses per week, we would allow twice a month.
    - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
  - If sampling only once a month, need to run QC once a month.

Calculations

- % Recovery for LFB
  - $= \frac{\text{LFB Result}}{\text{Expected Concentration}} \times 100\%$
- RPD – relative percent differences for duplicates and LFM/LFMD
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$
- % Recovery for LFM – when using less than or equal to 1% spike volume compared to sample volume
  - $= \frac{\text{LFM Result} - \text{Sample Result}}{\text{Actual Concentration of spike}} \times 100\%$

Oxygen (Dissolved), Luminescence Measurement of Dissolved Oxygen, Hach Method 10360, Revision 1.2, October 2011

Initial Demonstration of Capability (DOC)

- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.
- Calibrate daily according to manufacturer's instructions
- Hach Method 10360 9.2.1 – Prepare and measure four samples of air-saturated water according to section 7.2.
    - 7.2.1 – Add approximately 1500 mL of organic-free water or BOD dilution water to a 2-L beaker or PET bottle
    - 7.2.2 – Allow the water to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
    - 7.2.3 – With a steady gentle stream of filtered air (≈ 10-40 mL per minute), aerate the water for a minimum of 30 minutes. Alternatively, vigorously shake the reagent water or BOD dilution water for several minutes.
    - 7.2.4 – At the completion of aeration, let water re-equilibrate to room temperature (20 ± 3°C) for 30 minutes and note the barometric pressure [uncorrected] of the laboratory during preparation. The barometric temperature reading is used in the calculation and determination of the theoretical DO concentration for the preparation of air-saturated water.
    - 7.2.5 – Transfer the aerated water to a BOD bottle until overflowing and stopper.
    - 7.2.6 – Calculate the theoretical dissolved oxygen concentration using a dissolved oxygen table such as Hitchman…
- **Real people language – each analyst should calibrate the probe, in accordance with manufacturer's instruction, prepare dilution water that is air-saturated and analyze four bottles and compare to the theoretical dissolved oxygen concentration (± 0.2 mg/L).**
    - **Theoretical dissolved oxygen can be found at USGS's website at http://water.usgs.gov/software/DOTABLES/ or by using a DO Saturation Table.**

Method Detection Limit (MDL)

- None

Initial Calibration Verification (ICV)

- 7.1.1 – Add approximately 1 inch (2.54 cm) of reagent water to a clean BOD bottle and stopper).
- 7.1.2 – Shake vigorously for ~ 10 seconds.
- 7.1.3 – Allow for the BOD bottle and its contents to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
- 7.1.4 – The stopper may now be removed from the BOD bottle and the LBOD probe inserted for calibration purposes.
- **Real people language – calibrate daily (day of) by following manufacturer's instructions.**

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate

- **Real people language – on a 5% basis (see batch size for more information) analyze 2 samples for DO.**
  - **First sample is result, second sample is duplicate**
  - **Target value is to be close to the first value and have a small difference (≤ 0.2 mg/L)**
- **For reporting purposes, all duplicates should be reported according to your permit limits. If your permit sets a minimum, then the minimum value should be reported even if falls outside your permit limit.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Continuing Calibration Verification (CCV)

- 7.2.1 – Add approximately 1500 mL of organic-free water or BOD dilution water to a 2-L beaker or PET bottle
- 7.2.2 – Allow the water to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
- 7.2.3 – With a steady gentle stream of filtered air (≈ 10-40 mL per minute), aerate the water for a minimum of 30 minutes. Alternatively, vigorously shake the reagent water or BOD dilution water for several minutes.
- 7.2.4 – At the completion of aeration, let water re-equilibrate to room temperature (20 ± 3°C) for 30 minutes and note the barometric pressure of the laboratory during preparation. The barometric temperature reading is used in the calculation and determination of the theoretical DO concentration for the preparation of air-saturated water.
- 7.2.5 – Transfer the aerated water to a BOD bottle until overflowing and stopper.
- 7.2.6 – Calculate the theoretical dissolved oxygen concentration using a dissolved oxygen table such as Hitchman…
- 9.3.1 – Upon air calibration, prepare a calibration verification standard with each analytical batch of 20 samples or less in an 8-hour period.
- 9.4.3 – Initially and at the end of each analytical batch of samples, analyze a dilution water sample that is air-saturated
- **Real people language – prepare dilution water that is air-saturated and analyze bottles and compare to the theoretical dissolved oxygen concentration (± 0.2 mg/L) after daily samples or with each batch of 20 samples or less in an 8-hour period.**
  - **Theoretical dissolved oxygen can be found at USGS's website at http://water.usgs.gov/software/DOTABLES/ or by using a DO Saturation Table.**

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

Batch Size

- 9.3.1 – … with each analytical batch of 20 samples or less in an 8 hour period.
- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would allow twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Oxygen (Dissolved), SM 4500-O G, 22nd edition (2001) – Membrane Electrode Method

Initial Demonstration of Capability (DOC)

- Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.
- Calibrate daily according to manufacturer's instructions
- Follow Hach Method 10360 9.2.1 – Prepare and measure four samples of air-saturated water according to section 7.2.
    - 7.2.1 – Add approximately 1500 mL of organic-free water or BOD dilution water to a 2-L beaker or PET bottle
    - 7.2.2 – Allow the water to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
    - 7.2.3 – With a steady gentle stream of filtered air (≈ 10-40 mL per minute), aerate the water for a minimum of 30 minutes. Alternatively, vigorously shake the reagent water or BOD dilution water for several minutes.
    - 7.2.4 – At the completion of aeration, let water re-equilibrate to room temperature (20 ± 3°C) for 30 minutes and note the barometric pressure [uncorrected] of the laboratory during preparation. The barometric temperature reading is used in the calculation and determination of the theoretical DO concentration for the preparation of air-saturated water.
    - 7.2.5 – Transfer the aerated water to a BOD bottle until overflowing and stopper.
    - 7.2.6 – Calculate the theoretical dissolved oxygen concentration using a dissolved oxygen table such as Hitchman…
- **Real people language – each analyst should calibrate the probe, in accordance with manufacturer's instruction, prepare dilution water that is air-saturated and analyze four bottles and compare to the theoretical dissolved oxygen concentration (± 0.2 mg/L).**
    - **Theoretical dissolved oxygen can be found at USGS's website at http://water.usgs.gov/software/DOTABLES/ or by using a DO Saturation Table.**

Method Detection Limit (MDL)

- None

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration
- **Real people language – calibrate daily (day of) by following manufacturer's instructions.**

Method Blank

- NONE

Laboratory Fortified Blank (LFB)

- NONE

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 4020 B.2.f. – Randomly select routine samples to be analyzed twice.

- Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – on a 5% basis (see batch size for more information) analyze 2 samples for DO.**
    - **First sample is result, second sample is duplicate**
    - **Target value is to be close to the first value and have a small difference (≤ 0.2 mg/L)**
- **For reporting purposes, all duplicates should be reported according to your permit limits. If your permit sets a minimum, then the minimum value should be reported even if falls outside your permit limit.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Continuing Calibration Verification (CCV)

- Follow Hach Method 7.2.1 – Add approximately 1500 mL of organic-free water or BOD dilution water to a 2-L beaker or PET bottle
- 7.2.2 – Allow the water to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
- 7.2.3 – With a steady gentle stream of filtered air (≈ 10-40 mL per minute), aerate the water for a minimum of 30 minutes. Alternatively, vigorously shake the reagent water or BOD dilution water for several minutes.
- 7.2.4 – At the completion of aeration, let water re-equilibrate to room temperature (20 ± 3°C) for 30 minutes and note the barometric pressure of the laboratory during preparation. The barometric temperature reading is used in the calculation and determination of the theoretical DO concentration for the preparation of air-saturated water.
- 7.2.5 – Transfer the aerated water to a BOD bottle until overflowing and stopper.
- 7.2.6 – Calculate the theoretical dissolved oxygen concentration using a dissolved oxygen table such as Hitchman…
- 9.3.1 – Upon air calibration, prepare a calibration verification standard with each analytical batch of 20 samples or less in an 8 hour period.
- 9.4.3 – Initially and at the end of each analytical batch of samples, analyze a dilution water sample that is air-saturated
- **Real people language – prepare dilution water that is air-saturated and analyze bottles and compare to the theoretical dissolved oxygen concentration (± 0.2 mg/L) after daily samples or with each batch of 20 samples or less in an 8-hour period.**
    - **Theoretical dissolved oxygen can be found at USGS's website at http://water.usgs.gov/software/DOTABLES/ or by using a DO Saturation Table.**

Control Charts

- NONE

Corrective Action - 1020 B.5., B.8,. & B.15.

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would allow twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Total Phosphorus, SM 4500-P B (Sample Prep) and E, 22nd edition (1999) – Ascorbic Acid Method

Minimum Detectable Concentration **–** 4500-P E.1.c. – approximately 10 μg/L (0.010 mg/L)

Initial Demonstration of Capability (DOC)

- 1020 B. 1 – As a minimum, include a reagent blank and at least 4 LFBs at a concentration between 10 times the MDL and the midpoint of a calibration curve.
- 4020 B.1.a. - each analyst must run a known standard concentration at least four times and compare limits listed in the method.
- **Real people language – each operator running this test needs to analyze 4 samples of Phosphorus standard at a concentration of about 0.5 mg/L**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- 1020 B. 4 – As a starting point for selecting the concentration to use when determining the MDL, us an estimate of five times the estimated true detection level (5 x 0.010 mg/L = 0.050 mg/L).
    - Ideally, prepare and analyze at least seven (7) portions of this solution over a 3-day period to ensure that the MDL determination is more representative of routine measurements as performed in the laboratory.
    - The replicate measurements should be in the range of one to five times the estimated MDL, and recoveries of the known addition should be between 50 and 150%, with %RSD (relative standard deviation) values ≤ 20%.
- 4020 B.1.b. – Verify MDL at least ***annually***.
    - Ideally use pooled data from several analysts rather than data from one analyst.
- **Real people language – have several operators, who run this test, analyze a Phosphorus standard at a concentration of 0.05 mg/L over several days with a total of at least 7 samples**
    - **Joe analyzes 3 samples on Monday**
    - **Bob analyzes 3 samples on Tuesday**
    - **Mary analyzes 3 samples on Wednesday**
- **Run this once a year**

Initial Calibration Verification (ICV) – does not go through digestion

- 1020 B.11.b. – Perform initial calibration using at least three concentrations of standards for linear curves.
- 4020.B.2.a. – Calibrate initially with at least one blank and three calibration standards.
    - The appropriate linear correlation coefficient for standard concentration-to-instrument response should be greater than or equal to 0.995.
    - The back-calculated and true concentrations should agree within ± 10%.

- **Real people language – prepare a set of Phosphorus standards (4-5 standards) to verify the factory pre-set calibration curve monthly or more frequently if reagent lot # changes.**

Method Blank – goes through digestion

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 4020 B.2.d. – Include at least one method blank daily or with each batch of 20 or fewer samples, whichever is more frequent.
    - If any method blank measurements are at or above the reporting level, take immediate corrective action.
- **Real people language – analyze distilled water as a sample by going through all digestion and reagent addition before reading.**
    - **Target value is less than reporting limit.**
        - **Reporting limit will be equal to your Method Detection Limit (MDL)**
    - **Run on a 5% basis (see batch size for more information).**

Laboratory Fortified Blank (LFB) – goes through digestion

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis = 1 every 20 samples
    - Use an added concentration of at least 10 times the MDL, less than or equal to the midpoint of the calibration curve.
- 4020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits (see Control Charts below)
- **Real people language – analyze Phosphorus standard at a concentration of 0.5 mg/L**
    - **Run on a 5% basis (see batch size for more information).**

Duplicate –

- NONE

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD) – goes through digestion

- 1020 B.7.– A laboratory fortified matrix (LFM) is an additional portion of a sample to which a known amount of the analyte of interest is added before sample preparation
    - The LFM is used to evaluate analyte recover in a sample
    - Sample batch = 5% basis = 1 every 20 samples
    - Add a concentration that is at least 10 times the MRL (minimum reporting level), less than or equal to the midpoint of the calibration curve.
    - Preferably use the same concentration as the LFB
- 4020 B.2.g. – When appropriate for the analyte, include at least one LFM/LFMD daily or with each batch of 20 or fewer samples
    - Add a known concentration of analyte to a randomly selected routine sample
    - Calculate percent recovery and relative percent difference, plot control charts and determine control limits for spikes at different concentrations (see Control Charts below)

- **Real people language – add a known amount of phosphorus to a sample and expect that amount to increase your sample concentration**
    - **Run on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent), see batch size for more information**
    - **Calculate RPD between spiked sample and spiked duplicate, target value should be close to the first value and have a small RPD (less than 20%).**
    - **Spike volume should be less than 1% of the volume.**
        - **Example: spike with 0.1 mL of 100 mg/L into 10 mL sample will equal a 1 mg/L increase in phosphorus concentration.**

Continuing Calibration Verification (CCV) – does not go through digestion

- 1020 B.11.c. – Analysts periodically use a calibration standard to confirm that the instrument performance has not changed significantly since initial calibration.
    - Verify calibration by analyzing one standard at a concentration near or at the mid-point of the calibration range.
- 4020.B.2.b. – Verify calibration by periodically analyzing a calibration standard and calibration blank during a run – typically after each batch of 10 samples and at the end of the run.
    - For the calibration verification to be valid, check standards must not exceed 10% of its true value
- **Real people language – analyze mid-range Phosphorus standard daily (day of).**

Control Charts – 1020 B.13.

- **Real people language**
    - **Create and maintain control charts if you have 20-30 data points within 90 days.**
    - **If you do not meet the above criteria, follow QC Acceptance Criteria below.**

Corrective Action - 1020 B.5., B.8,. & B.15.

QC Acceptance Criteria

- Blanks < MDL
- LFB ± 15%
- ICV/CCV ± 10%
- LFM/LFMD ± 20%
- RPD < 20%
- Reporting Limit = MDL

Batch Size –

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
    - If a permit stated that 3 analyses per week, we would allow for a duplicate to be analyzed at least once per month.
        - Pick a date and be consistent, the 1st of every month or the 1st Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, we would suggest twice a month.

- Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!

Calculations –

- % Recovery for LFB
  - = $\frac{\text{LFB concentration}}{\text{Expected concentration}}$ X 100%
- RPD – relative percent differences for duplicates and LFM/LFMD
  - = $\frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}}$ X 100%
- % Recovery for LFM – when using less than or equal to 1% spike volume compared to sample volume
  - = $\frac{\text{LFM concentration – Sample concentration}}{\text{Concentration of spike}}$ X 100%

Biochemical Oxygen Demand (BOD), SM 5210 B, 22nd edition (2001) – 5-Day BOD Test

Initial Demonstration of Capability (DOC)

- 1020 B. 1 – As a minimum, include a reagent blank and at least 4 LFBs
- 4020 B.1.a. – Before analysts run any samples, verify their capability with the method. Run a laboratory fortified blank at least four times and compare to the limits listed in the method.
    - If no limit is specified, use the following procedure to establish limits.
    - Calculate the standard deviation of the four samples. Then calculate the LFB's recovery limits (see formula at end)
- **Real people language – each operator running this test needs to analyze 4 samples of GGA at a concentration of 198 ±30.5 mg/L**
    - **Keep a folder for each analyst, keep a copy here**
    - **Documentation (signed form) that analyst has read and understands all appropriate SOPs and Methods.**
    - **Recommend backup analyst do this once a year.**

Method Detection Limit (MDL)

- NONE

Initial Calibration Verification (ICV)

- 1020 B.11.b. – Perform initial calibration
- Hach's Method: 7.1.1 – Add approximately 1 inch (2.54 cm) of reagent water to a clean BOD bottle and stopper).
- 7.1.2 – Shake vigorously for ~ 10 seconds.
- 7.1.3 – Allow for the BOD bottle and its contents to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
- 7.1.4 – The stopper may now be removed from the BOD bottle and the LBOD probe inserted for calibration purposes.
- **Real people language – calibrate DO probe daily (day of) by following manufacturer's instructions.**

Method Blank

- 1020 B.5.– A reagent blank (method blank) consists of reagent water and all reagents that normally are in contact with a sample during the entire analytical procedure.
- 5020 B.2.d. – Include at least one method blank daily or with each batch of 20 or fewer samples, whichever is more frequent.
- 5210 B.6.c. – With each batch of samples, incubate one or more bottles of dilution water that contains nutrient, mineral and buffer solutions but no seed or nitrification inhibitor.
    - The DO uptake in 5 days must not be more than 0.20 mg/L and preferably not more than 0.10 mg/L, before making seed corrections.
- **Real people language – analyze dilution water blanks *daily* *(day of)*, preferably one at beginning and one at end**
    - **Target value is less than 0.20 mg/L (preferably less than 0.10 mg/L)**

Laboratory Fortified Blank (LFB)

- 1020 B.6.– A laboratory-fortified blank is a reagent water sample to which a known concentration of the analyte of interest has been added.
    - Sample batch = 5% basis
- 5020 B.2.e. – Calculate percent recovery, plot control charts and determine control limits (see Control Charts below)
    - When appropriate, include at least one LFB daily or per each batch of 20 or fewer samples.
- **Real people language – analyze GGA sample at a concentration of 198 ±30.5 mg/L**
    - **Run on a 5% basis (see batch size for more information).**
    - **If permit requires cBOD, add nitrification inhibitor (NI) to one GGA bottle once/quarter (or more often if the Lot # of NI changes), which should be equal to 164 ±30.7 mg/L**

Duplicate

- 1020 B.12.f. – Calculate RPD (relative percent difference)
- 5020 B.2.f. – Randomly select routine samples to be analyzed twice.
    - Process duplicate sample independently through the entire sample preparation and analysis.
    - Include at least one duplicate for each matrix type daily or with each batch of 20 or fewer samples.
- **Real people language – analyze 2 samples for BOD or cBOD, run an extra sample dilution bottle**
    - **Example: if you run 100mL, 200mL and 300mL for your effluent, run a second 300mL sample. You will have 4 bottles total for your effluent dilutions.**
    - **Target value should be close to the first value (same dilution) and have a small RPD (less than 20%)**
- **For reporting purposes, average results that meet method criteria.**

Laboratory Fortified Matrix (LFM)/Laboratory Fortified Matrix Duplicate (LFMD)

- NONE

Continuing Calibration Verification (CCV)

- Hach Method 10360 7.2 and 9.4 – Calibration Verification for membranes and LDO probes
    - 7.2.1 – Add approximately 1500 mL of organic-free water or BOD dilution water to a 2-L beaker or PET bottle
    - 7.2.2 – Allow the water to equilibrate to room temperature. Room temperature should be approximately 20 ± 3°C.
    - 7.2.3 – With a steady gentle stream of filtered air (≈ 10-40 mL per minute), aerate the water for a minimum of 30 minutes. Alternatively, vigorously shake the reagent water or BOD dilution water for several minutes.
    - 7.2.4 – At the completion of aeration, let water re-equilibrate to room temperature (20 ± 3°C) for 30 minutes and note the barometric pressure of the laboratory during preparation. The barometric temperature reading is used in the calculation and

determination of the theoretical DO concentration for the preparation of air-saturated water.
    - 7.2.5 – Transfer the aerated water to a BOD bottle until overflowing and stopper.
    - 7.2.6 – Calculate the theoretical dissolved oxygen concentration using a dissolved oxygen table such as Hitchman…
    - 9.4.3 – Initially and at the end of each analytical batch of samples, analyze a dilution water sample that is air-saturated
- **Real people language – prepare dilution water that is air-saturated and analyze bottles and compare to the theoretical dissolved oxygen concentration (± 0.2 mg/L).**
    - **Theoretical dissolved oxygen can be found at USGS's website at http://water.usgs.gov/software/DOTABLES/ or by using a DO Saturation Table.**

Control Charts – 1020 B.13.

- **Real people language**
    - **Create and maintain control charts if you have 20-30 data points within 90 days.**
    - **If you do not meet the above criteria, follow QC Acceptance Criteria below.**

Corrective Action - 1020 B.5., B.8,. & B.15.

