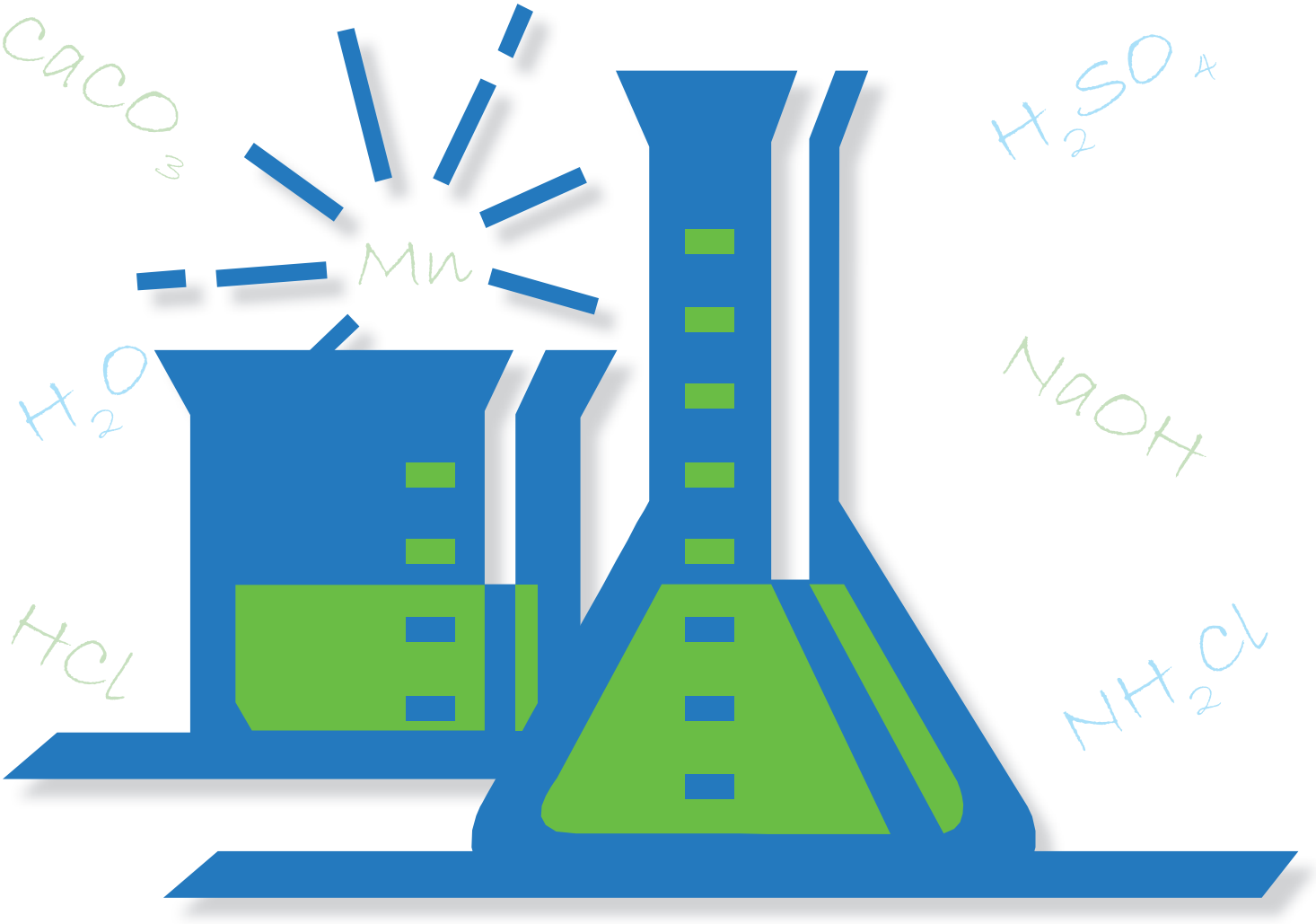
C Level
Water Laboratory Manual

State of Oklahoma
Department of Environmental Quality
Water Quality Division
Operator Certification Section



Department of Environmental Quality

NOTICE

NEW PROCEDURES FOR OBTAINING AGENCY ISSUED LICENSES/CERTIFICATIONS

Effective November 1, 2007

In order to comply with Oklahoma's new immigration law, 56 Okla. Stat. § 71, the Oklahoma Department of Environmental Quality has established the following new procedures for an individual to obtain an agency-issued license/certification.

A. **In order to obtain a license/certification or to renew an existing license/certification, the documentation requested in Sections C and E, including a signed Affidavit Regarding Citizenship, is required. In the absence of the required documentation, citizenship and immigration status cannot be determined and applicants may not be eligible for the license/certification for which they are applying.**

B. **The Department of Environmental Quality will have available notary public services for the Affidavit Regarding Citizenship at no cost to the applicant at the main office located at 707 N. Robinson, Oklahoma City, Oklahoma 73101 during regular business hours (8:00 a.m. – 4:30 p.m. Monday through Friday, except holidays).**

C. **The following documents must be provided to the agency with the relevant license/certification application in order to establish eligibility:**

ALL U.S. CITIZENS

1. A copy of a valid, unexpired **Driver's License** or **Photo-Identification Card** from your state of residency; AND
2. An original or certified copy of a **Birth Certificate,** a photocopy of a valid, unexpired **U.S. Passport,** a photocopy of a **Certificate of Citizenship (N-560 or N-561),** or a photocopy of a **Naturalization Certificate (N-550 or N-570);** AND
3. A signed and notarized **Affidavit Regarding Citizenship (see attached affidavit)**

ALL NON-U.S. CITIZENS:

If you are not a U.S. Citizen, but are a qualified alien under the federal Immigration and Nationality Act and are lawfully present in the U.S. to work, please provide one of the documents listed in Section E, along with the Affidavit Regarding Citizenship.

D. **The Oklahoma Department of Environmental Quality participates in the Systematic Alien Verification for Entitlements (SAVE) Program, which is an intergovernmental information-sharing initiative designed to aid in determining a non-citizen applicant's immigration status (lawful presence), and thereby ensuring only eligible non-citizens receive government benefits, such as licenses/certifications.**

E. The Oklahoma Department of Environmental Quality will only issue licenses/certifications to Qualified Aliens (non-U.S. citizens) who present valid documentary evidence of one (1) of the following:

- ☐ Unexpired foreign passport, with I-551 stamp, or attached Form I-94 indicating unexpired employment authorization;
- ☐ Permanent Resident Card or Alien Registration Receipt Card with photograph (Form I-151, or I-551);
- ☐ Unexpired Temporary Resident Card (Form I-688);
- ☐ Unexpired Employment Authorization Card (Form I-688A)
- ☐ Unexpired Reentry Permit (Form I-327);
- ☐ Unexpired Refugee Travel Document (Form I-571);
- ☐ Unexpired Employment Authorization Document issued by Department of Homeland Security ("DHS") containing a photograph (Form I-688B);
- ☐ Valid unexpired immigrant or non-immigrant visa status for admission into the United States;
- ☐ Pending or approved application for asylum in the United States;
- ☐ Pending or approved application for temporary protected status in the United States;
- ☐ Approved deferred action status (Aliens whose deportation is being withheld under (1) § 243(h) of the Immigration and Nationality Act ("INA") as in effect prior to April 1, 1997 or (2) § 241(b)(3) of the INA;
- ☐ Pending application for adjustment of status to legal permanent resident or conditional resident status. (Aliens granted conditional entry under § 2039 (a)(7) of the INA before April 1, 1980). (Upon approval, the applicant may be issued a temporary license/certification for the period of time of the authorized stay in the U.S., or if there is no definite end to the period of authorized stay, then for period of one (1) year);
- ☐ Cuban and Haitian Entrants, as defined in § 501(e) of the Refugee Education Assistance Act of 1980;
- ☐ Aliens granted parole for at least one year under § 212(d)(5) of the INA;
- ☐ Battered aliens, who meet the conditions set forth in § 431(c) of Personal Responsibility and Work Opportunity Reconciliation Act ("PRWORA") as added by § 501 of the Illegal Immigration Reform and Immigrant Responsibility Act of 1996, P.L. 104-208 (IIRIRA), and amended by § 5571 of the Balanced Budget Act of 1997, P.L. 105-33 (BBA), and § 1508 of the Violence against Women Act of 2000, P.L. 106-386. Section 431(c) of PRWORA, as amended, is codified at 8 U.S.C. 1641(c);
- ☐ Victims of a severe form of trafficking, in accordance with § 107(b)(1) of the Trafficking Victims Protection Act of 2000, P.L. 106-386.

F. Complying with the above requirements does not guarantee issuance of a license/certification. Applicants must still satisfy all other required qualifications of the respective licenses/certifications for which they are applying.

G. <u>RENEWALS:</u>

Effective November 1, 2007, all applicants will be required to present the documentation listed in Sections C and E to establish eligibility. All licenses/certifications may be renewed upon expiration by, in addition to satisfying any other preconditions required by the particular license/certification, mailing a renewal application and any applicable renewal fee. For renewal applicants that have already demonstrated citizenship by satisfying the requirements set forth in Section C above in his/her original application or a prior renewal application, the applicant shall not be required to resubmit such documentation. For renewal applicants that identify themselves as a "qualified alien lawfully present" in the Affidavit Regarding Citizenship, the documents listed in Section E must be resubmitted to the Oklahoma Department of Environmental Quality with the renewal application in order to demonstrate that the applicant's lawful status has not changed.

Department of Environmental Quality

AFFIDAVIT REGARDING CITIZENSHIP

I, _____ swear under a penalty of perjury, that I am

_____ a United States citizen; or

_____ a qualified alien lawfully present in the United States, and I authorize the United States Department of Homeland Security to release my citizenship and immigration status to the Oklahoma Department of Environmental Quality in order to be eligible to receive the benefit/license/certification for which I am applying*

_____
License/certification Applicant

* Any person who knowingly and willfully makes a false, fictitious, or fraudulent statement or representation in this affidavit shall be subject to criminal penalties applicable in the State of Oklahoma for fraudulently obtaining a public assistance program benefit (a license/certification). If the affidavit constitutes a false claim of U.S. citizenship under 18 U.S.C. Section 911, a complaint will be filed by the Oklahoma Department of Environmental Quality with the United States Attorney for the applicable district based upon the venue in which the affidavit was executed.

ACKNOWLEDGEMENT

State of _____)
) ss:
County of _____)

Subscribed and sworn to before me this _____ day of _____, 200____.

_____
Notary Public

My Commission expires:_____

The Oklahoma Department of Environmental Quality

INSTRUCTIONS for OPERATOR CERTIFICATION EXAM APPLICATION

1. If you are applying for certification as water, wastewater or laboratory operator by **RECIPROCITY** from another state. Please fill out this section along with the rest of the application.