- 5210 B.7.b. – Identify results in the test reports when any of the following quality control parameters is not met:
    - Dilution water exceeds 0.20 mg/L (5210B.6c)
    - Glucose-glutamic acid check falls outside of acceptable limits (5210B.6b)
    - Test replicates show more than 30% difference between high and low values
    - Seed control samples do not meet the above criteria in all dilutions (5210B.6d) or
    - Minimum DO is less than 1.0 mg/L (5210B.7a3)

QC Acceptance Criteria

- Blanks < 0.20 mg/L
- GGA = 198 ± 30.5 mg/L (if running cBOD, add NI to one bottle once/quarter or more often if NI Lot# changes, and it should = 164 ± 30.7 mg/L)
- RPD < 20%
- Minimum of three dilutions for each sample, at least one sample must have valid data with at least 2.0 mg/L depletion and a residual of 1.0 mg/L

Batch Size

- For samples that need to be analyzed on a 5% basis (1 for every 20 samples or once per month, whichever is more frequent) follow these criteria:
- *Influent and Effluent are 2 different samples*
    - If a permit stated that 3 analyses per week, that would be 6 samples per week, we would allow for a duplicate to be analyzed at least twice a month.
        - Pick a date and be consistent, the 1st and 15th of every month or the 1st and 3rd Thursday of every month. Mark your calendar!!
    - If a permit stated 5 analyses per week, that would be 10 samples per week, we would allow once a week.
        - Pick a date and be consistent, every Monday. Mark your calendar!!

- If sampling only once a month, need to run QC once a month.

Calculations

- % Recovery for LFB
  - $= \frac{\text{LFB concentration}}{\text{Expected concentration}} \times 100\%$
- RPD – relative percent differences for duplicates
  - $= \frac{\text{Difference between sample and duplicate}}{\text{Average of the sample and duplicate}} \times 100\%$
- Unseeded - $BOD_5, mg/L = \frac{D_1 - D_2}{P}$
- Seeded - $BOD_5, mg/L = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$
  - Where:
    - D_1 = Initial Dissolved Oxygen Concentration in Sample, mg/L
    - D_2 = Final Dissolved Oxygen Concentration in Sample, mg/L
    - B_1 = Initial Dissolved Oxygen Concentration in Seed Control, mg/L
    - B_2 = Final Dissolved Oxygen Concentration in Seed Control, mg/L
    - P = Sample Concentration, % (expressed as a decimal)
    - $f = \frac{\text{Seed in Sample, \%}}{\text{Seed in Seed Control, \%}}$

phosphorus, as long as complete oxidation can be demonstrated.

(xxii) Use of an axially viewed torch with Method 200.7.

■ 7. Add new § 136.7 to read as follows:

§ 136.7 Quality assurance and quality control.

The permittee/laboratory shall use suitable QA/QC procedures when conducting compliance analyses with any Part 136 chemical method or an alternative method specified by the permitting authority. These QA/QC procedures are generally included in the analytical method or may be part of the methods compendium for approved Part 136 methods from a consensus organization. For example, Standard Methods contains QA/QC procedures in the Part 1000 section of the Standard Methods Compendium. The permittee/laboratory shall follow these QA/QC procedures, as described in the method or methods compendium. If the method lacks QA/QC procedures, the permittee/laboratory has the following options to comply with the QA/QC requirements:

(a) Refer to and follow the QA/QC published in the ''equivalent'' EPA method for that parameter that has such QA/QC procedures;

(b) Refer to the appropriate QA/QC section(s) of an approved Part 136 method from a consensus organization compendium;

(c)(1) Incorporate the following twelve quality control elements, where applicable, into the laboratory's documented standard operating procedure (SOP) for performing compliance analyses when using an approved Part 136 method when the method lacks such QA/QC procedures. One or more of the twelve QC elements may not apply to a given method and may be omitted if a written rationale is provided indicating why the element(s) is/are inappropriate for a specific method.

(i) Demonstration of Capability (DOC);

(ii) Method Detection Limit (MDL);

(iii) Laboratory reagent blank (LRB), also referred to as method blank (MB);

(iv) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);

(v) Matrix spike (MS) and matrix spike duplicate (MSD), or laboratory fortified matrix (LFM) and LFM duplicate, may be used for suspected matrix interference problems to assess precision;

(vi) Internal standards (for GC/MS analyses), surrogate standards (for organic analysis) or tracers (for radiochemistry);

(vii) Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);

(viii) Control charts (or other trend analyses of quality control results);

(ix) Corrective action (root cause analysis);

(x) QC acceptance criteria;

(xi) Definitions of preparation and analytical batches that may drive QC frequencies; and

(xii) Minimum frequency for conducting all QC elements.

(2) These twelve quality control elements must be clearly documented in the written standard operating procedure for each analytical method not containing QA/QC procedures, where applicable.

■ 8. Revise Appendix C to Part 136 to read as follows.

APPENDIX C TO PART 136—DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA–ATOMIC EMISSION SPECTROMETRY METHOD 200.7

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP–AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1–4] (For analysis of petroleum products see References 5 and 6, Section 16.0). This method is applicable to the following analytes:

Analyte	Chemical abstract services registry number (CASRN)
Aluminum (Al)	7429–90–5
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Boron (B)	7440–42–8
Cadmium (Cd)	7440–43–9
Calcium (Ca)	7440–70–2
Cerium [a] (Cr)	7440–45–1
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Iron (Fe)	7439–89–6
Lead (Pb)	7439–92–1
Lithium (Li)	7439–93–2
Magnesium (Mg)	7439–95–4
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Molybdenum (Mo)	7439–98–7
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Potassium (K)	7440–09–7
Selenium (Se)	7782–49–2
Silica [b] (SiO_2)	7631–86–9
Silver (Ag)	7440–22–4
Sodium (Na)	7440–23–5
Strontium (Sr)	7440–24–6
Thallium (Tl)	7440–28–0
Tin (Sn)	7440–31–5
Titanium (Ti)	7440–32–6
Vanadium (V)	7440–62–2
Zinc (Zn)	7440–66–6

[a] Cerium has been included as method analyte for correction of potential interelement spectral interference.

[b] This method is *not* suitable for the determination of silica in solids.

1.2 For reference where this method is approved for use in compliance monitoring programs [*e.g.,* Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest **Federal Register** announcements.

1.3 ICP–AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as ''direct analysis''. However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (*e.g.,* soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by ''direct analysis'' where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver.

Section 3
Approved Methods and NPDES Permit

40CFR136

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Part II

Environmental Protection Agency

40 CFR Parts 136, 260, et al.
Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; Final Rule

TABLE IA—LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER AND SEWAGE SLUDGE

Parameter and units	Method [1]	EPA	Standard methods	AOAC, ASTM, USGS	Other
Bacteria:					
1. Coliform (fecal), number per 100 mL or number per gram dry weight.	Most Probable Number (MPN), 5 tube, 3 dilution, or	p. 132 [3] ..... 1680 [11,15]. 1681 [11,20].	9221 C E–2006.		
	Membrane filter (MF) [2], single step	p. 124 [3]	9222 D–1997	B–0050–85 [4].	
2. Coliform (fecal) in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 132 [3]	9221 C E–2006.		
	MF [2], single step [5]	p. 124 [3]	9222 D–1997.		
3. Coliform (total), number per 100 mL.	MPN, 5 tube, 3 dilution, or.	p. 114 [3]	9221 B–2006.		
	MF [2], single step or two step.	p. 108 [3]	9222 B–1997	B–0025–85 [4]	
4. Coliform (total), in presence of chlorine, number per 100 mL.	MPN, 5 tube, 3 dilution, or	p. 114 [3]	9221 B–2006		
	MF [2] with enrichment [5]	p. 111 [3]	9222 (B + B.5c) – 1997		
5. *E. coli,* number per 100 mL [21].	MPN [6,8,16] multiple tube, or.	.....	9221B.1–2006/9221F–2006 [12,14].		
	multiple tube/multiple well, or	.....	9223 B–2004 [13]	991.15 [10]	Colilert® [13,18] Colilert-18® [13,17,18]
	MF [2,6,7,8] single step ...	1603 [22]	.....	.....	mColiBlue-24® [19]
6. Fecal streptococci, number per 100 mL.	MPN, 5 tube 3 dilution, or	p. 139 [3]	9230 B–2007.		
	MF [2], or	p. 136 [3]	9230 C–2007	B–0055–85 [4]	
	Plate count	p. 143 [3].			
7. Enterococci, number per 100 mL [22].	MPN [6,8], multiple tube/multiple well, or	.....	.....	D6503–99 [9]	Enterolert® [13,24]
	MF [2,6,7,8] single step or	1600 [25]	9230 C–2007		
	Plate count	p. 143 [3].			
8. *Salmonella,* number per gram dry weight [11].	MPN multiple tube	1682 [23].			
Aquatic Toxicity:					
9. Toxicity, acute, fresh water organisms, LC_{50}, percent effluent.	*Ceriodaphnia dubia* acute.	2002.0. [26]			
	Daphnia puplex and *Daphnia magna* acute.	2021.0. [26]			
	Fathead Minnow, *Pimephales promelas,* and Bannerfin shiner, *Cyprinella leedsi,* acute.	2000.0. [26]			
	Rainbow Trout, *Oncorhynchus mykiss,* and brook trout, *Salvelinus fontinalis,* acute.	2019.0. [26]			
10. Toxicity, acute, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, LC_{50}, percent effluent.	Mysid, *Mysidopsis bahia,* acute.	2007.0. [26]			

TABLE IA—LIST OF APPROVED BIOLOGICAL METHODS FOR WASTEWATER AND SEWAGE SLUDGE—Continued

Parameter and units	Method [1]	EPA	Standard methods	AOAC, ASTM, USGS	Other
	Sheepshead Minnow, *Cyprinodon variegatus,* acute.	2004.0 [26]			
	Silverside, *Menidia beryllina, Menidia menidia,* and *Menidia peninsulae,* acute.	2006.0 [26]			
11. Toxicity, chronic, fresh water organisms, NOEC or IC_{25}, percent effluent.	Fathead minnow, *Pimephales promelas,* larval survival and growth.	1000.0.[27]			
	Fathead minnow, *Pimephales promelas,* embryo-larval survival and teratogenicity.	1001.0.[27]			
	Daphnia, *Ceriodaphnia dubia,* survival and reproduction.	1002.0.[27]			
	Green alga, *Selenastrum capricornutum,* growth.	1003.0.[27]			
12. Toxicity, chronic, estuarine and marine organisms of the Atlantic Ocean and Gulf of Mexico, NOEC or IC_{25}, percent effluent.	Sheepshead minnow, *Cyprinodon variegatus,* larval survival and growth.	1004.0.[28]			
	Sheepshead minnow, *Cyprinodon variegatus,* embryo-larval survival and teratogenicity.	1005.0.[28]			
	Inland silverside, *Menidia beryllina,* larval survival and growth.	1006.0.[28]			
	Mysid, *Mysidopsis bahia,* survival, growth, and fecundity.	1007.0.[28]			
	Sea urchin, *Arbacia punctulata,* fertilization.	1008.0.[28]			

Table IA notes:

[1] The method must be specified when results are reported.

[2] A 0.45-µm membrane filter (MF) or other pore size certified by the manufacturer to fully retain organisms to be cultivated and to be free of extractables which could interfere with their growth.

[3] Microbiological Methods for Monitoring the Environment, Water, and Wastes, EPA/600/8–78/017. 1978. US EPA.

[4] U.S. Geological Survey Techniques of Water-Resource Investigations, Book 5, Laboratory Analysis, Chapter A4, Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. 1989. USGS.

[5] Because the MF technique usually yields low and variable recovery from chlorinated wastewaters, the Most Probable Number method will be required to resolve any controversies.

[6] Tests must be conducted to provide organism enumeration (density). Select the appropriate configuration of tubes/filtrations and dilutions/volumes to account for the quality, character, consistency, and anticipated organism density of the water sample.

[7] When the MF method has been used previously to test waters with high turbidity, large numbers of noncoliform bacteria, or samples that may contain organisms stressed by chlorine, a parallel test should be conducted with a multiple-tube technique to demonstrate applicability and comparability of results.

[8] To assess the comparability of results obtained with individual methods, it is suggested that side-by-side tests be conducted across seasons of the year with the water samples routinely tested in accordance with the most current Standard Methods for the Examination of Water and Wastewater or EPA alternate test procedure (ATP) guidelines.

[9] Annual Book of ASTM Standards–Water and Environmental Technology, Section 11.02. 2000, 1999, 1996. ASTM International.

[10] Official Methods of Analysis of AOAC International. 16th Edition, 4th Revision, 1998. AOAC International.

[11] Recommended for enumeration of target organism in sewage sludge.

[12] The multiple-tube fermentation test is used in 9221B.1–2006. Lactose broth may be used in lieu of lauryl tryptose broth (LTB), if at least 25 parallel tests are conducted between this broth and LTB using the water samples normally tested, and this comparison demonstrates that the false-positive rate and false-negative rate for total coliform using lactose broth is less than 10 percent. No requirement exists to run the completed phase on 10 percent of all total coliform-positive tubes on a seasonal basis.

[13] These tests are collectively known as defined enzyme substrate tests, where, for example, a substrate is used to detect the enzyme β-glucuronidase produced by *E. coli.*

[14] After prior enrichment in a presumptive medium for total coliform using 9221B.1–2006, all presumptive tubes or bottles showing any amount of gas, growth or acidity within 48 h ± 3 h of incubation shall be submitted to 9221F–2006. Commercially available EC–MUG media or EC media supplemented in the laboratory with 50 µg/mL of MUG may be used.

[15] Method 1680: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation Using Lauryl-Tryptose Broth (LTB) and EC Medium, EPA–821–R–10–003. April 2010. U.S. EPA.

[16] Samples shall be enumerated by the multiple-tube or multiple-well procedure. Using multiple-tube procedures, employ an appropriate tube and dilution configuration of the sample as needed and report the Most Probable Number (MPN). Samples tested with Colilert® may be enumerated with the multiple-well procedures, Quanti-Tray®, Quanti-Tray®/2000, and the MPN calculated from the table provided by the manufacturer.

[17] Colilert-18® is an optimized formulation of the Colilert® for the determination of total coliforms and *E. coli* that provides results within 18 h of incubation at 35 °C rather than the 24 h required for the Colilert® test and is recommended for marine water samples.

[18] Descriptions of the Colilert®, Colilert-18®, Quanti-Tray®, and Quanti-Tray®/2000 may be obtained from IDEXX Laboratories, Inc.

[19] A description of the mColiBlue24® test, is available from Hach Company.

[20] Method 1681: Fecal Coliforms in Sewage Sludge (Biosolids) by Multiple-Tube Fermentation using A–1 Medium, EPA–821–R–06–013. July 2006. U.S. EPA.

[21] Recommended for enumeration of target organism in wastewater effluent.

[22] Method 1603: *Escherichia coli* (*E. coli*) in Water by Membrane Filtration Using Modified membrane-Thermotolerant *Escherichia coli* Agar (modified mTEC), EPA–821–R–09–007. December 2009. U.S. EPA.

[23] Method 1682: *Salmonella* in Sewage Sludge (Biosolids) by Modified Semisolid Rappaport-Vassiliadis (MSRV) Medium, EPA–821–R–06–014. July 2006. U.S. EPA.

[24] A description of the Enterolert® test may be obtained from IDEXX Laboratories Inc.

[25] Method 1600: Enterococci in Water by Membrane Filtration Using membrane-Enterococcus Indoxyl-β-D–Glucoside Agar (mEI), EPA–821–R–09–016. December 2009. U.S. EPA.

[26] Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms. EPA–821–R–02–012. Fifth Edition, October 2002. U.S. EPA.

[27] Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. EPA–821–R–02–013. Fourth Edition, October 2002. U.S. EPA.

[28] Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. EPA–821–R–02–014. Third Edition, October 2002. U.S. EPA.

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
1. Acidity, as $CaCO_3$, mg/L.	Electrometric endpoint or phenolphthalein endpoint.	.....	2310 B–1997	D1067–06	I–1020–85.[2]
2. Alkalinity, as $CaCO_3$, mg/L.	Electrometric or Colorimetric titration to pH 4.5, Manual.	.....	2320 B–1997	D1067–06	973.43 [3], I–1030–85.[2]
	Automatic	310.2 (Rev. 1974)[1] ..	.....	.....	I–2030–85.[2]
3. Aluminum—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36]	.....	3111 D–1999 or 3111 E–1999.	.....	I–3051–85.[2]
	AA furnace	.....	3113 B–2004.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	Direct Current Plasma (DCP) [36].	.....	.....	D4190–08	See footnote.[34]
	Colorimetric (Eriochrome cyanine R).	.....	3500–Al B–2001.		
4. Ammonia (as N), mg/L.	Manual distillation [6] or gas diffusion (pH > 11), followed by any of the following:	350.1, Rev. 2.0 (1993).	4500–NH_3 B–1997 ..	.....	973.49[3].
	Nesslerization	.....	.....	D1426–08 (A)	973.49[3], I–3520–85.[2]
	Titration	.....	4500–NH_3 C–1997.		
	Electrode	.....	4500–NH_3 D–1997 or E–1997.	D1426–08 (B).	
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	.....	4500–NH_3 F–1997 ...	.....	See footnote.[60]
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.	350.1[30], Rev. 2.0 (1993).	4500–NH_3 G–1997 4500–NH_3 H–1997.	.....	I–4523–85.[2]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Automated electrode	Ion Chromatography	.....	D6919–09	See footnote.[7]
5. Antimony—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–1999.		
	AA furnace	.....	3113 B–2004.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
6. Arsenic–Total,[4] mg/L.	Digestion,[4] followed by any of the following:	206.5 (Issued 1978) [1].			
	AA gaseous hydride	.....	3114 B–2009 or 3114 C–2009	D2972–08 (B)	I–3062–85.[2]
	AA furnace	.....	3113 B–2004	D2972–08 (C)	I–4063–98.[49]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	Colorimetric (SDDC)	.....	3500–As B–1997	D2972–08 (A)	I–3060–85.[2]
7. Barium–Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration [36].	.....	3111 D–1999	.....	I–3084–85.[2]
	AA furnace	.....	3113 B–2004	D4382–02(07).	
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	.....	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP [36]	.....	.....	.....	See footnote.[34]
8. Beryllium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	.....	3111 D–1999 or 3111 E–1999	D3645–08 (A)	I–3095–85.[2]
	AA furnace	.....	3113 B–2004	D3645–08 (B).	
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP	.....	.....	D4190–08	See footnote.[34]
	Colorimetric (aluminon).	.....	See footnote [61].		
9. Biochemical oxygen demand (BOD5), mg/L.	Dissolved Oxygen Depletion.	.....	5210 B–2001	.....	973.44[3], p. 17.[9], I–1578–78,[8] See footnote.[10,63]
10. Boron—Total,[37] mg/L.	Colorimetric (curcumin) ..	.....	4500–B B –2000	.....	I–3112–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP	.....	.....	D4190–08	See footnote.[34]
11. Bromide, mg/L	Electrode	.....	.....	D1246–05	I–1125–85.[2]
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000, C–2000, D–2000.	D4327–03	993.30.[3]
	CIE/UV	.....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
12. Cadmium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].	.....	3111 B–1999 ..... or 3111 C–1999	D3557–02(07) (A or B).	974.27,[3] p. 37.[9], I–3135–85 [2] or I–3136–85.[2]
	AA furnace	.....	3113 B–2004	D3557–02(07) (D)	I–4138–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–1472–85 [2] or I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP[36]	.....	.....	D4190–08	See footnote.[34]
	Voltametry[11]	.....	.....	D3557–02(07) (C).	
	Colorimetric (Dithizone).	.....	3500–Cd-D–1990.		
13. Calcium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999	D511–08(B)	I–3152–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	.....	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP	.....	.....	.....	See footnote.[34]
	Titrimetric (EDTA) ...	.....	3500–Ca B–1997	D511–08 (A).	
	Ion Chromatography	.....	.....	D6919–09.	
14. Carbonaceous biochemical oxygen demand ($CBOD_5$), mg/L[12].	Dissolved Oxygen Depletion with nitrification inhibitor.	.....	5210 B–2001	.....	See footnote.[35,63]
15. Chemical oxygen demand (COD), mg/L.	Titrimetric	410.3 (Rev. 1978)[1] ..	5220 B–1997 ..... or C–1997	D1252–06 (A)	973.46,[3] p. 17,[9] I–3560–85.[2]
	Spectrophotometric, manual or automatic.	410.4, Rev. 2.0 (1993).	5220 D–1997	D1252–06 (B)	See footnotes.[13,14] I–3561–85.[2]
16. Chloride, mg/L	Titrimetric: (silver nitrate)	.....	4500–Cl^- B–1997 ...	D512–04 (B)	I–1183–85.[2]
	(Mercuric nitrate)	.....	4500–Cl^- C–1997 ...	D512–04 (A)	973.51,[3] I–1184–85.[2]
	Colorimetric: manual	.....	.....	.....	I–1187–85.[2]
	Automated (Ferricyanide)	.....	4500–Cl^- E–1997 ...	.....	I–2187–85.[2]
	Potentiometric Titration ..	.....	4500–Cl^- D–1997.		
	Ion Selective Electrode ..	.....	.....	D512–04 (C).	
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or 4110 C–2000	D4327–03	993.30[3] , I–2057–90.[51]
	CIE/UV	.....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
17. Chlorine–Total residual, mg/L.	Amperometric direct	.....	4500–Cl D–2000	D1253–08.	
	Amperometric direct (low level).	.....	4500–Cl E–2000.		
	Iodometric direct	.....	4500–Cl B–2000.		
	Back titration ether end–point[15].	.....	4500–Cl C–2000.		
	DPD–FAS	.....	4500–Cl F–2000.		
	Spectrophotometric, DPD	.....	4500–Cl G–2000.		
	Electrode	.....	.....	.....	See footnote.[16]
17A. Chlorine–Free Available, mg/L.	Amperometric direct	.....	4500–Cl D–2000	D1253–08.	
	Amperometric direct (low level).	.....	4500–Cl E–2000.		
	DPD–FAS	.....	4500–Cl F–2000.		
	Spectrophotometric, DPD	.....	4500–Cl G–2000.		
18. Chromium VI dissolved, mg/L.	0.45-micron Filtration followed by any of the following:				
	AA chelation–extraction.	.....	3111 C–1999	.....	I–1232–85.[2]
	Ion Chromatography	218.6, Rev. 3.3 (1994).	3500–Cr C–2009	D5257–03	993.23.
	Colorimetric (Diphenyl–carbazide).	.....	3500–Cr B–2009	D1687–02(07) (A)	I–1230–85.[2]
19. Chromium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].	.....	3111 B–1999	D1687–02(07) (B)	974.27,[3] I–3236–85.[2]
	AA chelation–extraction.	.....	3111 C–1999.		
	AA furnace	.....	3113 B–2004	D1687–02(07) (C)	I–3233–93.[46]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003),[68] 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP [36]	.....	.....	D4190–08	See footnote.[34]
	Colorimetric (Diphenyl–carbazide).	.....	3500–Cr B–2009.		
20. Cobalt—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999 or 3111 C–1999.	D3558–08 (A or B) ..	p. 37,[9] I–3239–85.[2]
	AA furnace	.....	3113 B–2004	D3558–08 (C)	I–4243–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP	.....	.....	D4190–08	See footnote.[34]
21. Color, platinum cobalt units or dominant wavelength, hue, luminance purity.	Colorimetric (ADMI)	.....	.....	.....	See footnote.[18]
	(Platinum cobalt) ..... Spectrophotometric.	.....	2120 B–2001	.....	I–1250–85.[2]
22. Copper—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–1999 or 3111 C–1999	D1688–07 (A or B) ..	974.27,[3] p. 37,[9] I–3270–85 [2] or I–3271–85.[2]
	AA furnace	.....	3113 B–2004	D1688–07 (C)	I–4274–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP [36]	.....	.....	D4190–08	See footnote.[34]
	Colorimetric (Neocuproine).	.....	3500–Cu B–1999.		
	(Bathocuproine)	.....	3500–Cu C–1999	.....	See footnote.[19]
23. Cyanide—Total, mg/L.	Automated UV digestion/distillation and Colorimetry.	.....	.....	.....	Kelada–01.[55]
	Segmented Flow Injection, In-Line Ultraviolet Digestion, followed by gas diffusion amperometry.	.....	.....	D7511–09.	
	Manual distillation with $MgCl_2$, followed by any of the following:	335.4, Rev. 1.0 (1993) [57].	4500–CN^- B–1999 or C–1999.	D2036–09(A), D7284–08.	10–204–00–1–X.[56]
	Flow Injection, gas diffusion amperometry.	.....	.....	D2036–09(A) D7284–08.	
	Titrimetric	.....	4500–CN^- D–1999	D2036–09(A)	p. 22.[9]
	Spectrophotometric, manual.	.....	4500–CN^- E–1999	D2036–09(A)	I–3300–85.[2]
	Semi-Automated [20] ..	335.4, Rev. 1.0 (1993) [57].	.....	.....	10–204–00–1–X,[56] I–4302–85.[2]
	Ion Chromatography	.....	.....	D2036–09(A).	