2. List the **CITY** and **DATE** of the exam you wish to take. Exam dates may be found in the current "MAIN EVENT" newsletter, or the Operator Certification website at www.deq.state.ok.us/WQDnew/opcert/index.html.

3. Print your **NAME**, **HOME ADDRESS**, **CITY**, **STATE**, etc. Your **BIRTHDATE** and **SOCIAL SECURITY NUMBER** must be shown.

4. List **YOUR JOB TITLE**: (Water Plant Supt, Wastewater Plant Supt, Water Plant Operator, etc).
   LICENSE NUMBER: If you are an Operator, Temporary operator or Helper in the State of Oklahoma, your **LICENSE NUMBER** may be found on the pocket card you are to carry with you at all times. If you are not certified, leave the space blank and a number will be assigned to you.
   DO YOU SUPERVISE OTHER EMPLOYEES? Answer yes or no. **IF YES**, list the number of employees you supervise. Please list the **NAME OF YOUR SUPERVISOR** and his/her **LICENSE NUMBER**.

5. List your **PLACE OF EMPLOYMENT'S** name, **ADDRESS**, **CITY**, **STATE**, etc.

6. **EMPLOYER'S WATER FACILITY / SEWER FACILITY ID NUMBERS**: The Water Facility Number is a seven-digit **NUMBER** and the Wastewater Facility **NUMBER** usually has 5 digits. These numbers identify the type of system. They can be obtained from your Supervisor or Employer.

7. **CHECK** (X) the box on the left of the exam you wish to take. Be sure notice that there are separate boxes for water and wastewater.

8. List your **EXPERIENCE** in Water, Wastewater, Laboratory, or Distribution/Collection which will be used to qualify for this examination. Be sure to list **"TO"** and **"FROM"** dates as well as **DESCRIBE YOUR DUTIES**. Make sure to list the required amount of experience for the exam you wish to take. A chart of requirements for each exam is located at the bottom of the first page of the exam application.
   NOTE: It is important to update this information each time you apply. DO NOT rely on this office to maintain the information. The regulation states this is the responsibility of the Operator.

9. **TRAINING CREDIT** - Please read carefully and enter **TITLE, LOCATION, DATES, HOURS** and **CLASS NUMBERS** as requested. Be sure to list any training you will be taking prior to the exam**.** Make sure to list the required amount of training for the exam you wish to take. A chart of requirements for each exam is located at the bottom of the first page of the exam application. **The training credit section cannot be left blank**. Submit verification of required training, Academic Transcripts, Attendance Records, etc.
   NOTE: It is important to update this information each time you apply. DO NOT rely on this office to maintain the information. The regulation states this is the responsibility of the Operator.

10. Read the **"STATEMENT OF UNDERSTANDING", SIGN**, **DATE.** Must be original signature, not a photocopy.

FEES: The application fee is a **non-refundable, nontransferable fee of $40 per exam.**
Please choose form of payment on the **PAYMENT FORM** located at the bottom of page 2 of the exam application.

Make your check or money order payable to: Dept of Environmental Quality and mail it with the exam application to:

DEPT OF ENVIRONMENTAL QUALITY
FINANCIAL & HUMAN RESOURCES
PO BOX 2036
OKLAHOMA CITY, OK 73I01-2036

FAXED APPLICATIONS WILL NOT BE ACCEPTED

The application must be postmarked at least **THREE** weeks prior to the date on which you wish to take the exam.

- √ Check your application to make sure that you have completed all blanks. If any information is not listed, your application is subject to being returned and not being approved.
- √ If you need assistance contact the operator certification section at (405) 702-8150 or (405) 702-8100.
- √ After you submit your exam application, you will receive a letter regarding approval/disapproval. If your application is returned to you with a disapproval letter, please make corrections and resubmit your application.

YOU ARE NOT APPROVED TO TAKE AN EXAM UNTIL YOU RECEIVE A LETTER OF APPROVAL FROM DEQ.

Rev. 7/2007

Class_____Water Exam – Score _____%
Class_____Sewer Exam – Score _____%
Dist\Coll Operator Exam – Score _____%
Class_____Water Lab Exam – Score _____%
Class_____Sewer Lab Exam – Score _____%
Dist\Coll Technician Exam – Score _____%

Date Results Mailed_____ ☐ Internet exam **THIS BOX FOR DEQ OFFICE USE ONLY**

PLEASE RETURN THE APPLICATION AND APPLICATION FEE TO: Dept. of Environmental Quality
Financial & Human Resources
PO Box 2036
Oklahoma City, OK 73101-2036

Must be postmarked 3 weeks prior to exam date.

PAYMENT INFORMATION

Payment must be included with this application. The **non-refundable** and **non-transferable** application fee is $40.00 per exam. Payment form is located at the bottom of page 2.

1. Are you applying for this certification by reciprocity? _____From what state? _____What classification? _____

Reciprocity may be granted when certification held in another state is current, in good standing and is comparable to Oklahoma Operator Certification rules.

2. **LOCATION** and **DATE OF EXAM YOU WISH TO TAKE**: **City** _____ **Date** _____

3. Name - Last: _____ **First:** _____ **MI**: _____

Address_____**City**_____ **State**_____ **Zip**_____

Social Security#_____/____/_____ **Birthdate**_____/_____/_____ **Home Phone #** ( ) _____

4. Your Job Title_____ **Your License #**_____

Do you supervise other operators or helpers? _____ If yes, how many? _____

Name of Immediate Supervisor_____ **Supervisor's License #**_____

5. Employer_____ **Address**_____**City**_____

State_____ **Zip**_____ **Office Phone #** ( ) _____

6. Water Facility ID#_____ **Wastewater Facility ID#**_____

7. Please place an X in the box to the left of the exam(s) you are applying for.

	WATER		WASTEWATER	REQUIRED AMOUNT OF TRAINING	REQUIRED EXPERIENCE
	D		D	16 hours	None
	C		C	36 hours	1 year
	B		B	100 hours	3 years
	A		A	200 hours	5 years
	C LAB		C LAB	32 hours of C lab training *	None
	B LAB		B LAB	32 hours of C lab training * & 32 hours of B level lab training	6 months
	A LAB		A LAB	32 hours of B lab training	5 years **
	DISTRIBUTION / COLLECTION				
	C OPERATOR			36 hours	1 year
	TECHNICIAN			8 hours	None

* An Associates Degree or greater in chemistry, biology, engineering, physical science, hydrology, geology, math, env. science, microbiology, toxicology, or civil, chemical, sanitary or env. engineering may be substituted for the 32 hours of DEQ approved C level training.

** Only 3 years of laboratory experience required with an Associates Degree in chemistry, microbiology, instrumental analysis or other field of science approved by the DEQ.

** **OR** 1 year of laboratory experience required with a Bachelor of Science degree in chemistry, microbiology, instrumental analysis or other field of science approved by the DEQ.

Exam Application Continued on Page 2

8. **Experience**: List your experience in water and/or wastewater system operations or maintenance. **YOU MUST LIST AT LEAST THE REQUIRED AMOUNT OF EXPERIENCE FOR THE LEVEL OF EXAM YOU WISH TO TAKE.** You can find the required amount of experience for each level in the chart at the bottom of the first page. List your present job first. Attach additional sheets if needed.

1. From_____ To_____ Name of Employer_____

   Employer's Address_____City_____State___Zip_____

   Describe your duties in detail: _____
   _____

2. From_____ To_____ Name of Employer_____

   Employer's Address_____City_____State___Zip_____

   Describe your duties in detail: _____
   _____

9. **Training Credit**: Please list all water and/or wastewater classes you have attended and/or will be attending prior to the exam**. YOU MUST LIST AT LEAST THE REQUIRED AMOUNT OF TRAINING FOR THE LEVEL OF EXAM YOU WISH TO TAKE.** You can find the required amount of training for each level in the chart at the bottom of the first page. Applicants requesting credit for technical school or college hours must attach an official transcript for credit to be granted.

THIS SECTION CANNOT BE LEFT BLANK. If you are planning to attend an approved training class prior to the date of your exam session, you must list it below.

Class Title and Location	Class Date(s)	Training Hours	Class Number

Total hours approved training _____

Highest high school grade or college degree completed: _____

10. **Statement of understanding**: I hereby certify under penalty of law that this application and any attachments contain no willful or negligent misrepresentation or falsification and that all information is true, accurate and complete. I understand that any misrepresentation or falsification may result in rejection of my application or in revocation of any certificate issued as a result of this application.

Signature of Applicant_____**Date**_____

Please Choose Form of Payment

___ Check Enclosed - Made Payable to DEQ
__ Money Order Enclosed - Made Payable to DEQ
___ Credit Card No: __ __ __ __ __ __ __ __ __ __ __ __ __ __ __ __
(**Must be Visa or MasterCard ONLY**)

Exp. (mm/yy) __ __/__ __

Authorized Signature: _____

___ Purchase Order No.: _____

Rev. 7/2007

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INTRODUCTION

This manual is not designed to replace the references, Standard Methods For the Examination Of Water And Wastewater, 20th Edition, 1998, Water Treatment Plant Operation, Third Edition, California State University, Sacramento, Volumes I and II, or any other comprehensive procedures manual. This is an introduction to common, inexpensive and readily available testing materials and simple techniques. Commercially available tests kits are emphasized because of their simple techniques, availability, and widespread use. Simplified and inexpensive instrumentation for basic spectroscopic examinations are included in additional to the required routine tests.

Laboratory control tests are the tools by which the efficiency of the processes at the water treatment plant are monitored and the proper process control procedures are chosen. By using accurate laboratory data, the operator can select the most effective process control changes and identify potential problems before they arise.

This manual is meant to be a study guide for the formal classroom courses. The Oklahoma Administrative Code ("OAC") Title 252, Department of Environmental Quality ("DEQ"), Chapter 710, Waterworks and Wastewater Works Operator Certification requires thirty-two (32) hours of approved classroom training presented by various training organizations within the state. In addition to receiving a passing grade for the written examination, an equally important hands-on or practical examination must be taken during the class room instruction. Both the written and the practical examinations must be successfully passed with a grade of at least 70%. These examinations will not be averaged; both must be passed.

This manual is designed for laboratory analysis for a Class "C" water treatment facility as required by the OAC, Title 252, DEQ Chapter 631, Public Water Supply Operation.

The subjects of laboratory safety, basic chemistry, the metric system, glassware, and equipment will not be discussed in this manual. These are indeed important and necessary subjects to know, but these particular subjects will be covered in the required thirty-two (32) hours of classroom instruction.