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Ion Selective Electrode.	.....	4500–CN^- F–1999	D2036–09(A).	
24. Cyanide–Available, mg/L.	Cyanide Amenable to Chlorination (CATC); Manual distillation with $MgCl_2$, followed by Titrimetric or Spectrophotometric.	.....	4500–CN^- G–1999	D2036–09(B).	
	Flow injection and ligand exchange, followed by gas diffusion amperometry [59].	.....	.....	D6888–09	OIA–1677–09.[44]
	Automated Distillation and Colorimetry (no UV digestion).	.....	.....	.....	Kelada–01.[55]
24.A Cyanide-Free, mg/L.	Flow Injection, followed by gas diffusion amperometry.	.....	.....	D7237–10	OIA–1677–09.[44]
	Manual micro-diffusion and colorimetry.	.....	.....	D4282–02.	
25. Fluoride—Total, mg/L.	Manual distillation,[6] followed by any of the following:	.....	4500–F^- B–1997.		
	Electrode, manual ...	.....	4500–F^- C–1997	D1179–04 (B).	
	Electrode, automated.	.....	.....	.....	I–4327–85.[2]
	Colorimetric, (SPADNS).	.....	4500–F^- D–1997	D1179–04 (A).	
	Automated complexone.	.....	4500–F^- E–1997.		
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV	.....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
26. Gold—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999.		
	AA furnace	231.2 (Issued 1978)[1]	3113 B–2004.		
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP	.....	.....	.....	See footnote.[34]
27. Hardness—Total, as $CaCO_3$, mg/L.	Automated colorimetric ...	130.1 (Issued 1971)[1].			
	Titrimetric (EDTA)	.....	2340 C–1997	D1126–02(07)	973.52B,[3] I–1338–85.[2]
	Ca plus Mg as their carbonates, by inductively coupled plasma or AA direct aspiration. (See Parameters 13 and 33)..	.....	2340 B–1997.		
28. Hydrogen ion (pH), pH units.	Electrometric measurement.	.....	4500–H^+ B–2000	D1293–99 (A or B) ..	973.41,[3] I–1586–85.[2]
	Automated electrode	150.2 (Dec. 1982)[1] ..	.....	.....	See footnote,[21] I–2587–85.[2]
29. Iridium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999.		
	AA furnace	235.2 (Issued 1978)[1].			
	ICP/MS	.....	3125 B–2009.		
30. Iron—Total,[4] mg/L	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–1999 or 3111 C–1999	D1068–05 (A or B) ..	974.27,[3] I–3381–85.[2]
	AA furnace	.....	3113 B–2004	D1068–05 (C).	
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	DCP [36]			D4190–08	See footnote.[34]
	Colorimetric (Phenanthroline).		3500–Fe-1997	D1068–05 (D)	See footnote.[22]
31. Kjeldahl Nitrogen [5]—Total, (as N), mg/L.	Manual digestion [20] and distillation or gas diffusion, followed by any of the following:		4500–N_{org} B–1997 or C–1997 and 4500–NH_3 B–1997.	D3590–02(06) (A)	I–4515–91.[45]
	Titration		4500–NH_3 C–1997		973.48.[3]
	Nesslerization			D1426–08 (A).	
	Electrode		4500–NH_3 D–1997 or E–1997.	D1426–08 (B).	
	Semi-automated phenate.	350.1 Rev 2.0 1993	4500–NH_3 G–1997. 4500–NH_3 H–1997.		
	Manual phenate, salicylate, or other substituted phenols in Berthelot reaction based methods.		4500–NH_3 F–1997		See footnote.[60]
	Automated Methods for TKN that do not require manual distillation				
	Automated phenate, salicylate, or other substituted phenols in Berthelot reaction based methods colorimetric (auto digestion and distillation).	351.1 (Rev. 1978)[1]			I–4551–78.[8]
	Semi-automated block digestor colorimetric (distillation not required).	351.2, Rev. 2.0 (1993).	4500–N_{org} D–1997	D3590–02(06) (B)	I–4515–91.[45]
	Block digester, followed by Auto distillation and Titration.				See footnote.[39]
	Block digester, followed by Auto distillation and Nesslerization.				See footnote.[40]
	Block Digester, followed by Flow injection gas diffusion (distillation not required).				See footnote.[41]
32. Lead—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration [36].		3111 B–1999 or 3111 C–1999.	D3559–08 (A or B)	974.27,[3] I–3399–85.[2]
	AA furnace		3113 B–2004	D3559–08 (D)	I–4403–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP [36]			D4190–08	See footnote.[34]
	Voltametry[11]			D3559–08 (C).	
	Colorimetric (Dithizone).		3500–Pb B–1997.		
33. Magnesium—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration		3111 B–1999	D511–08 (B)	974.27,[3] I–3447–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP				See footnote.[34]
	Gravimetric.				
	Ion Chromatography			D6919–09.	
34. Manganese—Total,[4] mg/L.	Digestion [4] followed by any of the following:				

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	AA direct aspiration [36].	.....	3111 B–1999	D858–07 (A or B)	974.27,[3] I–3454–85.[2]
	AA furnace	.....	3113 B–2004	D858–07 (C).	
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP [36]	.....	.....	D4190–08	See footnote.[34]
	Colorimetric (Persulfate).	.....	3500–Mn B–1999	.....	920.203.[3]
	(Periodate)	.....	.....	.....	See footnote.[23]
35. Mercury—Total,[4] mg/L.	Cold vapor, Manual	245.1, Rev. 3.0 (1994).	3112 B–2009	D3223–02(07)	977.22,[3] I–3462–85.[2]
	Cold vapor, Automated ..	245.2 (Issued 1974)[1].			
	Cold vapor atomic fluorescence spectrometry (CVAFS).	245.7 Rev. 2.0 (2005)[17].	.....	.....	I–4464–01.[71]
	Purge and Trap CVAFS	1631E[43].			
36. Molybdenum—Total,[4] mg/L.	Digestion,[4] followed by any of the following:				
	AA direct aspiration	.....	3111 D–1999	.....	I–3490–85.[2]
	AA furnace	.....	3113 B–2004	.....	I–3492–96.[47]
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4471–97.[50]
	DCP	.....	.....	.....	See footnote.[34]
37. Nickel—Total,[4] mg/L.	Digestion [4] followed by any of the following:				
	AA direct aspiration [36].	.....	3111 B–1999 or 3111 C–1999	D1886–08 (A or B) ..	I–3499–85.[2]
	AA furnace	.....	3113 B–2004	D1886–08 (C)	I–4503–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES [36]	200.5, Rev 4.2 (2003) [68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14,[3] I–4020–05.[70]
	DCP [36]	.....	.....	D4190–08	See footnote.[34]
38. Nitrate (as N), mg/L.	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV	.....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
	Ion Selective Electrode.	.....	4500–NO_3^- D–2000.		
	Colorimetric (Brucine sulfate).	352.1 (Issued 1971)[1]	.....	.....	973.50,[3] 419D[1,7], p. 28.[9]
	Nitrate-nitrite N minus Nitrite N (See parameters 39 and 40).	.....	.....	.....	See footnote.[62]
39. Nitrate-nitrite (as N), mg/L.	Cadmium reduction, Manual.	.....	4500–NO_3^- E–2000	D3867–04 (B).	
	Cadmium reduction, Automated.	353.2, Rev. 2.0 (1993).	4500–NO_3^- F–2000	D3867–04 (A)	I–2545–90.[51]
	Automated hydrazine.	.....	4500–NO_3^- H–2000.		
	Reduction/Colorimetric.	.....	.....	.....	See footnote.[62]
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV	.....	4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
40. Nitrite (as N), mg/L	Spectrophotometric: Manual.	.....	4500–NO_2^- B–2000	.....	See footnote.[25]
	Automated (Diazotization).	.....	.....	.....	I–4540–85[2], See footnote.[62]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Automated (*bypass cadmium reduction).	353.2, Rev. 2.0 (1993).	4500–NO_3^- F–2000	D3867–04 (A)	I–4545–85.[2]
	Manual (*bypass cadmium reduction).		4500–NO_3^- E–2000	D3867–04 (B).	
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
41. Oil and grease—Total recoverable, mg/L.	Hexane extractable material (HEM): n–Hexane extraction and gravimetry.	1664 Rev. A; 1664 Rev. B[42].	5520 B–2001[38].		
	Silica gel treated HEM (SGT–HEM): Silica gel treatment and gravimetry.	1664 Rev. A; 1664 Rev. B[42].	5520 B–2001[38] and 5520 F–2001[38].		
42. Organic carbon—Total (TOC), mg/L.	Combustion		5310 B–2000	D7573–09	973.47[3], p. 14.[24]
	Heated persulfate or UV persulfate oxidation.		5310 C 2000 5310 D 2000.	D4839–03	973.47[3], p. 14.[24]
43. Organic nitrogen (as N), mg/L.	Total Kjeldahl N (Parameter 31) minus ammonia N (Parameter 4).				
44. Ortho-phosphate (as P), mg/L.		Ascorbic acid method:			
	Automated	365.1, Rev. 2.0 (1993).	4500–P F–1999 or G–1999.		973.56[3], I–4601–85.[2]
	Manual single reagent.		4500–P E–1999	D515–88(A)	973.55.[3]
	Manual two reagent	365.3 (Issued 1978)[1].			
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30.[3]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
45. Osmium—Total[4], mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration,		3111 D–1999.		
	AA furnace	252.2 (Issued 1978)[1].			
46. Oxygen, dissolved, mg/L.	Winkler (Azide modification).		4500–O B–2001, C–2001, D–2001, E–2001, F–2001.	D888–09 (A)	973.45B[3], I–1575–78.[8]
	Electrode		4500–O G–2001	D888–09 (B)	I–1576–78.[8]
	Luminescence Based Sensor.			D888–09 (C)	See footnote[63] See footnote.[64]
47. Palladium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999.		
	AA furnace	253.2[1](Issued 1978).			
	ICP/MS		3125 B–2009.		
	DCP				See footnote.[34]
48. Phenols, mg/L	Manual distillation[26], followed by any of the following:	420.1[1](Rev. 1978)	5530 B–2005	D1783–01.	
	Colorimetric (4AAP) manual.	420.1[1](Rev. 1978)	5530 D–2005[27]	D1783–01 (A or B).	
	Automated colorimetric (4AAP).	420.4 Rev. 1.0 (1993).			
49. Phosphorus (elemental), mg/L.	Gas–liquid chromatography.				See footnote.[28]
50. Phosphorus—Total, mg/L.	Digestion[20], followed by any of the following:		4500–P B(5)-1999		973.55.[3]
	Manual	365.3[1](Issued 1978)	4500–P E–1999	D515–88 (A).	
	Automated ascorbic acid reduction.	365.1 Rev. 2.0 (1993).	4500–P F–1999, G–1999, H–1999.		973.56[3], I–4600–85.[2]
	ICP/AES[4, 36]	200.7, Rev. 4.4 (1994).	3120 B–1999		I–4471–97.[50]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	Semi–automated block digestor (TKP digestion).	365.4[1] (Issued 1974)	.....	D515–88 (B)	I–4610–91.[48]
51. Platinum—Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999.		
	AA furnace	255.2 (Issued 1978)[1].			
	ICP/MS	.....	3125 B–2009.		
	DCP	.....	.....	.....	See footnote.[34]
52. Potassium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999	.....	973.53[3], I–3630–85.[2]
	ICP/AES	200.7, Rev. 4.4 (1994).	3120 B–1999.		
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	Flame photometric ..	.....	3500–K B–1997.		
	Electrode	.....	3500–K C–1997.		
	Ion Chromatography	.....	.....	D6919–09.	
53. Residue—Total, mg/L.	Gravimetric, 103–105°	.....	2540 B–1997	.....	I–3750–85.[2]
54. Residue—filterable, mg/L.	Gravimetric, 180°	.....	2540 C–1997	D5907–03	I–1750–85.[2]
55. Residue—non–filterable (TSS), mg/L.	Gravimetric, 103–105° post washing of residue.	.....	2540 D–1997	D5907–03	I–3765–85.[2]
56. Residue—settleable, mg/L.	Volumetric, (Imhoff cone), or gravimetric.	.....	2540 F–1997.		
57. Residue—Volatile, mg/L.	Gravimetric, 550°	160.4 (Issued 1971)[1]	2540–E–1997	.....	I–3753–85.[2]
58. Rhodium—Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration, or.	.....	3111 B–1999.		
	AA furnace	265.2 (Issued 1978)[1].			
	ICP/MS	.....	3125 B–2009.		
59. Ruthenium—Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration, or.	.....	3111 B–1999.		
	AA furnace	267.2[1].			
	ICP/MS	.....	3125 B–2009.		
60. Selenium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA furnace	.....	3113 B–2004	D3859–08 (B)	I–4668–98.[49]
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES[36]	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4020–05.[70]
	AA gaseous hydride	.....	3114 B–2009, or 3111 C–2009.	D3859–08 (A)	I–3667–85.[2]
61. Silica—Dissolved,[37] mg/L.	0.45-micron filtration followed by any of the following:				
	Colorimetric, Manual	.....	4500–SiO_2 C–1997 ..	D859–05	I–1700–85.[2]
	Automated (Molybdosilicate).	.....	4500–SiO_2 E–1997 or F–1997.	.....	I–2700–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	.....	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
62. Silver—Total,[4, 31] mg/L.	Digestion[4, 29], followed by any of the following:				
	AA direct aspiration	.....	3111 B–1999 or 3111 C–1999	.....	974.27[3], p. 37[9], I–3720–85.[2]
	AA furnace	.....	3113 B–2004	.....	I–4724–89.[51]
	STGFAA	200.9, Rev. 2.2 (1994).			

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4471–97.[50]
	DCP				See footnote.[34]
63. Sodium—Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999		973.54[3], I–3735–85.[2]
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999		I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
	DCP				See footnote.[34]
	Flame photometric		3500–Na B–1997.		
	Ion Chromatography			D6919–09.	
64. Specific conductance, micromhos/cm at 25°C.	Wheatstone bridge	120.1[1](Rev. 1982)	2510 B–1997	D1125–95(99) (A)	973.40[3], I–2781–85.[2]
65. Sulfate (as SO_4), mg/L.	Automated colorimetric	375.2, Rev. 2.0 (1993).	4500–SO_4[2] F–1997 or G–1997.		
	Gravimetric		4500–SO_4[2] C–1997 or D–1997.		925.54.[3]
	Turbidimetric		4500–SO_4[2] E–1997.	D516–07.	
	Ion Chromatography	300.0, Rev 2.1 (1993) and 300.1–1, Rev 1.0 (1997).	4110 B–2000 or C–2000.	D4327–03	993.30[3], I–4020–05.[70]
	CIE/UV		4140 B–1997	D6508–00(05)	D6508, Rev. 2.[54]
66. Sulfide (as S), mg/L.	Sample Pretreatment		4500–S^{2-} B, C–2000.		
	Titrimetric (iodine)		4500–S^{2-} F–2000		I–3840–85.[2]
	Colorimetric (methylene blue).		4500–S^{2-} D–2000.		
	Ion Selective Electrode.		4500–S^{2-} G–2000	D4658–08.	
67. Sulfite (as SO_3), mg/L.	Titrimetric (iodine-iodate)		4500–SO_3^{2-} B–2000.		
68. Surfactants, mg/L	Colorimetric (methylene blue).		5540 C–2000	D2330–02.	
69. Temperature, °C	Thermometric		2550 B–2000		See footnote.[32]
70. Thallium–Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 B–1999.		
	AA furnace	279.2[1](Issued 1978)	3113 B–2004.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.7, Rev. 4.4 (1994); 200.5 Rev. 4.2 (2003)[68].	3120 B–1999	D1976–07.	
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4471–97.[50]
71. Tin–Total,[4] mg/L	Digestion[4], followed by any of the following:.				
	AA direct aspiration		3111 B–1999		I–3850–78.[8]
	AA furnace		3113 B–2004.		
	STGFAA	200.9, Rev. 2.2 (1994).			
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).			
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]
72. Titanium–Total,[4] mg/L.	Digestion[4] followed by any of the following:				
	AA direct aspiration		3111 D–1999.		
	AA furnace	283.2[1](Issued 1978).			
	ICP/AES	200.7, Rev. 4.4 (1994).			
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14.[3]

TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter	Methodology [58]	EPA [52]	Standard methods	ASTM	USGS/AOAC/Other
	DCP				See footnote.[34]
73. Turbidity, NTU[53]	Nephelometric	180.1, Rev. 2.0 (1993).	2130 B–2001	D1889–00	I–3860–85.[2] See footnote.[65] See footnote.[66] See footnote.[67]
74. Vanadium–Total,[4] mg/L.	Digestion[4], followed by any of the following:				
	AA direct aspiration		3111 D–1999.		
	AA furnace		3113 B–2004	D3373–03(07).	
	ICP/AES	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4020–05.[70]
	DCP			D4190–08	See footnote.[34]
	Colorimetric (Gallic Acid).		3500–V B–1997.		
75. Zinc–Total[4], mg/L	Digestion[4], followed by any of the following:				
	AA direct aspiration[36].		3111 B–1999 or 3111 C–1999.	D1691–02(07) (A or B).	974.27[3], p. 37[9], I–3900–85.[2]
	AA furnace	289.2[1](Issued 1978).			
	ICP/AES[36]	200.5, Rev 4.2 (2003)[68]; 200.7, Rev. 4.4 (1994).	3120 B–1999	D1976–07	I–4471–97.[50]
	ICP/MS	200.8, Rev. 5.4 (1994).	3125 B–2009	D5673–05	993.14[3], I–4020–05.[70]
	DCP[36]			D4190–08	See footnote.[34]
	Colorimetric (Zincon)		3500 Zn B–1997		See footnote.[33]
76. Acid Mine Drainage.		1627[69].			

Table IB Notes:

[1] Methods for Chemical Analysis of Water and Wastes, EPA–600/4–79–020. Revised March 1983 and 1979, where applicable. U.S. EPA.

[2] Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resource Investigations of the U.S. Geological Survey, Book 5, Chapter A1., unless otherwise stated. 1989. USGS.

[3] Official Methods of Analysis of the Association of Official Analytical Chemists, Methods Manual, Sixteenth Edition, 4th Revision, 1998. AOAC International.

[4] For the determination of total metals (which are equivalent to total recoverable metals) the sample is not filtered before processing. A digestion procedure is required to solubilize analytes in suspended material and to break down organic-metal complexes (to convert the analyte to a detectable form for colorimetric analysis). For non–platform graphite furnace atomic absorption determinations a digestion using nitric acid (as specified in Section 4.1.3 of Methods for the Chemical Analysis of Water and Wastes) is required prior to analysis. The procedure used should subject the sample to gentle, acid refluxing and at no time should the sample be taken to dryness. For direct aspiration flame atomic absorption determinations (FLAA) a combination acid (nitric and hydrochloric acids) digestion is preferred prior to analysis. The approved total recoverable digestion is described as Method 200.2 in Supplement I of ''Methods for the Determination of Metals in Environmental Samples'' EPA/600R–94/111, May, 1994, and is reproduced in EPA Methods 200.7, 200.8, and 200.9 from the same Supplement. However, when using the gaseous hydride technique or for the determination of certain elements such as antimony, arsenic, selenium, silver, and tin by non–EPA graphite furnace atomic absorption methods, mercury by cold vapor atomic absorption, the noble metals and titanium by FLAA, a specific or modified sample digestion procedure may be required and in all cases the referenced method write–up should be consulted for specific instruction and/or cautions. For analyses using inductively coupled plasma-atomic emission spectrometry (ICP–AES), the direct current plasma (DCP) technique or the EPA spectrochemical techniques (platform furnace AA, ICP–AES, and ICP–MS) use EPA Method 200.2 or an approved alternate procedure (*e.g.,* CEM microwave digestion, which may be used with certain analytes as indicated in Table IB); the total recoverable digestion procedures in EPA Methods 200.7, 200.8, and 200.9 may be used for those respective methods. Regardless of the digestion procedure, the results of the analysis after digestion procedure are reported as ''total'' metals.

[5] Copper sulfate or other catalysts that have been found suitable may be used in place of mercuric sulfate.

[6] Manual distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary: however, manual distillation will be required to resolve any controversies. In general, the analytical method should be consulted regarding the need for distillation. If the method is not clear, the laboratory may compare a minimum of 9 different sample matrices to evaluate the need for distillation. For each matrix, a matrix spike and matrix spike duplicate are analyzed both with and without the distillation step. (A total of 36 samples, assuming 9 matrices). If results are comparable, the laboratory may dispense with the distillation step for future analysis. Comparable is defined as < 20% RPD for all tested matrices). Alternatively the two populations of spike recovery percentages may be compared using a recognized statistical test.

[7] Industrial Method Number 379–75 WE Ammonia, Automated Electrode Method, Technicon Auto Analyzer II. February 19, 1976. Bran & Luebbe Analyzing Technologies Inc.

[8] The approved method is that cited in Methods for Determination of Inorganic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A1. 1979. USGS.

[9] American National Standard on Photographic Processing Effluents. April 2, 1975. American National Standards Institute.

[10] In-Situ Method 1003–8–2009, Biochemical Oxygen Demand (BOD) Measurement by Optical Probe. 2009. In-Situ Incorporated.

[11] The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

[12] Carbonaceous biochemical oxygen demand ($CBOD_5$) must not be confused with the traditional BOD_5 test method which measures ''total BOD.'' The addition of the nitrification inhibitor is not a procedural option, but must be included to report the $CBOD_5$ parameter. A discharger whose permit requires reporting the traditional BOD_5 may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states $CBOD_5$ is required can the permittee report data using a nitrification inhibitor.

[13] OIC Chemical Oxygen Demand Method. 1978. Oceanography International Corporation.

[14] Method 8000, Chemical Oxygen Demand, Hach Handbook of Water Analysis, 1979. Hach Company.

[15] The back titration method will be used to resolve controversy.

[16] Orion Research Instruction Manual, Residual Chlorine Electrode Model 97–70. 1977. Orion Research Incorporated. The calibration graph for the Orion residual chlorine method must be derived using a reagent blank and three standard solutions, containing 0.2, 1.0, and 5.0 mL 0.00281 N potassium iodate/100 mL solution, respectively.

[17] Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, EPA–821–R–05–001. Revision 2.0, February 2005. US EPA.

[18] National Council of the Paper Industry for Air and Stream Improvement (NCASI) Technical Bulletin 253, December 1971.

[19] Method 8506, Biocinchoninate Method for Copper, Hach Handbook of Water Analysis. 1979. Hach Company.

[20] When using a method with block digestion, this treatment is not required.

[21] Industrial Method Number 378–75WA, Hydrogen ion (pH) Automated Electrode Method, Bran & Luebbe (Technicon) Autoanalyzer II. October 1976. Bran & Luebbe Analyzing Technologies.

[22] Method 8008, 1,10–Phenanthroline Method using FerroVer Iron Reagent for Water. 1980. Hach Company.

[23] Method 8034, Periodate Oxidation Method for Manganese, Hach Handbook of Wastewater Analysis. 1979. Hach Company.

[24] Methods for Analysis of Organic Substances in Water and Fluvial Sediments, Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 5, Chapter A3, (1972 Revised 1987) p. 14. 1987. USGS.

[25] Method 8507, Nitrogen, Nitrite-Low Range, Diazotization Method for Water and Wastewater. 1979. Hach Company.

[26] Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH.

[27] The colorimetric reaction must be conducted at a pH of 10.0 ± 0.2.

[28] Addison, R.F., and R.G. Ackman. 1970. Direct Determination of Elemental Phosphorus by Gas–Liquid Chromatography, *Journal of Chromatography*, 47(3):421–426.

[29] Approved methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M $Na_2S_2O_3$ and NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the approved method is satisfactory.

[30] The use of EDTA decreases method sensitivity. Analysts may omit EDTA or replace with another suitable complexing reagent provided that all method specified quality control acceptance criteria are met.

[31] For samples known or suspected to contain high levels of silver (*e.g.,* in excess of 4 mg/L), cyanogen iodide should be used to keep the silver in solution for analysis. Prepare a cyanogen iodide solution by adding 4.0 mL of concentrated NH_4OH, 6.5 g of KCN, and 5.0 mL of a 1.0 N solution of I2 to 50 mL of reagent water in a volumetric flask and dilute to 100.0 mL. After digestion of the sample, adjust the pH of the digestate to >7 to prevent the formation of HCN under acidic conditions. Add 1 mL of the cyanogen iodide solution to the sample digestate and adjust the volume to 100 mL with reagent water (NOT acid). If cyanogen iodide is added to sample digestates, then silver standards must be prepared that contain cyanogen iodide as well. Prepare working standards by diluting a small volume of a silver stock solution with water and adjusting the pH≤7 with NH_4OH. Add 1 mL of the cyanogen iodide solution and let stand 1 hour. Transfer to a 100-mL volumetric flask and dilute to volume with water.

[32] ''Water Temperature–Influential Factors, Field Measurement and Data Presentation,'' Techniques of Water-Resources Investigations of the U.S. Geological Survey, Book 1, Chapter D1. 1975. USGS.

[33] Method 8009, Zincon Method for Zinc, Hach Handbook of Water Analysis, 1979. Hach Company.

[34] Method AES0029, Direct Current Plasma (DCP) Optical Emission Spectrometric Method for Trace Elemental Analysis of Water and Wastes. 1986–Revised 1991. Thermo Jarrell Ash Corporation.

[35] In-Situ Method 1004–8–2009, Carbonaceous Biochemical Oxygen Demand (CBOD) Measurement by Optical Probe. 2009. In-Situ Incorporated.

[36] Microwave-assisted digestion may be employed for this metal, when analyzed by this methodology. Closed Vessel Microwave Digestion of Wastewater Samples for Determination of Metals. April 16, 1992. CEM Corporation

[37] When determining boron and silica, only plastic, PTFE, or quartz laboratory ware may be used from start until completion of analysis.

[38] Only use n-hexane (n-Hexane—85% minimum purity, 99.0% min. saturated C6 isomers, residue less than 1 mg/L) extraction solvent when determining Oil and Grease parameters—Hexane Extractable Material (HEM), or Silica Gel Treated HEM (analogous to EPA Methods 1664 Rev. A and 1664 Rev. B). Use of other extraction solvents is prohibited.

[39] Method PAI–DK01, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Titrimetric Detection. Revised December 22, 1994. OI Analytical.

[40] Method PAI–DK02, Nitrogen, Total Kjeldahl, Block Digestion, Steam Distillation, Colorimetric Detection. Revised December 22, 1994. OI Analytical.

[41] Method PAI–DK03, Nitrogen, Total Kjeldahl, Block Digestion, Automated FIA Gas Diffusion. Revised December 22, 1994. OI Analytical.

[42] Method 1664 Rev. B is the revised version of EPA Method 1664 Rev. A. U.S. EPA. February 1999, Revision A. Method 1664, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT–HEM; Non-polar Material) by Extraction and Gravimetry. EPA–821–R–98–002. U.S. EPA. February 2010, Revision B. Method 1664, n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT–HEM; Non-polar Material) by Extraction and Gravimetry. EPA–821–R–10–001.

[43] Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, EPA–821–R–02–019. Revision E. August 2002, U.S. EPA. The application of clean techniques described in EPA's Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels,* EPA–821–R–96–011, are recommended to preclude contamination at low-level, trace metal determinations.

[44] Method OIA–1677–09, Available Cyanide by Ligand Exchange and Flow Injection Analysis (FIA). 2010. OI Analytical.

[45] Open File Report 00–170, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Ammonium Plus Organic Nitrogen by a Kjeldahl Digestion Method and an Automated Photometric Finish that Includes Digest Cleanup by Gas Diffusion. 2000. USGS.

[46] Open File Report 93–449, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Chromium in Water by Graphite Furnace Atomic Absorption Spectrophotometry. 1993. USGS.

[47] Open File Report 97–198, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Molybdenum by Graphite Furnace Atomic Absorption Spectrophotometry. 1997.. USGS.

[48] Open File Report 92–146, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Total Phosphorus by Kjeldahl Digestion Method and an Automated Colorimetric Finish That Includes Dialysis. 1992. USGS.

[49] Open File Report 98–639, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Arsenic and Selenium in Water and Sediment by Graphite Furnace-Atomic Absorption Spectrometry. 1999. USGS.

[50] Open File Report 98–165, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry. 1998. USGS.

[51] Open File Report 93–125, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediments. 1993.. USGS.

[52] Unless otherwise indicated, all EPA methods, excluding EPA Method 300.1–1, are published in U.S. EPA. May 1994. Methods for the Determination of Metals in Environmental Samples, Supplement I, EPA/600/R–94/111; or U.S. EPA. August 1993. Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R–93/100. EPA Method 300.1 is US EPA. Revision 1.0, 1997, including errata cover sheet April 27, 1999. Determination of Inorganic Ions in Drinking Water by Ion Chromatography.

[53] Styrene divinyl benzene beads (*e.g.,* AMCO–AEPA–1 or equivalent) and stabilized formazin (*e.g.,* Hach StablCal™ or equivalent) are acceptable substitutes for formazin.

[54] Method D6508, Test Method for Determination of Dissolved Inorganic Anions in Aqueous Matrices Using Capillary Ion Electrophoresis and Chromate Electrolyte. December 2000. Waters Corp.

[55] Kelada-01, Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate, EPA 821–B–01–009, Revision 1.2, August 2001. US EPA. Note: A 450–W UV lamp may be used in this method instead of the 550–W lamp specified if it provides performance within the quality control (QC) acceptance criteria of the method in a given instrument. Similarly, modified flow cell configurations and flow conditions may be used in the method, provided that the QC acceptance criteria are met.

[56] QuikChem Method 10–204–00–1–X, Digestion and Distillation of Total Cyanide in Drinking and Wastewaters using MICRO DIST and Determination of Cyanide by Flow Injection Analysis. Revision 2.2, March 2005. Lachat Instruments.

[57] When using sulfide removal test procedures described in EPA Method 335.4–1, reconstitute particulate that is filtered with the sample prior to distillation.

[58] Unless otherwise stated, if the language of this table specifies a sample digestion and/or distillation ''followed by'' analysis with a method, approved digestion and/or distillation are required prior to analysis.

[59] Samples analyzed for available cyanide using OI Analytical method OIA–1677–09 or ASTM method D6888–09 that contain particulate matter may be filtered only after the ligand exchange reagents have been added to the samples, because the ligand exchange process converts complexes containing available cyanide to free cyanide, which is not removed by filtration. Analysts are further cautioned to limit the time between the addition of the ligand exchange reagents and sample filtration to no more than 30 minutes to preclude settling of materials in samples.

[60] Analysts should be aware that pH optima and chromophore absorption maxima might differ when phenol is replaced by a substituted phenol as the color reagent in Berthelot Reaction (''phenol-hypochlorite reaction'') colorimetric ammonium determination methods. For example when phenol is used as the color reagent, pH optimum and wavelength of maximum absorbance are about 11.5 and 635 nm, respectively—see, Patton, C.J. and S.R. Crouch. March 1977. Anal. Chem. 49:464–469. These reaction parameters increase to pH > 12.6 and 665 nm when salicylate is used as the color reagent—see, Krom, M.D. April 1980. The Analyst 105:305–316.

[61] If atomic absorption or ICP instrumentation is not available, the aluminon colorimetric method detailed in the 19th Edition of *Standard Methods* may be used. This method has poorer precision and bias than the methods of choice.

[62] Easy (1–Reagent) Nitrate Method, Revision November 12, 2011. Craig Chinchilla.

[63] Hach Method 10360, Luminescence Measurement of Dissolved Oxygen in Water and Wastewater and for Use in the Determination of BOD_5 and $cBOD_5$. Revision 1.2, October 2011. Hach Company. This method may be used to measure dissolved oxygen when performing the methods approved in Table IB for measurement of biochemical oxygen demand (BOD) and carbonaceous biochemical oxygen demand (CBOD).

[64] In-Situ Method 1002–8–2009, Dissolved Oxygen (DO) Measurement by Optical Probe. 2009. In-Situ Incorporated.

[65] Mitchell Method M5331, Determination of Turbidity by Nephelometry. Revision 1.0, July 31, 2008. Leck Mitchell.

[66] Mitchell Method M5271, Determination of Turbidity by Nephelometry. Revision 1.0, July 31, 2008. Leck Mitchell.

[67] Orion Method AQ4500, Determination of Turbidity by Nephelometry. Revision 5, March 12, 2009. Thermo Scientific.

[68] EPA Method 200.5, Determination of Trace Elements in Drinking Water by Axially Viewed Inductively Coupled Plasma-Atomic Emission Spectrometry, EPA/600/R–06/115. Revision 4.2, October 2003. US EPA.

[69] Method 1627, Kinetic Test Method for the Prediction of Mine Drainage Quality, EPA–821–R–09–002. December 2011. US EPA.

[70] Techniques and Methods Book 5–B1, Determination of Elements in Natural-Water, Biota, Sediment and Soil Samples Using Collision/Reaction Cell Inductively Coupled Plasma-Mass Spectrometry, Chapter 1, Section B, Methods of the National Water Quality Laboratory, Book 5, Laboratory Analysis, 2006. USGS.

[71] Water-Resources Investigations Report 01–4132, Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Organic Plus Inorganic Mercury in Filtered and Unfiltered Natural Water With Cold Vapor-Atomic Fluorescence Spectrometry, 2001. USGS.

TABLE IC—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

Parameter [1]	Method	EPA [2,7]	Standard methods	ASTM	Other
1. Acenaphthene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98)	
2. Acenaphthylene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
3. Acrolein	GC	603.			
	GC/MS	624 [4], 1624B.			
4. Acrylonitrile	GC	603.			
	GC/MS	624 [4], 1624B.			
5. Anthracene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440B–2000	D4657–92 (98).	
6. Benzene	GC	602	6200 C–1997.		
	GC/MS	624, 1624B	6200 B–1997.		
7. Benzidine	Spectro-photo-metric.				See footnote [3], p.1.
	GC/MS	625 [5], 1625B	6410 B–2000.		
	HPLC	605.			
8. Benzo(a)anthracene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
9. Benzo(a)pyrene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
10. Benzo(b)fluoranthene	GC	610.			
	GC/MS	625, 1625B	6410 B–2000		See footnote [9], p. 27.
	HPLC	610	6440 B–2000	D4657–92 (98).	
11. Benzo(g,h,i)perylene	GC	610.			

provided to assure such changes in sample preservation, containers or holding times do not adversely affect the integrity of the sample. The Regional ATP Coordinator or permitting authority will review the application and then notify the applicant and the appropriate State agency of approval or rejection of the use of the alternate test procedure. A decision to approve or deny any request on deviations from the prescribed Table II requirements will be made within 90 days of receipt of the application by the Regional Administrator. An analyst may not modify any sample preservation and/or holding time requirements of an approved method unless the requirements of this section are met.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter number/name	Container [1]	Preservation [2,3]	Maximum holding time [4]
Table IA—Bacterial Tests:			
1–5. Coliform, total, fecal, and *E. coli*	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22,23]
6. Fecal streptococci	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
7. Enterococci	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
8. *Salmonella*	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
Table IA—Aquatic Toxicity Tests:			
9–12. Toxicity, acute and chronic	P, FP, G	Cool, ≤6 °C [16]	36 hours.
Table IB—Inorganic Tests:			
1. Acidity	P, FP, G	Cool, ≤6 °C [18]	14 days.
2. Alkalinity	P, FP, G	Cool, ≤6 °C [18]	14 days.
4. Ammonia	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
9. Biochemical oxygen demand	P, FP, G	Cool, ≤6 °C [18]	48 hours.
10. Boron	P, FP, or Quartz	HNO_3 to pH <2	6 months.
11. Bromide	P, FP, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, FP G	Cool, ≤6 °C [18]	48 hours.
15. Chemical oxygen demand	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
16. Chloride	P, FP, G	None required	28 days.
17. Chlorine, total residual	P, G	None required	Analyze within 15 minutes.
21. Color	P, FP, G	Cool, ≤6 °C [18]	48 hours.
23–24. Cyanide, total or available (or CATC) and free.	P, FP, G	Cool, ≤6 °C [18], NaOH to pH >10 [5,6], reducing agent if oxidizer present.	14 days.
25. Fluoride	P	None required	28 days.
27. Hardness	P, FP, G	HNO_3 or H_2SO_4 to pH <2	6 months.
28. Hydrogen ion (pH)	P, FP, G	None required	Analyze within 15 minutes.
31, 43. Kjeldahl and organic N	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2.	28 days.
Table IB—Metals: [7]			
18. Chromium VI	P, FP, G	Cool, ≤6 °C[18], pH = 9.3–9.7 [20].	28 days.
35. Mercury (CVAA)	P, FP, G	HNO_3 to pH <2	28 days.
35. Mercury (CVAFS)	FP, G; and FP-lined cap [17]	5 mL/L 12N HCl or 5 mL/L BrCl [17].	90 days.[17]
3, 5–8, 12, 13, 19, 20, 22, 26, 29, 30, 32–34, 36, 37, 45, 47, 51, 52, 58–60, 62, 63, 70–72, 74, 75. Metals, except boron, chromium VI, and mercury.	P, FP, G	HNO_3 to pH <2, or at least 24 hours prior to analysis [19].	6 months.
38. Nitrate	P, FP, G	Cool, ≤6 °C [18]	48 hours.
39. Nitrate-nitrite	P, FP, G	Cool, ≤6 °C[18], H_2SO_4 to pH <2.	28 days.
40. Nitrite	P, FP, G	Cool, ≤6 °C [18]	48 hours.
41. Oil and grease	G	Cool to ≤6 °C[18], HCl or H_2SO_4 to pH <2.	28 days.
42. Organic Carbon	P, FP, G	Cool to ≤6 °C [18], HCl, H_2SO_4, or H_3PO_4 to pH <2.	28 days.
44. Orthophosphate	P, FP, G	Cool, to ≤6 °C [18,24]	Filter within 15 minutes; Analyze within 48 hours.
46. Oxygen, Dissolved Probe	G, Bottle and top	None required	Analyze within 15 minutes.
47. Winkler	G, Bottle and top	Fix on site and store in dark.	8 hours.
48. Phenols	G	Cool, ≤6 °C[18], H_2SO_4 to pH <2.	28 days.
49. Phosphorous (elemental)	G	Cool, ≤6 °C [18]	48 hours.
50. Phosphorous, total	P, FP, G	Cool, ≤6 °C [18], H_2SO_4 to pH <2.	28 days.
53. Residue, total	P, FP, G	Cool, ≤6 °C [18]	7 days.
54. Residue, Filterable	P, FP, G	Cool, ≤6 °C [18]	7 days.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES—Continued