RULES

The OAC Rules 252:710-5-53(a) states that "All duties relating to the laboratory analysis of water quality samples from water treatment plants, groundwater systems, storage and distribution systems (including purchased-water systems) must be performed by or under the general supervision of a laboratory operator certified by the DEQ."

A person who is certified in laboratory operation may perform the laboratory analysis, but the person can not interpret the results of the laboratory data or give orders that will determine the method of working on the works or to change the quality of the water directly or indirectly by order unless that individual is properly certified as a waterworks operator.

If the waterworks contracts all or a portion of the required laboratory analysis with an associated laboratory, the owner of that works shall notify the DEQ in writing within ten (10) days. The notification shall include:

1. Which of the required analysis will be performed by the associated laboratory;
2. Whether the associated laboratory is currently certified by the DEQ;
3. Whether the associated laboratory will only be performing operational testing for the works;
4. Whether the laboratory operator has the responsibility or authority to determine the method of working on the works or to change the quality of water of the waterworks directly or by order.

Certified laboratory operators of laboratories owned by or associated with waterworks shall record, at the time of the analysis, the results of all required analysis in a bound volume. Each entry shall be dated and signed by the individual who performed the analysis. Each volume shall be kept on file at the laboratory for inspection and review for ten (10) years.

LABORATORY PROCEDURES LIST

STANDARD AND STOCK SOLUTIONS ---------- make-up

SAMPLING ---------- types and techniques

BACTERIOLOGICAL ---------- sampling only

QUALITY ASSUARANCE ---------- quality control and quality assessment

TEMPERATURE ---------- Celsius and Fahrenheit

TURBIDITY ---------- nephelometric only

pH ---------- meter only

CHLORINE RESIDUAL – FREE & TOTAL ---------- commercial kits & bench titration

ALKALINITY – P & TOTAL ---------- commercial kits & bench titration

$CaCO_3$ STABILITY – MARBLE TEST ---------- procedure & interpretation

* JAR TEST ---------- procedure & interpretation

** FLUORIDE ---------- SPADNS and ELECTRODE method

*** HARDNESS ---------- EDTA titrimetric titration

*** MANGANESE ---------- Persulfate method & DR 4000 Perodate method

*** IRON ---------- Phenanthroline method & DR 4000 FerroVer method

* When required to meet turbidity requirements
** When fluoridation is practiced
*** When required for process control or to meet DEQ requirements

LABORATORY PROCEDURES

SAMPLING AND PRESERVATION

The most common remark a person hears about sampling is that the results of the analysis are no better than the sample. Not only is this statement true, but it is one of the most important aspects of laboratory procedure.

The objective of sampling is to collect a portion of material small enough in volume to be transported conveniently and handled in the laboratory, while still accurately representing the material being sampled. This assumes that the proportions or concentrations of the components being tested are the same in the sample as in the body of the material being sampled. It is also assumed that the handling of the material from the act of sampling, to the laboratory, and throughout the analysis has not resulted in any significant change in the composition or concentration of the components being tested.

In many cases, the sampling is to show the compliance with regulatory requirements. Due to the increasing importance of being able to verify the accuracy and representation of data, greater emphasis is placed on the proper sample collection and preservation.

Often in waterworks, the laboratory determines the specific sampling program, which is determined by the user of the test results. Such determinations are important to insure that the selection of samples and the methods of analysis provide correct and accurate data necessary to answer the questions that resulted in the sampling being done.

PRECAUTIONS

Note: Check Table #1 for the proper container and preservation of samples.

When no preservative or dechlorinating agent is present in the sample container, rinse the container two (2) or three (3) times with the water that is being sampled.

If the container holds a preserving agent or any other compound, do not overfill because you will dilute or loose the preserving agent. Leave an air space in the container of about 1% of the volume to allow for thermal expansion.

The choice of sampling method must be defined in your sampling plan.

Separate any suspended or floating matter by decanting, centrifuging, or filtering.

For metals, it is appropriate to collect filtered and unfiltered samples to differentiate between total and dissolved compounds.

Determine the acid requirements beforehand to bring the pH to <2 and add the same amount to all containers.

Filter the sample in the field or at the time of collection before adding the acid to lower the pH <2.

Make a record of every sample collected and identify every bottle. (Date, time, location, test, and sampler initials.)

Before collecting sample from distribution lines, flush the lines with three (3) to five (5) times the volume of the line. Calculation of the time required to adequately flush a line two (2) times its volume is shown below.

$$\text{Pipe volume (cu. Ft.)} = \frac{\text{(pipe area. Sq. in.)} \quad \text{(pipe length, ft.)}}{\text{144 sq. in./sq. ft.}}$$

$$\text{Flushing Time (min.)} = \frac{\text{(pipe volume, gal.)} \quad \text{(2 times)}}{\text{Flow, gal./min.}}$$

At individual taps, flush the line for three (3) to five (5) minutes.

If sampling from a well, pump the well long enough to ensure that the sample represents the groundwater source.

When sampling a small stream for a grab or catch sample, take it in the middle of the stream at mid-depth. For a larger stream or river, more than one sample is usually required to obtain a representative sample. When sampling lakes or impoundments, choose the location, depth, number, and frequency of sampling, depending on the local conditions. This usually requires several samples mixed together to obtain a representative sample because of poor mixing and stratification of the lake waters.