Parameter number/name	Container [1]	Preservation [2,3]	Maximum holding time [4]
55. Residue, Nonfilterable (TSS)	P, FP, G	Cool, ≤6 °C [18]	7 days.
56. Residue, Settleable	P, FP, G	Cool, ≤6 °C [18]	48 hours.
57. Residue, Volatile	P, FP, G	Cool, ≤6 °C [18]	7 days.
61. Silica	P or Quartz	Cool, ≤6 °C [18]	28 days.
64. Specific conductance	P, FP, G	Cool, ≤6 °C [18]	28 days.
65. Sulfate	P, FP, G	Cool, ≤6 °C [18]	28 days.
66. Sulfide	P, FP, G	Cool, ≤6 °C [18], add zinc acetate plus sodium hydroxide to pH >9.	7 days.
67. Sulfite	P, FP, G	None required	Analyze within 15 minutes.
68. Surfactants	P, FP, G	Cool, ≤6 °C [18]	48 hours.
69. Temperature	P, FP, G	None required	Analyze.
73. Turbidity	P, FP, G	Cool, ≤6 °C [18]	48 hours.
Table IC—Organic Tests: [8]	.		
13, 18–20, 22, 24–28, 34–37, 39–43, 45–47, 56, 76, 104, 105, 108–111, 113. Purgeable Halocarbons.	G, FP-lined septum	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5].	14 days.
6, 57, 106. Purgeable aromatic hydrocarbons	G, FP-lined septum	Cool, ≤6 °C[18], 0.008% $Na_2S_2O_3$ [5], HCl to pH 2 [9].	14 days.[9]
3, 4. Acrolein and acrylonitrile	G, FP-lined septum	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$, pH to 4–5[10].	14 days.[10]
23, 30, 44, 49, 53, 77, 80, 81, 98, 100, 112. Phenols [11].	G, FP-lined cap	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$.	7 days until extraction, 40 days after extraction.
7, 38. Benzidines [11,12]	G, FP-lined cap	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5].	7 days until extraction.[13]
14, 17, 48, 50–52. Phthalate esters [11]	G, FP-lined cap	Cool, ≤6 °C [18]	7 days until extraction, 40 days after extraction.
82–84. Nitrosamines [11,14]	G, FP-lined cap	Cool, ≤6 °C[18], store in dark, 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
88–94. PCBs [11]	G, FP-lined cap	Cool, ≤6 °C [18]	1 year until extraction, 1 year after extraction.
54, 55, 75, 79. Nitroaromatics and isophorone [11]	G, FP-lined cap	Cool, ≤6 °C [18], store in dark, 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
1, 2, 5, 8–12, 32, 33, 58, 59, 74, 78, 99, 101. Polynuclear aromatic hydrocarbons [11].	G, FP-lined cap	Cool, ≤6 °C [18], store in dark, 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
15, 16, 21, 31, 87. Haloethers [11]	G, FP-lined cap	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5].	7 days until extraction, 40 days after extraction.
29, 35–37, 63–65, 107. Chlorinated hydrocarbons [11].	G, FP-lined cap	Cool, ≤6 °C [18]	7 days until extraction, 40 days after extraction.
60–62, 66–72, 85, 86, 95–97, 102, 103. CDDs/CDFs [11].	.		
Aqueous Samples: Field and Lab Preservation	G	Cool, ≤6 °C [18], 0.008% $Na_2S_2O_3$[5], pH <9.	1 year.
Solids and Mixed-Phase Samples: Field Preservation.	G	Cool, ≤6 °C [18]	7 days.
Tissue Samples: Field Preservation	G	Cool, ≤6 °C [18]	24 hours.
Solids, Mixed-Phase, and Tissue Samples: Lab Preservation.	G	Freeze, ≤ −10 °C	1 year.
114–118. Alkylated phenols	G	Cool, <6 °C, H_2SO_4 to pH <2.	28 days until extraction, 40 days after extraction.
119. Adsorbable Organic Halides (AOX)	G	Cool, <6 °C, 0.008% $Na_2S_2O_3$ HNO_3 to pH <2.	Hold *at least* 3 days, but not more than 6 months.
120. Chlorinated Phenolics		Cool, <6 °C, 0.008% $Na_2S_2O_3$ H_2SO_4 to pH <2.	30 days until acetylation, 30 days after acetylation.
Table ID—Pesticides Tests:			
1–70. Pesticides [11]	G, FP-lined cap	Cool, ≤6 °C[18], pH 5–9–[15]	7 days until extraction, 40 days after extraction.
Table IE—Radiological Tests:			
1–5. Alpha, beta, and radium	P, FP, G	HNO_3 to pH <2	6 months.
Table IH—Bacterial Tests:			
1. *E. coli*	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$[5].	8 hours.[22]
2. Enterococci	PA, G	Cool, <10 °C, 0.0008% $Na_2S_2O_3$ [5].	8 hours.[22]
Table IH—Protozoan Tests:	.		
8. *Cryptosporidium*	LDPE; field filtration	1–10 °C	96 hours.[21]
9. *Giardia*	LDPE; field filtration	1–10 °C	96 hours.[21]

[1] "P" is for polyethylene; "FP" is fluoropolymer (polytetrafluoroethylene (PTFE); Teflon®), or other fluoropolymer, unless stated otherwise in this Table II; "G" is glass; "PA" is any plastic that is made of a sterilizable material (polypropylene or other autoclavable plastic); "LDPE" is low density polyethylene.

[2] Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sample (*e.g.,* using a 24-hour composite sample; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), refrigerate the sample at ≤ 6 °C during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the sample at ≤ 6 °C, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or aliquot split from a composite sample within 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (*e.g.,* 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664 Rev. A (oil and grease) and the procedures at 40 CFR 141.34(f)(14)(iv) and (v) (volatile organics).

[3] When any sample is to be shipped by common carrier or sent via the U.S. Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirement of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater; Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[4] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before the start of analysis and still be considered valid. Samples may be held for longer periods only if the permittee or monitoring laboratory has data on file to show that, for the specific types of samples under study, the analytes are stable for the longer time, and has received a variance from the Regional Administrator under Sec. 136.3(e). For a grab sample, the holding time begins at the time of collection. For a composite sample collected with an automated sampler (*e.g.,* using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR part 403, Appendix E), the holding time begins at the time of the end of collection of the composite sample. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set. Some samples may not be stable for the maximum time period given in the table. A permittee or monitoring laboratory is obligated to hold the sample for a shorter time if it knows that a shorter time is necessary to maintain sample stability. See 136.3(e) for details. The date and time of collection of an individual grab sample is the date and time at which the sample is collected. For a set of grab samples to be composited, and that are all collected on the same calendar date, the date of collection is the date on which the samples are collected. For a set of grab samples to be composited, and that are collected across two calendar dates, the date of collection is the dates of the two days; *e.g.,* November 14–15. For a composite sample collected automatically on a given date, the date of collection is the date on which the sample is collected. For a composite sample collected automatically, and that is collected across two calendar dates, the date of collection is the dates of the two days; *e.g.,* November 14–15. For static-renewal toxicity tests, each grab or composite sample may also be used to prepare test solutions for renewal at 24 h, 48 h, and/or 72 h after first use, if stored at 0–6 °C, with minimum head space.

[5] ASTM D7365–09a specifies treatment options for samples containing oxidants (e.g., chlorine). Also, Section 9060A of Standard Methods for the Examination of Water and Wastewater (20th and 21st editions) addresses dechlorination procedures.

[6] Sampling, preservation and mitigating interferences in water samples for analysis of cyanide are described in ASTM D7365–09a. There may be interferences that are not mitigated by the analytical test methods or D7365–09a. Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal or suppression technique not described in D7365–09a or the analytical test method must be documented along with supporting data.

[7] For dissolved metals, filter grab samples within 15 minutes of collection and before adding preservatives. For a composite sample collected with an automated sampler (*e.g.,* using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), filter the sample within 15 minutes after completion of collection and before adding preservatives. If it is known or suspected that dissolved sample integrity will be compromised during collection of a composite sample collected automatically over time (*e.g.,* by interchange of a metal between dissolved and suspended forms), collect and filter grab samples to be composited (footnote 2) in place of a composite sample collected automatically.

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

[9] If the sample is not adjusted to pH 2, then the sample must be analyzed within seven days of sampling.

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

[11] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity (*i.e.,* use all necessary preservatives and hold for the shortest time listed). When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to ≤ 6 °C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6–9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (regarding the requirement for thiosulfate reduction), and footnotes 12, 13 (regarding the analysis of benzidine).

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

[13] Extracts may be stored up to 30 days at < 0 °C.

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7–10 with NaOH within 24 hours of sampling.

[15] The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

[16] Place sufficient ice with the samples in the shipping container to ensure that ice is still present when the samples arrive at the laboratory. However, even if ice is present when the samples arrive, immediately measure the temperature of the samples and confirm that the preservation temperature maximum has not been exceeded. In the isolated cases where it can be documented that this holding temperature cannot be met, the permittee can be given the option of on-site testing or can request a variance. The request for a variance should include supportive data which show that the toxicity of the effluent samples is not reduced because of the increased holding temperature. Aqueous samples must not be frozen. Hand-delivered samples used on the day of collection do not need to be cooled to 0 to 6 °C prior to test initiation.

[17] Samples collected for the determination of trace level mercury (<100 ng/L) using EPA Method 1631 must be collected in tightly-capped fluoropolymer or glass bottles and preserved with BrCl or HCl solution within 48 hours of sample collection. The time to preservation may be extended to 28 days if a sample is oxidized in the sample bottle. A sample collected for dissolved trace level mercury should be filtered in the laboratory within 24 hours of the time of collection. However, if circumstances preclude overnight shipment, the sample should be filtered in a designated clean area in the field in accordance with procedures given in Method 1669. If sample integrity will not be maintained by shipment to and filtration in the laboratory, the sample must be filtered in a designated clean area in the field within the time period necessary to maintain sample integrity. A sample that has been collected for determination of total or dissolved trace level mercury must be analyzed within 90 days of sample collection.

[18] Aqueous samples must be preserved at ≤ 6 °C, and should not be frozen unless data demonstrating that sample freezing does not adversely impact sample integrity is maintained on file and accepted as valid by the regulatory authority. Also, for purposes of NPDES monitoring, the specification of "≤ °C" is used in place of the "4 °C" and "< 4 °C" sample temperature requirements listed in some methods. It is not necessary to measure the sample temperature to three significant figures (1/100th of 1 degree); rather, three significant figures are specified so that rounding down to 6 °C may not be used to meet the ≤6 °C requirement. The preservation temperature does not apply to samples that are analyzed immediately (less than 15 minutes).

[19] An aqueous sample may be collected and shipped without acid preservation. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. If the sample must be analyzed within 24 hours of collection, add the acid immediately (see footnote 2). Soil and sediment samples do not need to be preserved with acid. The allowances in this footnote supersede the preservation and holding time requirements in the approved metals methods.

[20] To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

[21] Holding time is calculated from time of sample collection to elution for samples shipped to the laboratory in bulk and calculated from the time of sample filtration to elution for samples filtered in the field.

[22] Sample analysis should begin as soon as possible after receipt; sample incubation must be started no later than 8 hours from time of collection.

[23] For fecal coliform samples for sewage sludge (biosolids) only, the holding time is extended to 24 hours for the following sample types using either EPA Method 1680 (LTB–EC) or 1681 (A–1): Class A composted, Class B aerobically digested, and Class B anaerobically digested.

[24] The immediate filtration requirement in orthophosphate measurement is to assess the dissolved or bio-available form of orthophosphorus (*i.e.,* that which passes through a 0.45-micron filter), hence the requirement to filter the sample immediately upon collection (*i.e.,* within 15 minutes of collection).

■ 4. Section 136.4 is revised to read as follows:

§ 136.4 Application for and approval of alternate test procedures for nationwide use.

(a) A written application for review of an alternate test procedure (alternate method) for nationwide use may be made by letter via email or by hard copy in triplicate to the National Alternate Test Procedure (ATP) Program Coordinator (National Coordinator), Office of Science and Technology (4303T), Office of Water, U.S. Environmental Protection Agency, 1200 Pennsylvania Ave. NW., Washington, DC 20460. Any application for an alternate test procedure (ATP) under this paragraph (a) shall:

(1) Provide the name and address of the responsible person or firm making the application.

(2) Identify the pollutant(s) or parameter(s) for which nationwide approval of an alternate test procedure is being requested.

(3) Provide a detailed description of the proposed alternate test procedure, together with references to published or other studies confirming the general applicability of the alternate test procedure for the analysis of the pollutant(s) or parameter(s) in wastewater discharges from representative and specified industrial or other categories.

(4) Provide comparability data for the performance of the proposed alternative test procedure compared to the performance of the reference method.

(b) The National Coordinator may request additional information and analyses from the applicant in order to determine whether the alternate test procedure satisfies the applicable requirements of this Part.

(c) *Approval for nationwide use.* (1) After a review of the application and any additional analyses requested from the applicant, the National Coordinator will notify the applicant, in writing, of acceptance or rejection of the alternate test procedure for nationwide use in CWA programs. If the application is not approved, the National Coordinator will specify what additional information might lead to a reconsideration of the application, and notify the Regional Alternate Test Procedure Coordinators of such rejection. Based on the National Coordinator's rejection of a proposed alternate test procedure and an assessment of any approvals for limited uses for the unapproved method, the Regional ATP Coordinator or permitting authority may decide to withdraw approval of the method for limited use in the Region.

(2) Where the National Coordinator approved an applicant's request for nationwide use of an alternate test procedure, the National Coordinator will notify the applicant that the National Coordinator will recommend rulemaking to approve the alternate test procedure. The National Coordinator will notify the Regional ATP Coordinator or permitting authorities that they may consider approval of this alternate test procedure for limited use in their Regions based on the information and data provided in the applicant's application. The Regional ATP Coordinator or permitting authority will grant approval on a case-by-case basis prior to use of the alternate test procedure for compliance analyses until the alternate test procedure is approved by publication in a final rule in the **Federal Register**.

(3) EPA will propose to amend 40 CFR Part 136 to include the alternate test procedure in § 136.3. EPA shall make available for review all the factual bases for its proposal, including any performance data submitted by the applicant and any available EPA analysis of those data.

(4) Following public comment, EPA shall publish in the **Federal Register** a final decision on whether to amend 40 CFR Part 136 to include the alternate test procedure as an approved analytical method.

(5) Whenever the National Coordinator has approved an applicant's request for nationwide use of an alternate test procedure, any person may request an approval of the method for limited use under § 136.5 from the EPA Region.

■ 5. Section 136.5 is revised to read as follows:

§ 136.5 Approval of alternate test procedures for limited use.

(a) Any person may request the Regional Alternate Test Procedure (ATP) Coordinator or permitting authority to approve the use of an alternate test procedure in the Region.

(b) When the request for the use of an alternate test procedure concerns use in a State with an NPDES permit program approved pursuant to section 402 of the Act, the requestor shall first submit an application for limited use to the Director of the State agency having responsibility for issuance of NPDES permits within such State (*i.e.,* permitting authority). The Director will forward the application to the Regional ATP Coordinator or permitting authority with a recommendation for or against approval.

(c) Any application for approval of an alternate test procedure for limited use may be made by letter, email or by hard copy. The application shall include the following:

(1) Provide the name and address of the applicant and the applicable ID number of the existing or pending permit and issuing agency for which use of the alternate test procedure is requested, and the discharge serial number.

(2) Identify the pollutant or parameter for which approval of an alternate test procedure is being requested.

(3) Provide justification for using testing procedures other than those specified in Tables IA through IH of § 136.3, or in the NPDES permit.

(4) Provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

phosphorus, as long as complete oxidation can be demonstrated.

(xxii) Use of an axially viewed torch with Method 200.7.

■ 7. Add new § 136.7 to read as follows:

§ 136.7 Quality assurance and quality control.

The permittee/laboratory shall use suitable QA/QC procedures when conducting compliance analyses with any Part 136 chemical method or an alternative method specified by the permitting authority. These QA/QC procedures are generally included in the analytical method or may be part of the methods compendium for approved Part 136 methods from a consensus organization. For example, Standard Methods contains QA/QC procedures in the Part 1000 section of the Standard Methods Compendium. The permittee/laboratory shall follow these QA/QC procedures, as described in the method or methods compendium. If the method lacks QA/QC procedures, the permittee/laboratory has the following options to comply with the QA/QC requirements:

(a) Refer to and follow the QA/QC published in the ''equivalent'' EPA method for that parameter that has such QA/QC procedures;

(b) Refer to the appropriate QA/QC section(s) of an approved Part 136 method from a consensus organization compendium;

(c)(1) Incorporate the following twelve quality control elements, where applicable, into the laboratory's documented standard operating procedure (SOP) for performing compliance analyses when using an approved Part 136 method when the method lacks such QA/QC procedures. One or more of the twelve QC elements may not apply to a given method and may be omitted if a written rationale is provided indicating why the element(s) is/are inappropriate for a specific method.

(i) Demonstration of Capability (DOC);

(ii) Method Detection Limit (MDL);

(iii) Laboratory reagent blank (LRB), also referred to as method blank (MB);

(iv) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);

(v) Matrix spike (MS) and matrix spike duplicate (MSD), or laboratory fortified matrix (LFM) and LFM duplicate, may be used for suspected matrix interference problems to assess precision;

(vi) Internal standards (for GC/MS analyses), surrogate standards (for organic analysis) or tracers (for radiochemistry);

(vii) Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);

(viii) Control charts (or other trend analyses of quality control results);

(ix) Corrective action (root cause analysis);

(x) QC acceptance criteria;

(xi) Definitions of preparation and analytical batches that may drive QC frequencies; and

(xii) Minimum frequency for conducting all QC elements.

(2) These twelve quality control elements must be clearly documented in the written standard operating procedure for each analytical method not containing QA/QC procedures, where applicable.

■ 8. Revise Appendix C to Part 136 to read as follows.

APPENDIX C TO PART 136—DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA–ATOMIC EMISSION SPECTROMETRY METHOD 200.7

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP–AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1–4] (For analysis of petroleum products see References 5 and 6, Section 16.0). This method is applicable to the following analytes:

Analyte	Chemical abstract services registry number (CASRN)
Aluminum (Al)	7429–90–5
Antimony (Sb)	7440–36–0
Arsenic (As)	7440–38–2
Barium (Ba)	7440–39–3
Beryllium (Be)	7440–41–7
Boron (B)	7440–42–8
Cadmium (Cd)	7440–43–9
Calcium (Ca)	7440–70–2
Cerium [a] (Cr)	7440–45–1
Chromium (Cr)	7440–47–3
Cobalt (Co)	7440–48–4
Copper (Cu)	7440–50–8
Iron (Fe)	7439–89–6
Lead (Pb)	7439–92–1
Lithium (Li)	7439–93–2
Magnesium (Mg)	7439–95–4
Manganese (Mn)	7439–96–5
Mercury (Hg)	7439–97–6
Molybdenum (Mo)	7439–98–7
Nickel (Ni)	7440–02–0
Phosphorus (P)	7723–14–0
Potassium (K)	7440–09–7
Selenium (Se)	7782–49–2
Silica [b] (SiO_2)	7631–86–9
Silver (Ag)	7440–22–4
Sodium (Na)	7440–23–5
Strontium (Sr)	7440–24–6
Thallium (Tl)	7440–28–0
Tin (Sn)	7440–31–5
Titanium (Ti)	7440–32–6
Vanadium (V)	7440–62–2
Zinc (Zn)	7440–66–6

[a] Cerium has been included as method analyte for correction of potential interelement spectral interference.

[b] This method is *not* suitable for the determination of silica in solids.

1.2 For reference where this method is approved for use in compliance monitoring programs [*e.g.,* Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest **Federal Register** announcements.

1.3 ICP–AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as ''direct analysis''. However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (*e.g.,* soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by ''direct analysis'' where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver.

STATE OF TENNESSEE

NPDES PERMIT

No. TN00.....

Authorization to discharge under the
National Pollutant Discharge Elimination System (NPDES)

Issued By

STATE OF TENNESSEE
DEPARTMENT OF ENVIRONMENT AND CONSERVATION
DIVISION OF WATER RESOURCES
William R. Snodgrass - Tennessee Tower
312 Rosa L. Parks Avenue, 11th Floor
Nashville, Tennessee 37243-1102

Under authority of the Tennessee Water Quality Control Act of 1977 (T.C.A. 69-3-101 et seq.) and the delegation of authority from the United States Environmental Protection Agency under the Federal Water Pollution Control Act, as amended by the Clean Water Act of 1977 (33 U.S.C. 1251, et seq.)

Discharger:

is authorized to discharge:

from a facility located:

to receiving waters named:

in accordance with effluent limitations, monitoring requirements and other conditions set forth herein.

This permit shall become effective on:

This permit shall expire on:

Issuance date:

_____
for Tisha Calabrese Benton
Director

CN-0759

RDA 2366

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TN0056332PMT.DOC

Nitrogen, Ammonia total (as N)	<=	2.8	mg/L	Composite	Three Per Week	Weekly Average

Description : External Outfall, Number : 001, Monitoring : Percent Removal, Season : All Year

Parameter	Qualifier	Value	Unit	Sample Type	Frequency	Statistical Base
CBOD, 5-day, 20 C, % removal	>=	40	%	Calculated	Three Per Week	Daily Minimum
CBOD, 5-day, 20 C, % removal	>=	85	%	Calculated	Three Per Week	Monthly Average Minimum
TSS, % removal	>=	85	%	Calculated	Three Per Week	Monthly Average Minimum
TSS, % removal	>=	40	%	Calculated	Three Per Week	Daily Minimum

Description : External Outfall, Number : 001, Monitoring : Raw Sewage Influent, Season : All Year

Parameter	Qualifier	Value	Unit	Sample Type	Frequency	Statistical Base
CBOD, 5-day, 20 C	Report	-	mg/L	Composite	Three Per Week	Monthly Average
CBOD, 5-day, 20 C	Report	-	mg/L	Composite	Three Per Week	Daily Maximum
Flow	Report	-	Mgal/d	Continuous	Daily	Daily Maximum
Flow	Report	-	Mgal/d	Continuous	Daily	Monthly Average
Total Suspended Solids (TSS)	Report	-	mg/L	Composite	Three Per Week	Monthly Average
Total Suspended Solids (TSS)	Report	-	mg/L	Composite	Three Per Week	Daily Maximum

Description : External Outfall, Number : 001, Monitoring : Wet Weather, Season : All Year

Parameter	Qualifier	Value	Unit	Sample Type	Frequency	Statistical Base
Bypass of Treatment	Report	-	occur/mo	Occurrences	Continuous	Monthly Total
Overflow use, occurrences	Report	-	occur/mo	Occurrences	Continuous	Monthly Total

Note: The permittee shall achieve 85% removal of $CBOD_5$ and TSS on a monthly average basis. The permittee shall report all instances of overflow and/or bypasses. See Part 2.3.3.a for the definition of overflow and Part 1.3.5.1 for reporting requirements.

Note: Unless elsewhere specified, summer months are May through October; winter months are November through April.

Note: See Part 1.2.3 for test procedures.

Note: See Part 3.4 for biomonitoring test and reporting requirements. See next page for percent removal calculations.

Total Suspended Solids (TSS)	<=	34	mg/L	Composite	Three Per Week	Daily Maximum
pH	>=	6	SU	Grab	Five Per Week	Minimum
pH	<=	9	SU	Grab	Five Per Week	Maximum

Description : External Outfall, Number : 001, Monitoring : Effluent Gross, Season : Summer

Parameter	Qualifier	Value	Unit	Sample Type	Frequency	Statistical Base
CBOD, 5-day, 20 C	<=	11.2	mg/L	Composite	Three Per Week	Monthly Average
CBOD, 5-day, 20 C	<=	20	mg/L	Composite	Three Per Week	Daily Maximum
CBOD, 5-day, 20 C	<=	15	mg/L	Composite	Three Per Week	Weekly Average
CBOD, 5-day, 20 C	<=	375	lb/d	Composite	Three Per Week	Monthly Average
CBOD, 5-day, 20 C	<=	500	lb/d	Composite	Three Per Week	Weekly Average
Nitrogen, Ammonia total (as N)	<=	52.5	lb/d	Composite	Three Per Week	Weekly Average
Nitrogen, Ammonia total (as N)	<=	2	mg/L	Composite	Three Per Week	Daily Maximum
Nitrogen, Ammonia total (as N)	<=	1	mg/L	Composite	Three Per Week	Monthly Average
Nitrogen, Ammonia total (as N)	<=	1.6	mg/L	Composite	Three Per Week	Weekly Average
Nitrogen, Ammonia total (as N)	<=	35	lb/d	Composite	Three Per Week	Monthly Average
Nitrogen, total (as N)	Report	-	mg/L	Composite	Twice Per Month	Daily Maximum
Nitrogen, total (as N)	<=	4	mg/L	Composite	Twice Per Month	Monthly Average
Phosphorus, total (as P)	Report	-	mg/L	Composite	Twice Per Month	Daily Maximum
Phosphorus, total (as P)	<=	3	mg/L	Composite	Twice Per Month	Monthly Average

Description : External Outfall, Number : 001, Monitoring : Effluent Gross, Season : Winter

Parameter	Qualifier	Value	Unit	Sample Type	Frequency	Statistical Base
CBOD, 5-day, 20 C	<=	18.7	mg/L	Composite	Three Per Week	Monthly Average
CBOD, 5-day, 20 C	<=	750	lb/d	Composite	Three Per Week	Weekly Average
CBOD, 5-day, 20 C	<=	625	lb/d	Composite	Three Per Week	Monthly Average
CBOD, 5-day, 20 C	<=	22.5	mg/L	Composite	Three Per Week	Weekly Average
CBOD, 5-day, 20 C	<=	30	mg/L	Composite	Three Per Week	Daily Maximum
Nitrogen, Ammonia total (as N)	<=	1.9	mg/L	Composite	Three Per Week	Monthly Average
Nitrogen, Ammonia total (as N)	<=	65	lb/d	Composite	Three Per Week	Monthly Average
Nitrogen, Ammonia total (as N)	<=	4	mg/L	Composite	Three Per Week	Daily Maximum
Nitrogen, Ammonia total (as N)	<=	95	lb/d	Composite	Three Per Week	Weekly Average

1.0. EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

1.1. NUMERIC AND NARRATIVE EFFLUENT LIMITATIONS

The City of Limestone is authorized to discharge treated domestic wastewater from Outfall 001 to the Big Limestone Creek at mile 3.8. Discharge 001 consists of municipal wastewater from a treatment facility with a design capacity of .005 MGD. Discharge 001 shall be limited and monitored by the permittee as specified below:

Notes: The permittee shall achieve % removal of $CBOD_5$ and TSS on a monthly average basis. The permittee shall report all instances of overflow and/or bypasses. See Part 2.3.3.a for the definition of overflow and Part 1.3.5.1 for reporting requirements.

Unless elsewhere specified, summer months are May through October; winter months are November through April.

See Part 1.2.3 for test procedures.

See Part 3.4 for biomonitoring test and reporting requirements. See next page for percent removal calculations.

See Part 1.2.3 for test procedures.

Total residual chlorine (TRC) monitoring shall be applicable when chlorine, bromine, or any other oxidants are added. The acceptable methods for analysis of TRC are any methods specified in Title 40 CFR, Part 136 as amended. The method detection level (MDL) for TRC shall not exceed 0.05 mg/l unless the permittee demonstrates that its MDL is higher. The permittee shall retain the documentation that justifies the higher MDL and have it available for review upon request. In cases where the permit limit is less that the MDL, the reporting of TRC at less than the MDL shall be interpreted to constitute compliance with the permit.

The wastewater discharge must be disinfected to the extent that viable coliform organisms are effectively eliminated. The concentration of the *E. coli* group after disinfection shall not exceed 126 cfu per 100 ml as the geometric mean calculated on the actual number of samples collected and tested for *E. coli* within the required reporting period. The permittee may collect more samples than specified as the monitoring frequency. Samples may not be collected at intervals of less than 12 hours. For the purpose of determining the geometric mean, individual samples having an *E. coli* group concentration of less than one (1) per 100 ml shall be considered as having a concentration of one (1) per 100 ml. In addition, the concentration of the *E. coli* group in any individual sample shall not exceed a specified maximum amount. A maximum daily limit of 487 colonies per 100 ml applies to lakes and exceptional Tennessee waters. A maximum daily limit of 941 colonies per 100 ml applies to all other recreational waters.

There shall be no distinctly visible floating scum, oil or other matter contained in the wastewater discharge. The wastewater discharge must not cause an objectionable color contrast in the receiving stream.

The wastewater discharge shall not contain pollutants in quantities that will be hazardous or otherwise detrimental to humans, livestock, wildlife, plant life, or fish and aquatic life in the receiving stream.

Sludge or any other material removed by any treatment works must be disposed of in a manner that prevents its entrance into or pollution of any surface or subsurface waters. Additionally, the disposal of such sludge or other material must be in compliance with the Tennessee Solid Waste Disposal Act, TCA 68-31-101 et seq. and the Tennessee Hazardous Waste Management Act, TCA 68-46-101 et seq.

Nothing in this permit authorizes take for the purposes of a facility's compliance with the Endangered Species Act. (40 C.F.R. 125.98(b)(1))

For the purpose of evaluating compliance with the permit limits established herein, where certain limits are below the State of Tennessee published required detection levels (RDLs) for any given effluent characteristics, the results of analyses below the RDL shall be reported as Below Detection Level (BDL), unless in specific cases other detection limits are demonstrated to be the best achievable because of the particular nature of the wastewater being analyzed.

For $CBOD_5$ and TSS, the treatment facility shall demonstrate a minimum of % removal efficiency on a monthly average basis. This is calculated by determining an average of all daily influent concentrations and comparing this to an average of all daily effluent concentrations. The formula for this calculation is as follows:

$$\left[1 - \frac{\text{average of daily effluent concentration}}{\text{average of daily influent concentration}}\right] \times 100\% = \%\ \text{removal}$$

The treatment facility will also demonstrate % minimum removal of the $CBOD_5$ and TSS based upon each daily composite sample. The formula for this calculation is as follows:

$$\left[1 - \frac{\text{daily effluent concentration}}{\text{daily influent concentration}}\right] \times 100\% = \%\ \text{removal}$$

1.2. MONITORING PROCEDURES

1.2.1. Representative Sampling

Appropriate flow measurement devices and methods consistent with accepted scientific practices shall be selected and used to insure the accuracy and reliability of measurements of the volume of monitored discharges. The devices shall be installed, calibrated and maintained to insure that the accuracy of the measurements is consistent with accepted capability of that type of device. Devices selected shall be capable of measuring flows with a maximum deviation of less than plus or minus

10% from the true discharge rates throughout the range of expected discharge volumes.

Samples and measurements taken in compliance with the monitoring requirements specified above shall be representative of the volume and nature of the monitored discharge, and shall be taken at the following location(s):

Influent samples must be collected prior to mixing with any other wastewater being returned to the head of the plant, such as sludge return. Those systems with more than one influent line must collect samples from each and proportion the results by the flow from each line.

Effluent samples must be representative of the wastewater being discharged and collected prior to mixing with any other discharge or the receiving stream. This can be a different point for different parameters, but must be after all treatment for that parameter or all expected change:

a. The chlorine residual must be measured after the chlorine contact chamber and any dechlorination. It may be to the advantage of the permittee to measure at the end of any long outfall lines.

b. Samples for *E. coli* can be collected at any point between disinfection and the actual discharge.

c. The dissolved oxygen can drop in the outfall line; therefore, D.O. measurements are required at the discharge end of outfall lines greater than one mile long. Systems with outfall lines less than one mile may measure dissolved oxygen as the wastewater leaves the treatment facility. For systems with dechlorination, dissolved oxygen must be measured after this step and as close to the end of the outfall line as possible.

d. Total suspended solids and settleable solids can be collected at any point after the final clarifier.

e. Biomonitoring tests (if required) shall be conducted on final effluent.

1.2.2. Sampling Frequency

Where the permit requires sampling and monitoring of a particular effluent characteristic(s) at a frequency of less than once per day or daily, the permittee is precluded from marking the "No Discharge" block on the Discharge Monitoring Report if there has been any discharge from that particular outfall during the period which coincides with the required monitoring frequency; i.e. if the required monitoring frequency is once per month or 1/month, the monitoring period is one month, and if the discharge occurs during only one day in that period then the permittee must sample on that day and report the results of analyses accordingly.

1.2.3. Test Procedures

a. Test procedures for the analysis of pollutants shall conform to regulations published pursuant to Section 304 (h) of the Clean Water Act (the "Act"), as amended, under which such procedures may be required.

b. Unless otherwise noted in the permit, all pollutant parameters shall be determined according to methods prescribed in Title 40, CFR, Part 136, as amended, promulgated pursuant to Section 304 (h) of the Act.

c. Composite samples must be proportioned by flow at time of sampling. Aliquots may be collected manually or automatically. The sample aliquots must be maintained at ≤ 6 degrees Celsius during the compositing period.

d. In instances where permit limits established through implementation of applicable water criteria are below analytical capabilities, compliance with those limits will be determined using the detection limits described in the TN Rules, Chapter 0400-40-03-.05(8).

e. All sampling for total mercury at the municipal wastewater plant (application, pretreatment, etc.) shall use Methods 1631, 245.7 or any additional method in 40 CFR 136 with a maximum detection limit of 5 ng/L.

1.2.4. Recording of Results

For each measurement or sample taken pursuant to the requirements of this permit, the permittee shall record the following information:

a. The exact place, date and time of sampling;

b. The exact person(s) collecting samples;

c. The dates and times the analyses were performed;

d. The person(s) or laboratory who performed the analyses;

e. The analytical techniques or methods used, and;

f. The results of all required analyses.

1.2.5. Records Retention

All records and information resulting from the monitoring activities required by this permit including all records of analyses performed and calibration and maintenance of instrumentation shall be retained for a minimum of three (3) years, or longer, if requested by the Division of Water Resources.

1.3. REPORTING

1.3.1. Monitoring Results

Monitoring results shall be recorded monthly and submitted monthly using Discharge Monitoring Report (DMR) forms supplied by the Division of Water Resources. Submittals shall be postmarked no later than 15 days after the completion of the reporting period. A completed DMR with an original signature shall be submitted to the following address:

STATE OF TENNESSEE
DEPARTMENT OF ENVIRONMENT AND CONSERVATION
DIVISION OF WATER RESOURCES
COMPLIANCE & ENFORCEMENT SECTION
William R. Snodgrass - Tennessee Tower
312 Rosa L. Parks Avenue, 11th Floor
Nashville, Tennessee 37243-1102

A copy of the completed and signed DMR shall be mailed to the Johnson City Environmental Field Office (EFO) at the following address:

STATE OF TENNESSEE
DEPARTMENT OF ENVIRONMENT AND CONSERVATION
DIVISION OF WATER RESOURCES
Johnson City Environmental Field Office
2305 Silverdale Road
Johnson City, Tennessee 37601

A copy should be retained for the permittee's files. In addition, any communication regarding compliance with the conditions of this permit must be sent to the two offices listed above.

The first DMR is due on the 15th of the month following permit effectiveness.

DMRs and any other information or report must be signed and certified by a responsible corporate officer as defined in 40 CFR 122.22, a general partner or proprietor, or a principal municipal executive officer or ranking elected official, or his duly authorized representative. Such authorization must be submitted in writing and must explain the duties and responsibilities of the authorized representative.

The electronic submission of DMR data will be accepted only if formally approved beforehand by the division. For purposes of determining compliance with this permit, data approved by the division to be submitted electronically is legally equivalent to data submitted on signed and certified DMR forms.

1.3.2. Additional Monitoring by Permittee

If the permittee monitors any pollutant specifically limited by this permit more frequently than required at the location(s) designated, using approved analytical methods as specified herein, the results of such monitoring shall be included in the

calculation and reporting of the values required in the DMR form. Such increased frequency shall also be indicated on the form.

1.3.3. Falsifying Results and/or Reports

Knowingly making any false statement on any report required by this permit or falsifying any result may result in the imposition of criminal penalties as provided for in Section 309 of the Federal Water Pollution Control Act, as amended, and in Section 69-3-115 of the Tennessee Water Quality Control Act.

1.3.4. Monthly Report of Operation

Monthly operational reports shall be submitted on standard forms to the appropriate Division of Water Resources Environmental Field Office in Jackson, Nashville, Chattanooga, Columbia, Cookeville, Memphis, Johnson City, or Knoxville. Reports shall be submitted by the 15th day of the month following data collection.

1.3.5. Bypass and Overflow Reporting

1.3.5.1. Report Requirements

A summary report of known or suspected instances of overflows in the collection system or bypass of wastewater treatment facilities shall accompany the Discharge Monitoring Report. The report must contain the date and duration of the instances of overflow and/or bypassing and the estimated quantity of wastewater released and/or bypassed.

The report must also detail activities undertaken during the reporting period to (1) determine if overflow is occurring in the collection system, (2) correct those known or suspected overflow points and (3) prevent future or possible overflows and any resulting bypassing at the treatment facility.

On the DMR, the permittee must report the number of sanitary sewer overflows, dry-weather overflows and in-plant bypasses separately. Three lines must be used on the DMR form, one for sanitary sewer overflows, one for dry-weather overflows and one for in-plant bypasses.

1.3.5.2. Anticipated Bypass Notification

If, because of unavoidable maintenance or construction, the permittee has need to create an in-plant bypass which would cause an effluent violation, the permittee must notify the division as soon as possible, but in any case, no later than 10 days prior to the date of the bypass.

1.3.6. Reporting Less Than Detection

A permit limit may be less than the accepted detection level. If the samples are below the detection level, then report "BDL" or "NODI =B" on the DMRs. The permittee must use the correct detection levels in all analytical testing required in the permit. The required detection levels are listed in the Rules of the Department of

Environment and Conservation, Division of Water Resources, Chapter 0400-40-03-.05(8).

For example, if the limit is 0.02 mg/l with a detection level of 0.05 mg/l and detection is shown; 0.05 mg/l must be reported. In contrast, if nothing is detected reporting "BDL" or "NODI =B" is acceptable.

1.4. COMPLIANCE WITH SECTION 208

The limits and conditions in this permit shall require compliance with an area-wide waste treatment plan (208 Water Quality Management Plan) where such approved plan is applicable.

1.5. REOPENER CLAUSE

This permit shall be modified, or alternatively revoked and reissued, to comply with any applicable effluent standard or limitation issued or approved under Sections 301(b)(2)(C) and (D), 307(a)(2) and 405(d)(2)(D) of the Clean Water Act, as amended, if the effluent standard, limitation or sludge disposal requirement so issued or approved:

a. Contains different conditions or is otherwise more stringent than any condition in the permit; or

b. Controls any pollutant or disposal method not addressed in the permit.

The permit as modified or reissued under this paragraph shall also contain any other requirements of the Act then applicable.

1.6. SCHEDULE OF COMPLIANCE

Full compliance and operational levels shall be attained from the effective date of this permit.

2.0. GENERAL PERMIT REQUIREMENTS

2.1. GENERAL PROVISIONS

2.1.1. Duty to Reapply

Permittee is not authorized to discharge after the expiration date of this permit. In order to receive authorization to discharge beyond the expiration date, the permittee shall submit such information and forms as are required to the Director of the Division of Water Resources (the "director") no later than 180 days prior to the expiration date. Such forms shall be properly signed and certified.

2.1.2. Right of Entry

The permittee shall allow the director, the Regional Administrator of the U.S. Environmental Protection Agency, or their authorized representatives, upon the presentation of credentials:

a. To enter upon the permittee's premises where an effluent source is located or where records are required to be kept under the terms and conditions of this permit, and at reasonable times to copy these records;

b. To inspect at reasonable times any monitoring equipment or method or any collection, treatment, pollution management, or discharge facilities required under this permit; and

c. To sample at reasonable times any discharge of pollutants.