TABLE #1
RECOMMENDATIONS FOR SAMPLING AND PRESERVATION

Measurement	Vol. Req. (mL)	Container	Preservative	Maximum Holding Time
PHYSICAL PROPERTIES				
Color	500	P,G	Cool, 4° C	48 hours
Conductance	500	P,G	Cool, 4° C	28 days
Hardness	100	P,G	Cool, 4° C HNO_3 to pH <2	6 months
Odor	200	G Only	Cool, 4° C	6 hours
pH	25	P,G	Det. on site	Immediately
Residue, Filterable	100	P,G	Cool, 4° C	7 days
Temperature	1000	P,G	Det. on site	Immediately
Turbidity	100	P,G	Immediately	
METALS (Fe, Mn)				
Dissolved	200	P,G	Filter on Site HNO_3 to pH <2	6 months
Suspended	200		Filter on site	6 months
Total	100	P,G	HNO_3 to pH <2	6 months
INORGANICS, NON-METALLICS				
Acidity	100	P,G	Cool, 4° C	14 days
Alkalinity	200	P,G	Immediately/within a few hours	
Bromide	100	P,G	None req.	28 days
Chloride	50	P,G	None req.	28 days
Chlorine	500	P,G	Det. on site	Immediately
Cyanide	500	P,G	Cool, 4° C NaOH to pH >12	14 days
Fluoride	300	P	None req.	28 days
Iodide	100	P,G	Cool, 4° C	24 hours
Nitrogen				
Ammonia	500	P,G	Cool, 4° C H_2SO_4 to pH <2	28 days
Kjeldahl, Total	500	P,G	Cool, 4° C H_2SO_4 to pH <2	28 days
Nitrate plus Nitrite	200	P,G	Cool, 4° C H_2SO_4 to pH <2	28 days
Nitrate	100	P,G	Cool, 4° C	48 hours
Nitrite	100	P,G	Cool, 4° C	48 hours
Dissolved Oxygen				
Probe	300	G Only	Det. on site	Immediately
Winkler	300	G Only	Fix on site	8 hours
Phosphorous				
Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4° C	48 hours
Hydrolyzable	50	P,G	Cool, 4° C H_2SO_4 to pH <2	24 hours
Total	50	P,G	Cool, 4° C H_2SO_4 to pH <2	28 days
Total, Dissolved	50	P,G	Filter on site Cool, 4° C H_2SO_4 to pH <2	24 hours
Silica	50	P Only	Cool, 4° C	28 days
Sulfate	100	P,G	Cool, 4° C	28 days
Sulfide	100	P,G	Cool, 4° C 2 mL zinc acetate	7 days
Sulfite	50	P,G	None Req.	Immediately
Bacteria	125	P, Sterile	$Na_2S_2O_3$	30 hours

TYPES OF SAMPLES

Grab Sample	A single sample of water collected at a particular time and place, which represents the composition of the water only at that time and place.
Composite Sample	A collection of individual samples obtained at regular intervals, usually every one (1) to two (2) hours during a twenty-four (24) hour time span. Each individual sample is combined with the others in proportion to the rate of flow when the sample was collected. The resulting mixture (composite sample) forms a representative sample and is analyzed to determine the average conditions during the sampling period.

The type and frequency of sampling to satisfy the regulatory requirements are determined by that regulatory agency.

SAMPLING METHODS

Manual Sampling	Manual sampling involves minimal equipment but may be too costly and time-consuming for routine or large-scale sampling programs.
Automatic Sampling	Automatic samplers can eliminate human errors that are frequent in manual sampling, reduce labor costs, and provide a way for more frequent sampling.
Caution	Be sure that the automatic sampler does not contaminate the sample. Periodically, clean the automatic sampler.

CHAIN-OF-CUSTODY PROCEDURES

It is very important to be sure of the sample integrity from the point of collection to the reporting of the laboratory data. This includes the ability to trace possession and handling of the sample through all the steps from collection to final deposit. This process is called chain-of-custody and is extremely important when legal litigation is involved.

A sample is considered to be under a person's custody if it is in the individual's physical possession, in the individual's sight, secured in a tamper-proof way by that individual, or secured in a restricted area. The following procedures summarize the major aspects of chain-of-custody.

1. Sample Labels – use labels to prevent sample misidentification.
2. Sample Seals – use seals to detect unauthorized tampering.

3. Field Log Book – record all information pertinent to a field survey or sampling in a bound log book.

4. Chain-of-Custody Record – fill out a chain-of-custody record to accompany each sample or group of samples.

5. Sample Analysis Request Sheet – the sample analysis request sheet accompanies the sample to the laboratory. The collector completes the field portion and the laboratory personnel completes the laboratory portion.

6. Sample Delivery to the Laboratory – deliver the sample to the laboratory as soon as practical after collection. If the sample is shipped by commercial carrier, be sure the way bill number and the chain-of-custody record accompanies the sample.

7. Receipt and Logging of Sample – sample custodian inspects the sample, checks the label information and seal against chain-of custody records, assigns a laboratory number, logs sample in laboratory log book and stores in a secure place.

8. Assignment for Analysis – the laboratory supervisor assigns the sample to an analyst who is responsible for its' care and custody.

BACTERIOLOGICAL SAMPLING

Bac-t sampling sites must be predetermined and then approved by the Water Quality Division (WQD) of the DEQ. These sampling sites must be adhered to and cannot be changed without the approval of the WQD. Listed below are important steps that should always be followed in order to assure yourself that you will have the best opportunity to obtain a safe sample.