2.1.3. Availability of Reports

Except for data determined to be confidential under Section 308 of the Federal Water Pollution Control Act, as amended, all reports prepared in accordance with the terms of this permit shall be available for public inspection at the offices of the Division of Water Resources. As required by the Federal Act, effluent data shall not be considered confidential.

2.1.4. Proper Operation and Maintenance

a. The permittee shall at all times properly operate and maintain all facilities and systems (and related appurtenances) for collection and treatment which are installed or used by the permittee to achieve compliance with the terms and conditions of this permit. Proper operation and maintenance also includes adequate laboratory and process controls and appropriate quality assurance procedures. This provision requires the operation of backup or auxiliary facilities or similar systems, which are installed by a permittee only when the operation is necessary to achieve compliance with the conditions of the permit. Backup continuous pH and flow monitoring equipment are not required.

b. Dilution water shall not be added to comply with effluent requirements to achieve BCT, BPT, BAT and or other technology based effluent limitations such as those in State of Tennessee Rule 0400-40-05-.09.

2.1.5. Treatment Facility Failure (Industrial Sources)

The permittee, in order to maintain compliance with this permit, shall control production, all discharges, or both, upon reduction, loss, or failure of the treatment facility, until the facility is restored or an alternative method of treatment is provided. This requirement applies in such situations as the reduction, loss, or failure of the primary source of power.

2.1.6. Property Rights

The issuance of this permit does not convey any property rights in either real or personal property, or any exclusive privileges, nor does it authorize any injury to private property or any invasion of personal rights, nor any infringement of federal, state, or local laws or regulations.

2.1.7. Severability

The provisions of this permit are severable. If any provision of this permit due to any circumstance, is held invalid, then the application of such provision to other circumstances and to the remainder of this permit shall not be affected thereby.

2.1.8. Other Information

If the permittee becomes aware of failure to submit any relevant facts in a permit application, or of submission of incorrect information in a permit application or in any report to the director, then the permittee shall promptly submit such facts or information.

2.2. CHANGES AFFECTING THE PERMIT

2.2.1. Planned Changes

The permittee shall give notice to the director as soon as possible of any planned physical alterations or additions to the permitted facility. Notice is required only when:

a. The alteration or addition to a permitted facility may meet one of the criteria for determining whether a facility is a new source in 40 CFR 122.29(b); or

b. The alteration or addition could significantly change the nature or increase the quantity of pollutants discharged. This notification applies to pollutants, which are subject neither to effluent limitations in the permit, nor to notification requirements under 40 CFR 122.42(a)(1).

2.2.2. Permit Modification, Revocation, or Termination

a. This permit may be modified, revoked and reissued, or terminated for cause as described in 40 CFR 122.62 and 122.64, Federal Register, Volume 49, No. 188 (Wednesday, September 26, 1984), as amended.

b. The permittee shall furnish to the director, within a reasonable time, any information which the director may request to determine whether cause exists for modifying, revoking and reissuing, or terminating this permit, or to determine compliance with this permit. The permittee shall also furnish to the director, upon request, copies of records required to be kept by this permit.

c. If any applicable effluent standard or prohibition (including any schedule of compliance specified in such effluent standard or prohibition) is established for any toxic pollutant under Section 307(a) of the Federal Water Pollution Control Act, as amended, the director shall modify or revoke and reissue the permit to conform to the prohibition or to the effluent standard, providing that the effluent standard is more stringent than the limitation in the permit on the toxic pollutant. The permittee shall comply with these effluent standards or prohibitions within the time provided in the regulations that establish these standards or prohibitions, even if the permit has not yet been modified or revoked and reissued to incorporate the requirement.

d. The filing of a request by the permittee for a modification, revocation, reissuance, termination, or notification of planned changes or anticipated noncompliance does not halt any permit condition.

2.2.3. Change of Ownership

This permit may be transferred to another party (provided there are neither modifications to the facility or its operations, nor any other changes which might affect the permit limits and conditions contained in the permit) by the permittee if:

a. The permittee notifies the director of the proposed transfer at least 30 days in advance of the proposed transfer date;

b. The notice includes a written agreement between the existing and new permittees containing a specified date for transfer of permit responsibility, coverage, and liability between them; and

c. The director, within 30 days, does not notify the current permittee and the new permittee of his intent to modify, revoke or reissue, or terminate the permit and to require that a new application be filed rather than agreeing to the transfer of the permit.

Pursuant to the requirements of 40 CFR 122.61, concerning transfer of ownership, the permittee must provide the following information to the division in their formal notice of intent to transfer ownership: 1) the NPDES permit number of the subject permit; 2) the effective date of the proposed transfer; 3) the name and address of the transferor; 4) the name and address of the transferee; 5) the names of the responsible parties for both the transferor and transferee; 6) a statement that the transferee assumes responsibility for the subject NPDES permit; 7) a statement that the transferor relinquishes responsibility for the subject NPDES permit; 8) the signatures of the responsible parties for both the transferor and transferee pursuant to the requirements of 40 CFR 122.22(a), "Signatories to permit applications"; and, 9) a statement regarding any proposed modifications to the facility, its operations, or any other changes which might affect the permit limits and conditions contained in the permit.

2.2.4. Change of Mailing Address

The permittee shall promptly provide to the director written notice of any change of mailing address. In the absence of such notice the original address of the permittee will be assumed to be correct.

2.3. NONCOMPLIANCE

2.3.1. Effect of Noncompliance

All discharges shall be consistent with the terms and conditions of this permit. Any permit noncompliance constitutes a violation of applicable state and federal laws and is grounds for enforcement action, permit termination, permit modification, or denial of permit reissuance.

2.3.2. Reporting of Noncompliance

a. 24-Hour Reporting

In the case of any noncompliance which could cause a threat to public drinking supplies, or any other discharge which could constitute a threat to human health or the environment, the required notice of non-compliance shall be provided to

the Division of Water Resources in the appropriate Environmental Field Office within 24-hours from the time the permittee becomes aware of the circumstances. (The Environmental Field Office should be contacted for names and phone numbers of environmental response team).

A written submission must be provided within five days of the time the permittee becomes aware of the circumstances unless the director on a case-by-case basis waives this requirement. The permittee shall provide the director with the following information:

i. A description of the discharge and cause of noncompliance;

ii. The period of noncompliance, including exact dates and times or, if not corrected, the anticipated time the noncompliance is expected to continue; and

iii. The steps being taken to reduce, eliminate, and prevent recurrence of the noncomplying discharge.

b. Scheduled Reporting

For instances of noncompliance which are not reported under subparagraph 2.3.2.a above, the permittee shall report the noncompliance on the Discharge Monitoring Report. The report shall contain all information concerning the steps taken, or planned, to reduce, eliminate, and prevent recurrence of the violation and the anticipated time the violation is expected to continue.

2.3.3. Overflow

a. "**Overflow**" means any release of sewage from any portion of the collection, transmission, or treatment system other than through permitted outfalls.

b. Overflows are prohibited.

c. The permittee shall operate the collection system so as to avoid overflows.

d. No new or additional flows shall be added upstream of any point in the collection system, which experiences chronic overflows (greater than 5 events per year) or would otherwise overload any portion of the system. Unless there is specific enforcement action to the contrary, the permittee is relieved of this requirement after: 1) an authorized representative of the Commissioner of the Department of Environment and Conservation has approved an engineering report and construction plans and specifications prepared in accordance with accepted engineering practices for correction of the problem; 2) the correction work is underway; and 3) the cumulative, peak-design, flows potentially added from new connections and line extensions upstream of any chronic overflow point are less than or proportional to the amount of inflow and infiltration removal documented upstream of that point. The inflow and infiltration reduction must be measured by the permittee using practices that are customary in the environmental engineering field and reported in an attachment to a Monthly Operating Report

submitted to the local TDEC Environmental Field Office. The data measurement period shall be sufficient to account for seasonal rainfall patterns and seasonal groundwater table elevations.

e. In the event that more than 5 overflows have occurred from a single point in the collection system for reasons that may not warrant the self-imposed moratorium or completion of the actions identified in this paragraph, the permittee may request a meeting with the Division of Water Resources EFO staff to petition for a waiver based on mitigating evidence.

2.3.4. Upset

a. "***Upset***" means an exceptional incident in which there is unintentional and temporary noncompliance with technology-based effluent limitations because of factors beyond the reasonable control of the permittee. An upset does not include noncompliance to the extent caused by operational error, improperly designed treatment facilities, inadequate treatment facilities, lack of preventive maintenance, or careless or improper operation.

b. An upset shall constitute an affirmative defense to an action brought for noncompliance with such technology-based permit effluent limitations if the permittee demonstrates, through properly signed, contemporaneous operating logs, or other relevant evidence that:

   i. An upset occurred and that the permittee can identify the cause(s) of the upset;

   ii. The permitted facility was at the time being operated in a prudent and workman-like manner and in compliance with proper operation and maintenance procedures;

   iii. The permittee submitted information required under "Reporting of Noncompliance" within 24-hours of becoming aware of the upset (if this information is provided orally, a written submission must be provided within five days); and

   iv. The permittee complied with any remedial measures required under "Adverse Impact."

2.3.5. Adverse Impact

The permittee shall take all reasonable steps to minimize any adverse impact to the waters of Tennessee resulting from noncompliance with this permit, including such accelerated or additional monitoring as necessary to determine the nature and impact of the noncomplying discharge. It shall not be a defense for the permittee in an enforcement action that it would have been necessary to halt or reduce the permitted activity in order to maintain compliance with the conditions of this permit.

Common Deficiencies Found in the Wastewater Treatment Plant Laboratory

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This handout has been prepared based on deficiencies found while performing Performance Audit Inspections (PAI) at wastewater treatment plants for the Tennessee Department of Environment and Conservation in the Division of Water Resources. Suggestions have been made in an effort to assist the operator of a wastewater treatment plant in performing his laboratory duties thus improving the self-monitoring program of the facility.

Every wastewater treatment plant has its own distinctive characteristics and needs. Many of the observations and suggestions provided may not apply to every facility.

Quality assurance and quality control requirements can be found in the 40CFR part 136.7 (promulgated May, 2012), method update rule (MUR). Guidance documents may be found on the Fleming Training Center web page. http://www.tn.gov/environment/article/wr-ftc-waste-water-information

The following are problems associated with records and reports:

1. Failure to keep permits and records at the wastewater treatment plant.
   (NPDES Permit Part 1, 2.1.3 & 1.2.5)
   All permits and records should be kept at the wastewater treatment plant. In most cases this is a requirement in the permits.

2. Failure to keep records for three years. **(NPDES Permit Part 1, 1.2.5)**
   All records and information resulting from the monitoring activities required by the permits are to be retained for a minimum of three (3) years, or longer, if requested by the Division of Water Resources. This includes all worksheets and scrap pieces of paper where calculations for analyses are performed and calibration and maintenance of instrumentation.

3. Uncertainty of what to do with records past the three (3)-year period.
   If this Division has not given instructions to retain them past the three (3)-year period then, the facility can either destroy or archive the records.

4. Inadequate or no worksheets on which to record data. Refer to permit.
   (NPDES Permit Part 1, 1.2.4)

5. Illegible and unorganized data recorded on worksheets.
   (NPDES Permit Part 1, 2.1.3)
   All work should be written in a manner where inspectors are able to interpret the data. Only the EPA approved methods may be used to perform the required analyses.

6. Failure to document calibration and maintenance of equipment.
   (NPDES Permit Part 1, 1.2.5)
   Documentation of calibration and maintenance of equipment should also be maintained.

7. Failure to monitor parameters at the required frequencies. **(NPDES Permit Part 1, 1.2.2)**

   Parameters should be monitored at their required frequencies (according to the permit). Analyses should not be locked into specific days during the week. These days should be changed to ascertain any potential problems that may occur during an entire week.

8. Inability to understand what should be recorded on Monthly Operational Reports (MORs).

   All columns on an MOR should be filled out to the best of the operator's ability.
   (NPDES Permit Part 1, 1.3.1)

9. Uncertainty of whether a computer-generated MOR is permissible or not.

   Should an operator want to submit his data on computer-generated MORs, he should use the same format as the State-provided MORs. The operator should provide both the MOR and the computer-generated MOR to the field office for approval.
   (NPDES Permit Part 1, 1.3.1)

   The initial documentation, even if hand-written, becomes the permanent record and must be maintained. Storage of data and other information generated on computer is acceptable but a very rigorous tracking system with passwords and control level for data must be in place. Also, all records must be backed up on routine schedule and second disc or tape stored at a secure second location. These all have to be in place before electronic data is acceptable.

10. Failure to fill out DMRs correctly.

    The Discharge Monitoring Reports (DMRs) are not being filled out correctly, due to a misleading feature of the pre-printed DMR form. The headings near the top of the sheet labeled. **(NPDES Permit Part 1, 1.3.1)**

| AVERAGE | MAXIMUM | UNITS | MINIMUM | AVERAGE | MAXIMUM | UNITS |

    These have caused some misunderstanding as to the information required. The sampling intervals and units typed in the stippled gray portion to the right of each parameter listed should be followed, even where there is a conflict with the pre-printed heading. For example, the entry for "Solids, Total Suspended, Effluent Gross Value", in the fourth column to the right, the monthly average value should be entered because "MO AVG." is typed in the stippled gray area. (The pre-printed column heading "MINIMUM" should be ignored.)

11. Failure to calculate weekly averages correctly.

    Weekly averages should be reported by averaging the data in each week (Sunday through Saturday) of the month, then reporting the maximum value of those averages. If the week is not complete by the end of one month, then that week's data should be reported with the month in which the week ends.

12. Failure to submit DMRs and MORs in a timely manner.

Discharge Monitoring Reports (DMRs) and Monthly Operational Reports (MORs) frequently arrive late. DMRs should be postmarked no later than 15 days after the

completion of the reporting period. (MORs) are to be submitted, in the field office, by the 15th day of the month following data collection. **(NPDES Permit Part 1, 1.3.1)**

13. Failure to have a Quality Control program. **(NPDES Permit Part 1, 1.2.3)**

A Quality Control (QC) program should be initiated by each facility. An acceptable QC program would incorporate both quality control (precise and accurate data, e.g. duplicates) and quality assurance (QA) (How closely the data agrees. Statistics are commonly used.). Blanks are used to indicate contamination, duplicates measure precision, and spike samples measure accuracy. Duplicates should be analyzed in accordance with the method of analyses and 40CFR part 136.7 (May, 2012).

Also, there is a QA section at the beginning of each part of Standard Methods for the Examination of Water and Wastewater (SM) e.g.1020, 2020, 3020, 4020, 5020, 6020, etc.

14. Failure to have an SOP. **(NPDES Permit Part 1, 2.1.4 and 40CFR part 136.7)**

Each facility should also have its own Standard Operations Procedure (SOP). An SOP would provide what is typically done at the laboratory and how operations are accomplished. This would include collection of samples to the actual method used for each laboratory analyses. An SOP should be available upon request and provide reference to EPA approved methods of analyses (e.g. SM and Hach methods).

15. Use of correction fluid to cover transcription errors.

It is unacceptable to use correction fluid to correct record keeping errors. Errors should be crossed out with a single line, initialed and the correct information entered.

THE FOLLOWING ARE PROBLEMS ASSOCIATED WITH THE LABORATORY.

General Laboratory Considerations

1. Failure to follow approved laboratory procedures. **(NPDES Permit Part 1, 1.2.3)**

The **40 *CFR* Part 136** provides the approved test procedures for the analysis of pollutants under the **Clean Water Act.**

Other equivalent, acceptable and approved laboratory procedures are

available (e.g. Hach Company products. See their EPA compliant methods for WW (wastewater) on the Hach website http://www.hach.com/epa). Any QA/QC must meet the requirements set forth in the 40CFR part 136.7. Not complying will make the self-monitoring data questionable and in some cases invalid; thus, resulting in violations.

2. Improperly marking containers.

   If samples from more than one wastewater treatment plant are analyzed, containers should be marked distinctly to avoid any confusion between samples.

3. Using expired chemicals in analyses.

   Chemicals should not be used beyond the expiration date. Doing so will place sample data in jeopardy of not being legally defensible. Purchase according to need. It won't be a bargain if the reagents expire before they are opened.

   Uncertainty of when reagents have expired.
   Mark the date received on the bottles and/or contact the manufacturer regarding expiration dates for the reagents.

4. Uncertainty on whether to purchase prepared reagents or prepare in-house reagents.

   Some reagents such as sodium thiosulfate, 10%, used for preservation and chlorine removal for bacteriological sample collection, can be prepared at the plant with minimal cost. Although prepared reagents tend to be costly they also can save valuable time.

5. Failure to properly label in-house prepared reagents.

   The in-house prepared reagents should be labeled with date, time, initials, and possible health hazards. A log of the reagents prepared should be kept. They should also be in compliance with OSHA regulations 29 CFR 1910.1200(f)(1)

6. Storing food and drink in ovens or refrigerators where samples are kept.

   Food and drink should not be stored in refrigerators or ovens that also contain chemicals and wastewater samples. Chemicals should be kept away from foods, as it is an unnecessary safety hazard. Some chemicals can be absorbed in food.

7. Failure to document dates, times and initials for collection and analyses.
(NPDES Permit Part 1, 1.2.4)

   The dates and times that the analyses were performed should be documented as should the name of the person who collected and analyzed the samples. This is especially important when transporting samples from one facility to another for analysis. The method of analyses should also be documented. This can either be referenced to the SOP or written directly on the daily worksheet. If the method can be found in SM, the method number should be followed by the SM committee's approval date. This can be found in the footnote in introductory section A of the method (e.g. 4500-NH_3 D-1997).

8. Failure to adequately clean glassware.

   Glassware should be washed thoroughly in a tub of soapy water (or dish washer) using phosphate-free detergent (preferably lab grade), rinsed well with tap water and a final rinse with distilled water. Just rinsing the glassware is not considered cleaning.
   Think … representative sample for the lab 24 hours.

9. Failure to maintain a log for equipment. **(NPDES Permit Part 1, 2.1.5)**

   A log should also be kept to record the temperatures of the ovens, water bath and incubator. It's advantageous to place the log near the equipment being monitored, but can also be recorded on the daily worksheet. This log should include the date, time, temperature and the initials of whomever is doing the checking.

The following are problems frequently found with the <u>Settleable Solids (SS)</u> analysis. (SM 2540 F-1997)

Failure to follow EPA approved methodology.

Too frequently, deviation of the SS methodology has been found. The appropriate methodology for SS requires that the sample be shaken well and be poured into an Imhoff cone; be allowed to settle for 45 minutes, and then very slowly stirred (one revolution) to dislodge material adhering to the sides. Do NOT stir fast. The solids in the sample should then be allowed to settle for another 15 minutes then be read to the nearest 0.1 mL/L mark.

Laboratories typically have either the glass or the plastic cones. The lowest marking on the glass cone is the 0.1 mL/L mark. The plastic cones have a screw cap at the tip and don't provide a reliable a reading that low. If the lowest marking is the 0.5 mL/L and the solids level is below this, the one would report <0.5 mL/L. You can't record < 0.1 mL/L if the lowest mark is 0.5 mL/L. If you happen to have a glass cone and a plastic cone, use the glass for the final and the plastic for the raw. Otherwise, you must properly record what you see.

The following are problems frequently found with <u>Dissolved Oxygen (DO)</u> analysis. (SM 4500-O G-2001 and Hach method 10360 for LDO)

1. Failure to collect DO sample properly.

   When collecting the sample be sure to collect the sample with a BOD bottle using the stopper. Fill the BOD bottle to near the top and then stopper immediately to avoid any further contact with the air. This assures that no air bubbles are caught between the stopper and the sample.

2. Failure to properly calibrate the DO meter.

   Air Calibration for the meter is acceptable by the EPA. If the air calibration method is used, the membranes must be kept fresh. Change the membrane at a minimum of once per

month. If air bubbles are visible under the membrane, the membrane must be changed. Follow manufacturer instructions for proper maintenance and calibration.

Winkler method is also acceptable by the EPA and is considered the better of the two methods used to calibrate the DO meter. Three bottles should be filled with distilled water. The first and third bottles should be titrated as required by the EPA approved method to determine the DO. The second bottle is used to adjust the setting on the meter to the averaged DO value found by titration of the other two bottles.

3. Failure to standardize the titrant.

   If the titrant, 0.0375 N sodium thiosulfate is used in the Winkler method, then it must be standardized daily according to the approved methodology.

   Another option is to titrate with a 0.03750N phenylarsine oxide (PAO) solution. This can be purchased pre-standardized. PAO solutions are stable. No further standardization would be necessary.

   Even the luminescent dissolved oxygen (LDO) probe must be calibrated properly. The cover for the probe typically replaced yearly.

   Currently, the barometric pressure and room temperature should be recorded at the same time that the DO meter is calibrated. The standard (or theoretical) DO value obtained from these readings should also be recorded. This can be found on the USGS website. http://water.usgs.gov/software/DOTABLES/ . A table can be tailored to one's specific needs on this website. This standard value and the value used to set the meter must lie within 10% of each other

4. Failure to store DO probes properly.

   DO probes can be stored in a BOD bottle containing at least 1 inch of water. Refer to the operations manual for the DO or LDO probe and meter or contact the YSI service center for assistance regarding proper maintenance of the equipment. Keep this bottle clean.

The following are problems frequently found with the Biochemical Oxygen Demand/Carbonaceous Biochemical Oxygen Demand (BOD/CBOD) analysis (SM 5210 B-2001)

1. Uncertainty of when to seed the sample. (5210B.4.d, 5.d. & 6.d.)

   If an effluent composite sample is collected prior to disinfection, no seeding is required for BOD. However, seeding is required for the CBOD method since the nitrification inhibitor must be added to the sample.

   Seeding is required for both influent and effluent samples for CBOD analysis. "*Comparing Apples to Apples*" as the saying goes.

If an effluent composite sample is collected following disinfection, the sample must be checked for any residual chlorine (if not UV disinfected) prior to setting up the CBOD samples. The samples then must be seeded.

2. Failure to adequately dechlorinate a sample. (5210B.4.b.2.)
   Just allowing the samples to sit for a short period of time in order to dissipate any residual chlorine is not as effective as chemical de-chlorination. Besides, the samples must be set up and analyzed within two hours of collection. Chemical dechlorination also eliminates the chlorine in a shorter period of time. Failure to properly dechlorinate would result in artificially low results.

3. Failure to allow the samples to come to room temperature before making dilutions. (5210B.4.b.4.)
   Since composite samples are kept at 6°C, or below, the samples should be warmed to 20 ± 3°C (comparable to 68°F) before making dilutions. This may be accomplished by allowing the samples to come to room temperature (approximately 68°F) or by setting the sample bottles in a warm water bath.

4. Initial DO values do not meet the method criteria. (5210B.8.b.)
   Samples with initial DO's that are greater than 9.0 mg/l at 20°C (e.g. stream samples) are considered supersaturated with oxygen. These samples may be vigorously shaken or aerated with clean, compressed air to bring down to saturation, less than or equal to 9.0 mg/l. (5210 B 4.b.4.) The samples should be brought to room temperature and the initial DO $\leq$9.0 mg/L before setting up dilutions and analyzed within two hours of collection.

5. Introducing contamination into the sample.
   Cross-contamination, which can produce inaccurately high results, can be avoided by properly rinsing the graduated cylinders between measuring sample volumes. Specific graduated cylinders can be delegated for each influent, effluent and stream sample. Clean, Clean, Clean!!!

6. Failure to adequately stir/shake the sample prior to making dilutions.
   Sample should be stirred or shaken thoroughly to obtain a representative sample.

7. Failure to set up the appropriate amount of dilutions. 5210B.5.c.
   At least three dilutions should be set up for both influent and effluent samples appropriate QA/QC measures.

8. Uncertainty of the purpose of the glucose-glutamic acid (GGA) check. 5210B.6.b.
   To check the quality of the seed material and analytical technique, it is recommended that a glucose-glutamic acid check be set up with each set of samples. A typical value of 198 mg/L ± 30.5 mg/L has been found for the GGA concentration. 164 ± 30.7 mg/L (nitrification inhibitor added) is recommended for GGA concentration in CBOD analysis.

A low value could be indicative of a toxic affect caused from trace metals in the dilution water (e.g. copper). It could also indicate that the seed material concentration is weak (relatively inactive).

A high value could be indicative of several factors e.g. contamination from improper rinsing of glassware after cleansing, imprecise measurement of standards, or too much seed material added to GGA.

Should the measurement fall outside the previously given range, the tests should be reported and flagged as to the findings. The problem should then be investigated in order to determine and eliminate the source.

9. Failure to follow the BOD criteria for reporting results. 5210B.6.a, 7. and 8.b.

Follow the BOD criteria for reporting the results. EPA approved methodology states that the initial DO must be less than or equal to 9.0 mg/l. The samples must deplete at least 2.0 mg/L DO and must leave 1.0 mg/L final DO. Results from dilutions that do not meet these criteria are considered invalid and should be discarded.

The blank oxygen depletion should be 0.2 mg/L or less as required by EPA approved methodology. Otherwise, an investigation should be initiated to determine the cause. Check for soap residue due to improper rinsing. The results still can be reported but must be marked that the blank is outside the guidelines. The blank oxygen depletion is NOT subtracted from the sample depletion. (5210 B. 7.a.3.)

Be wary of the existence of toxicity trending.

10. Uncertainty of which nitrification inhibitor to use.

There are two nitrification inhibitors available for use in the CBOD analysis method, **2-Chloro-6 (Trichloromethyl) Pyridine** and **Nitrification Inhibitor, Formula 2533™**. The biggest difference between the two is that Formula 2533™ is more soluble than the other, thereby yielding better results.

The dispenser cap for the nitrification inhibitor is well worth the money.

11. Failure to properly monitor the temperature of composite samplers. (40CFR part 136, table II)

The temperature of the composite samplers are not generally monitored or maintained at the required temperature of $\leq 6^{o}C$. During the collection of composite samples, the temperature of the samplers must maintain temperatures at $\leq 6^{o}C$ or below (but above freezing $0^{o}C$).

12. Failure to properly monitor the temperature of the BOD incubator. (5210 B. 5.h.)

    The BOD incubator temperature must be maintained at $20^{o} \pm 1^{o}C$. A log should be kept for each piece of equipment to record the date, time, temperature, and the initials of whoever was checking it. It is just as easy to record the temperature on the daily worksheet.

    Check and record the temperature using a *calibrated* thermometer placed in water inside the incubator. Do not use the digital thermometer found on top of the incubator.

The following are problems frequently found with the <u>pH</u> analysis.
(SM 4500-H B.-2000, revised 2011)

1. Failure to compensate for temperature.

   Since pH is temperature dependent, an automatic temperature compensator (ATC) probe must be use or the temperature must be measured and manually set on the instrument. This temperature of the samples should be recorded.

2. Failure to properly store the pH electrode.

   Store electrodes according to manufacturer instructions! Orion states using pH 7 buffer with 1 gram of KCl (potassium chloride).

3. Using expired pH standards.

   Do not use expired pH standards. Plan to buy what can be used before the expiration date.

4. Failure to properly calibrate the meter.

   A two-point calibration is a required. A two-point calibration brackets the normal pH range found at the plant. It provides a line on which the best possible data point for the sample can be found. If the sample falls outside the calibrated range, the instrument should be recalibrated.

   If the probe that you use has the capability of performing a 3-point calibration, follow manufacturer procedures. This is a great way to ensure that the samples will be bracketed by the calibration buffers.

5. Failure to use fresh standard solutions for calibration of the pH meter.

   Prepare fresh standard solutions for each daily use for calibration. If stock bottles are used, be sure to cap the bottle after pouring out an amount used for standardizing.
   Never pour used reagent back into the stock bottle. This is a big source of contamination. This method could jeopardize the integrity of the sample, which is directly related to the calibration of the meter.

6. Improper calibration procedure used in calibrating the pH meter.

   Start by adjusting the intercept knob with a pH 7 buffer (the isopotential point). The slope or calibrate function on the meter should be set with a second buffer. This buffer depends

on the desired range, either above pH 7 (e.g. pH 10) for the higher pH range, or below pH 7 (e.g. pH 4) for the lower pH range.

There are pH meters that provide a 3-point calibration allowing the use of pH buffers 7, 4 and 10. Follow the manufacturer directions.

7. Failure to rinse the electrode prior to reading the sample.
   Be sure to rinse the electrode well after standardizing the meter and prior to reading the pH of the sample. Pat the probe dry with a soft cloth or tissue to remove the liquid. This minimizes cross-contamination.

8. Failure to stir the sample.
   Stirring the sample at a rate of about one revolution/second is necessary in obtaining a quick and accurate reading.

9. Failure to run the sample immediately after collection.
   Don't collect the pH sample until the meter has been calibrated. The analysis of the samples should be run immediately. 40CFR part 136, table II states that the holding time is within 15 minutes of collection.

10. Failure to have a backup probe.
    An extra pH probe should be available in the event that the current probe malfunctions.

11. Uncertainty of how to maintain an electrode.
    The electrolyte should be added to the new electrode, through a filler hole in the side, when it is ready for use. After the electrolyte has been added, it should not be used for at least one hour. Be sure to rinse off any excess electrolyte and pat dry the electrode. Do not rub the electrode vigorously because it could create a static charge in the probe. This will assure that none of the electrolyte is introduced into the sample.

    Be sure to take the filler-hole cap off when taking readings for quicker response times. This cap may be replaced when not in use to prevent evaporation of the electrolyte.

The following are problems frequently found with the <u>Total Suspended Solids (TSS)</u> analysis. (SM 2540 D-1997)

1. Failure to adequately shake the sample.
   The biggest problem with the TSS is that operators are not shaking the sample well enough prior to analysis. This is necessary to obtain a representative sample.

2. Uncertainty of why results are too **high**. (When comparing results to another lab's results.)
   Frequently, sample volumes are too high for the amount of solids in the sample. This requires longer filtration periods for elimination of the liquid. Prolonged filtration times

may produce high results due to excessive solids on the clogged filter. By reducing the sample size, more satisfactory results should be obtained.

A constant weight must be demonstrated prior to reporting the results. This is to ensure that all the moisture has been eliminated. If this is not accomplished then erroneously high results may be obtained. The re-drying, cooling, desiccating and weighing cycle is

required unless shown otherwise. The weight change must be less than 4% of the previous weight or 0.5 mg, whichever is less. (2540 D.3.c.)

The drying oven should be kept clean to minimize contamination of samples.

3. Uncertainty of why results are too **low**. (When comparing results to another lab's results.)
   Solids can be lost under the filter paper when pouring in the sample. Wetting the filter paper with distilled water prior to pouring the sample will lessen the possibility of the solids being lost under the filter rather than collected on the filter.

   Filtered samples should not be placed directly on the oven rack. The filters could stick to the rack and lose fibers, which could change the weight of the sample. They could also gain contaminants or spill the filter contents. Aluminum weighing dishes are recommended.

4. Lack of good laboratory technique.
   Do not use fingers to pick up crucible or filter. The oil on your fingers adds weight.
   Use tongs instead.

5. Uncertainty of when to change the desiccant.
   Make sure that the color indicator desiccant is changed when the color turns to pink.

   An option would be to obtain the non-color indicator and mix it with the color indicator desiccant. This would incorporate cost with performance.

6. Failure to properly monitor the temperature of the drying oven.
   The oven should be maintained at a temperature between 103 - 105°C at all times.

7. Failure to perform quality control procedures (SM 2020I and II tables)
   A duplicate should be performed once every 20th sample.

   A distilled water blank should be analyzed with every 20th sample for quality assurance.

The following are problems frequently found with the <u>Total Chlorine Residual</u> analysis. (Hach method 8167)

1. Failure to calibrate the instrument prior to use (or check the calibration for Hach Pocket Colorimeters).

   The Instrument calibration should be checked prior to each use. Chlorine or $KMnO_4$ standards may be used. There are several companies that manufacture pre-made standards. The chlorine standards are typically added to samples that have already been analyzed (standard addition method). See Hach method of analysis.

2. Uncertainty of the proper method to use.

   The permit limit must be considered when deciding the appropriate method to use. The low limits presently being given require the lowest possible detection limits that a method can provide. DPD, electrode and amperometric methods are currently the methods that provide the lowest detection limits available. Current permits state the following:

   > *"Total residual chlorine (TRC) monitoring shall be applicable when chlorine, bromine, or any other oxidants are added. The acceptable methods for analysis of TRC are any methods specified in Title 40 CFR, Part 136 as amended. The method detection level (MDL) for TRC shall not exceed 0.05 mg/l unless the permittee demonstrates that its MDL is higher. The permittee shall retain the documentation that justifies the higher MDL and have it available for review upon request. In cases where the permit limit is less that the MDL, the reporting of TRC at less than the MDL shall be interpreted to constitute compliance with the permit."*

   Iron, manganese, nitrates and organic mercaptans can interfere with DPD readings giving a false positive for chlorine. Some facilities are unable to use the colorimeter due to these interferences.

   The amperometric method requires greater skill than the colorimetric method. However, less interference is found.

3. Uncertainty of what the lowest reportable value should be.

   The amperometric method requires greater skill than the colorimetric method but there are fewer problems with these interferences.

   The current instrument detection limit is 0.05 mg/L. Many permit limits lie below this value. Many operators have been reporting <0.1 mg/L. This was the old detection limit and should not be used anymore. If the value in the permit limit is within the capability of the instrument, it is preferable that the operators report the actual value that is obtained.

   However, MUR now requires that the method detection limit (MDL) must now be determined by the laboratory. However, follow permit requirements until the permit language changes.

The following are problems frequently found with the <u>Ammonia as Nitrogen (NH_3-N)</u> analysis. (SM 4500-NH_3 – 1997)

1. Failure to properly preserve samples. (4500-NH_3 A.3.)

   If samples are to be analyzed with within 24 hours of collection, refrigerate until removed for analysis. If the analysis cannot be performed within this time period, the samples must be preserved by acidifying to pH and store refrigerated to $\leq 6^{o}C$ for 28 days (40CFR part 136, table II).

   Oh, don't forget that this table can also provide guidance in which to store samples should a problem arises at the facility and the analysis cannot be performed.

2. Failure to adequately shake the sample.

   Thoroughly shaking the sample is necessary to obtain a more representative sampling.

3. Failure to distill samples.

   The analytical method should be consulted regarding the need for distillation. If this method is unclear, distillation is required. Distillation is required to remove impurities that would interfere with the analyses and produce erroneous results. (40CFR part 136 table 1B, footnote 6) It requires distillation for all methods unless comparability has been shown. "Manual Distillation is not required if comparability data on representative effluent samples are on file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies."
   Comparable is defined as <20 RPD (relative percent difference). Since the likelihood of the distilled and undistilled samples will meet this requirement, it recommended that a sample be distilled and compared with the undistilled sample, once per year.

   If distillation is required, guidance can be found in the 40CFR part 136 table 1B, footnote 6.

   Did you say Ammonia-free water? Hopefully, someone has found something out there to assist in this matter. Personally, I've had difficulty coming up with something. The EPA 350.2 method provides guidance

   <u>EPA Method 350.2</u>
   ……
   6.0 Reagents
   6.1 Distilled water should be free of ammonia. Such water is best prepared by passage through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.

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

Remember, not only does the air that we breathe have oxygen; it also has nitrogen which is a component of ammonia. So, when you distill the water minimize the exposure to the air as it is distilled off.

4. Failure to properly calibrate the instrument.
   Instrument calibration is required prior to running the analysis. At least two standards should be used to bracket the sample. If the sample falls outside this range, then the sample can be diluted or new standards prepared.

The following are problems frequently found with *Fecal Coliform* analysis. Some of this information may also apply to the *E.coli* analyses (Hach m-coli Blue method of analyses - comparable to EPA 1603)

1. Failure to use the approved method.
   Only use approved methods outlined in the 40CFR part 136 table 1A. Don't get this confused with total Coliform.

2. Failure to use a microscope with the appropriate magnification.
   A microscope with magnification of 10X to 15X is required to obtain a valid colony count. This magnification is necessary to determine the presence of small colonies in a sample that might otherwise be missed.

3. Failure to monitor the temperature of the water bath.
   Maintain the temperature of the water bath at a uniform and constant temperature of $44.5 \pm 0.2^{o}C$ at all times. *E.coli* incubator temperature should be maintained at $35 \pm 0.5^{o}C$.

   The thermometer must be graduated in 1/10 of ^{o}C which is needed for the $\pm$ 0.2 ^{o}C and **kept** clean**.**

4. Failure to follow proper sterilization procedures.
   0.1 mL of a 10% sodium thiosulfate solution should be added to each sample bottle prior to sterilization. Do not use the preservative N-10 (0.1005-0.0995) sodium thiosulfate. This is potentially harmful to the fecal coliform culture since this is stronger than the 10% (approximately 0.03N) solution stated in the EPA approved procedures.

   The sterilization procedure should be done for 15 - 20 minutes at $121^{o}C$ ($250^{o}F$).

   If you have to use a pressure cooker as an autoclave, do not close the petcock until steam comes out of the ports. When the sterilization period is complete, turn steam supply off; allow glassware to slowly cool before removing. The pressure cooker is only to be used as a **temporary** method of sterilization. The Autoclave is preferable.

5. Failure to properly collect the sample.

   While collecting the sample in the sterilized bottle, care must be taken to eliminate other sources of contamination (e.g. unsterilized dippers used to pour the sample into the sterilized sample bottles).

6. Uncertainty whether to use distilled water in place of buffered dilution water.

   Do **NOT** use distilled water in place of the buffered dilution water. EPA approved methodology requires the use of buffered dilution water in the procedures. The method shows you how to prepare this.

7. Failure to prepare the appropriate number of dilutions.

   Many operators are preparing only one dilution. Prepare three dilutions of the sample in order to obtain a 20 - 60-colony count. Do the same to obtain 20 - 80-colony counts for *E.coli*.

8. Performing analysis with faulty equipment.

   Avoid using a leaking filter apparatus. This could give erroneously low results.

9. Failure to perform quality control ("Quick Reference for *E.coli* Analysis) http://www.tn.gov/assets/entities/environment/attachments/wwt_quick_reference_e_coli.pdf

   It is recommended that a positive control sample be set up at least once per month as a quality control check (e.g. 1 mL of effluent prior to chlorination).

   Perform duplicate samples at least once every 10 samples.

10. Failure to perform analyses due to high flow conditions.

    Sampling during high flow events occasionally has been avoided by the operator due to frequently obtaining TNTC (Too Numerous To Count) data. (This is a violation of the permit since representative sampling is required at a specified frequency.) At several plants this occurrence is the norm rather than the exception. Operators who have worked at these plants for a number of years can probably guess as to the appropriate dilutions that could be used to obtain 20 - 60 colony counts. It's better to indicate what actually happens at the plants rather than indicate no problems. These problems would lend proof that there is a need for plant renovations.

11. Failure to report data correctly.

    There are specific guidelines that should be followed when reporting data. TNTC is not to be reported on the MOR. These guidelines are provided upon request or may be found in ***EPA Microbiological Methods for Monitoring the Environment Water and Wastes,*** EPA-600/8-78-017, December 1978.

The following are problems frequently found with the *E.coli* analysis.

1. Failure to use the methods approved for wastewater.

   In the March 2007 40 CFR part 136 the Colilert, Colilert 18 and mColiBlue 24 were approved for *E. coli* analyses. Well, there are others listed as well. But, these particular methods have fought long and hard for "approval".

2. Failure to use appropriate temperature.
   Follow instructions. Don't assume *E. coli* can be used at the same temperature as fecal coliform or visa versa.

3. Failure to count colonies in the appropriate range.
   The appropriate colony count range for Hach's m-Coli Blue method is 20 - 80.
   You are counting the blue colonies only and not the total colonies.

4. The "Quick Reference Guide to *E.coli* Analysis" can be found on the FTC website.
   http://www.tn.gov/environment/article/wr-ftc-waste-water-information

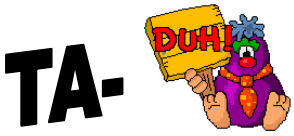
The following are problems frequently found with the IDEXX Colilert analysis.

1. Failure to monitor the incubator temperature at 35 $\pm$ 0.5^{o}C. The thermometer must be graduated in 1/10 of ^{o}C

2. Failure to have a color comparator available to confirm fluorescent blue wells. Yellow wells indicate the presence of total coliforms. The yellow wells that fluoresce under UV light indicate the presence of *Ecoli.*

3. Failure to have the correct Quanta Tray available for use in expected high count flows.
   Trays come in 51-well and 97-well sizes. The 51-well tray allows MPN counts up to 200 per 100 mL of sample. The 97-well tray allows MPN for up to 2419 per 100 mL of sample.

4. Failure to properly dispose of used Quanti trays.
   Samples, reference materials and equipment known or suspected to have viable bacteria attached or contained must be sterilized prior to disposal.

5. Failure to use **sterile water** for sample dilution.
   Do not use the sterile dilution water that is used in the fecal coliform or m-coli Blue analyses.

6. Failure to perform quality assurance controls.
   Purchase Quanti-Cult control samples (*Escherichia coli, Klebsiella pneumoniae, and Pseudomonas aeruginosa* cultures) to check the quality control of the method.