1. Remove any screen or aerator from the facuet. Do not use a swivel faucet.
2. Wash your hands thoroughly.
3. Leave the water running from the faucet for at least three minutes to clear out the line before taking your sample.
4. Carefully cut through the connecting seal below the arrow with a knife.
5. Open the lid very carefully, not touching the inside of the lid or container. If you do touch the inside of the lid or container, throw the container away and start with a new one.
6. Check for the sodium thiosulfate pill or powder. If the pill is not there, discard the container and start over.
7. Fill with the sample to the line between the mold shoulder and the EPA 100 ml fill line. Samples that are not filled to the proper line will not be tested. Your system will not receive credit for an incorrectly filled container.
8. Close the container, being careful not to touch the inside of the lid or container. Close the lid tightly to avoid any leakage.
9. Insert the barbed lock through the holes in the lid and flange and draw the barb through the lid, locking it to the flange.
10. Write the system name, I.D.# and the sample site three digit code on the container using a waterproof marker on a piece of tape. Flair type markers and ball point pens do not work.
11. Place in the mail with the completed Bac-t sampling log in form (form #407). Be sure you fill in the date, time, Cl residual and mailing address.
12. Mail by 1st class mail so it will reach the DEQ laboratory within twenty-four (24) hours.

QUALITY ASSURANCE

Quality Assurance (QA) is defined as a set of principles and techniques that, if followed and performed exactly according to the written guidelines for sample collection throughout the analysis, will produce data of known and defensible quality. In other words, the accuracy of the results of the analysis can be stated with a high degree of confidence. This is of the utmost importance if this data is questioned by any regulatory authority or in a court of law.

In any laboratory and with any laboratory operator, the quality and accuracy of the data cannot be proven without a well prepared and judiciously carried out program of quality assurance. However, no matter how thorough the quality assurance program and how carefully the program is implemented, the quality assurance program means nothing if accurate and complete records are not maintained. In any inquiry or in any court of law, your quality assurance program is useless without documentation of the proper control and application of all factors which affect the final results of the analysis.

Quality assurance in the laboratory may mean many different things to many people. To some it is merely judged on such factors as:

1. Adequately trained personnel;
2. Good physical facilities and equipment;
3. Certified reagents and standards;
4. Frequent servicing and calibration of instruments;
5. A knowledgeable and understanding management;
6. The use of duplicates and known additions; and/or
7. Documentation of lab results and quality control procedures.

All of these things are important, but none by themselves assures reliability of the laboratory data.

Any good quality assurance program must include:

1. Standard Methods – use only methods that have been accepted by Standard Methods or by the regulatory agency;
2. Internal quality control; and
3. External quality control (Quality Assessment).

Everyone realizes that it is a major effort in most small municipalities to retain an operator who is qualified to perform laboratory analysis and have some degree of confidence in the results reported. Often it is a major accomplishment just to arrive at theses results so why burden your lab operator with another chore called “Quality Control”? This could be answered with the old familiar phrase “If something is worth doing at all, its worth doing right”!

It is recognized that most lab operators practice quality control to some degree, (whether they know it or not), mostly depending upon the training, professional pride and awareness of the importance of the work they are doing. However, under the pressure of daily workload, many aspects of quality control may be easily neglected or ignored. Therefore, an established and documented routine quality control program applied to every analysis being performed is important in assuring the reliability of the final data.

The laboratory operator must always be aware that the recorded laboratory results can be challenged at any time by anyone. This is the reason the operator must be sure that the recorded results are the actual and accurate data obtained. If the original data from the analysis is not recorded or is changed by someone, this is a serious matter indeed. This is the primary reason for the rule OAC 252:710-5-53(b) which states that "Operators of laboratories owned by or associated with waterworks/wastewater works shall record the results of all laboratory analyses in a bound volume for each facility and shall date and sign each entry. Records shall be kept on file at the laboratory for inspection and review for ten (10) years for waterworks and three (3) years for wastewater works." This rule gives protection for the laboratory operator if the data is later changed on the required reporting forms by someone else.

If the data is changed from the original results and then recorded in the bound volume, this gives no protection for the operator. This bound volume must be a volume that no pages can be removed or torn out of without being noticed.

Falsification of data is a very serious offense which can result in revocation of certification, a fine, and/or jail time.

QUALITY CONTROL

Quality control is internal and external control measures. For this discussion, external control will be termed as quality assessment.

The internal quality control methods consist of at least the following seven elements.

1. Certification of operator competency. Before an analyst is permitted to perform reportable work, competency in making the analysis is to be demonstrated.
2. Recovery of known additions. Use the recovery of known additions (Spikes) as a part of your analysis 10% of the time or one for every batch, whichever is greater to verify the absence of matrix effects.
3. Analysis of externally supplied samples. As a minimum, analyze externally supplied standards whenever the analysis of known additions fails to result in 5% acceptable recovery, or at least once a day, whichever is more frequent.
4. Analysis of reagent blanks. Analyze reagents blanks whenever new reagents are used or required by specific methods. Always analyze a minimum of 5% of the sample load as reagent blanks.
5. Calibration with standards. As a minimum, measure at least three different dilutions of the standard when an analysis is started. Afterwards, verify the

standard curve daily by analyzing one or more standards within the linear range as specified in the individual method.

6. Analysis of duplicates. When measurable levels of the constituents being determined are present, the analysis of duplicates is valuable in determining precision. Analyze at least 10% of the samples in duplicate.

7. Control charts. Three types of control charts are commonly used in laboratories: a means chart for standards; a laboratory control standards chart; and a calibration check standards chart. For detailed discussion of these charts, consult Standard Methods.

Internal quality control of any laboratory analysis involves consideration and control of the many variables which affect the production of reliable data. The quality of the laboratory services available to the lab operator must be included among these variables:

1. The quality of distilled or de-ionized water;
2. Clean and dry compressed air;
3. Properly regulated electrical power;
4. Clean and proper glassware; and
5. Rotation of the chemical stock, mark date received and use old chemicals first.

Not all of these apply to all laboratories; however, every laboratory must address the importance of a good source of distilled water and clean glassware.

Standard Methods provides a good first step towards a good internal Quality Control program provided there are no "short cuts" employed. The next step is to rule out the introduction of outside interferences that can be controlled within the laboratory itself.

QUALITY ASSESMENT

Quality assessment is the process of using external control measures to determine the quality and validity of the data produced by the laboratory. This includes the items listed below:

1. Performance evaluation samples. Use samples with known amounts of the constituent being measured supplied by an outside agency or blind additions prepared independently within the laboratory to determine recovery achieved by the analyst. The recovery must fall within the acceptable range of recovery previously established.

2. Performance audits. Make unscheduled performance audits using a check list to document how the sample is treated from receipt of the sample to the final reporting of the result. The goal is to detect any deviation from the standard operating procedure so that corrective action may be taken if needed.

3. Laboratory intercomparison samples. Commercial and governmental programs supply samples containing different constituents in different matrices. A quality laboratory participates in a well planned inter comparison assessment program.

DATA QUALITY INDICATORS

The primary indicators of data quality are **bias** and **precision**. They are defined as the following:

Bias — Is the measure of systematic error. It has two components, one due to the method, which is measured by a laboratory inter-comparison study, which is the difference between the grand average and the true value.

The other is due to the laboratory's use of the method which is measured by the difference between the laboratory's average recovery and the true value. This bias is measured by recovery of known additions and/or duplicate samples.

Precision — Is a measure of the closeness of results in multiple duplicate samples, repeated analysis of a stable standard or repeated analysis of known additions to samples. The analysis of duplicate samples includes the random errors involved in sampling, as well as, sample preparation and analysis.

Precision is documented by Internal Quality Control

Accuracy — Is defined as the combination of bias and precision.

Accuracy is documented by External Quality Control

The relationship between precision and accuracy can be explained in this way. You are throwing darts at a target. You throw five darts at the bulls-eye and all the darts land very close together, but in a one inch circle in the lower left hand portion of the target. This is very inaccurate because you did not hit what you were aiming at and missed the bulls-eye by a mile.

However, you did throw the darts with precision, because all five darts are very close together. In other words, you repeated the placement of each dart very close to each other.

Then someone else throws the five darts at the bulls-eye and all five darts hit the bulls-eye. This accurate, because all five darts hit what they were thrown at. This is also called precision, because all five darts were very close together.

The external quality control (quality assessment) is a check on whether the laboratory has and practices an acceptable internal quality control program.

STANDARD AND STOCK SOLUTIONS

A standard solution is defined as a solution in which the exact concentration of a chemical or compound is known. A stock solution is defined as a strong solution of a chemical or compound of which the exact concentration is known and is used as a base for further dilutions.

The word "normal", abbreviated N, in front of a reagent or compound indicates the strength or concentration. Normal is defined as a solution that contains one gram equivalent weight of a compound/liter of solution. The equivalent weight of an acid is that weight which contains one gram atom of ionizable hydrogen or its chemical equivalent.

Another way to indicate the concentrations of solutions is the a+b system. This means that "a" volumes of a concentrated reagent is diluted with "b" volumes of water. For example: 1+1HCl means 1 volume of hydrochloric acid is diluted with 1 volume of water. If you have a solution with a normality of 0.02 N, this can also be expressed as N/50 or 1/50 N. They all mean the same thing, but are expressed in different ways.

PROCEDURE

When measuring chemicals or compounds for standard solutions, **always** use volumetric pipettes and volumetric flasks to insure accurate measurements.

When preparing a standard solution from a dry chemical, always weigh on an analytical balance for extreme accuracy.

When adding a dry chemical or a liquid solution in preparing a standard solution, add the chemical or liquid to a small amount of water in the volumetric flask and then add water to the volume mark.

As a general rule, stronger solutions usually store for longer periods of time than weak solutions.

Make up new standards periodically to check against old standards to determine if the old standard has lost strength.

If you have a lesser weight of a compound than it requires to make up 1 liter of solution, you can calculate how much water to add to make up the desired N. Use the following formula:

$$\text{Dilute to ml} = \frac{(\text{actual weight, gr.})(1000\text{ml})}{(\text{desired weight, gr.})}$$

TEMPERATURE

Temperature is one of the most frequent tests taken in the water laboratory. Temperature has a direct affect on almost any analysis you will perform in the laboratory or in the field.

The temperature of the water affects the rate of most chemical reactions. It affects pH, the amount of gasses dissolved in water, the amount of solids dissolved in water, biological growth rates, water stability, and many other aspects of water chemistry.

Temperature measurements are usually made with any good mercury filled thermometer. There are two different temperature scales. The one most people are familiar with is the Fahrenheit scale where the freezing point for water is 32° and the boiling point is 212°. The scale used in the laboratory is the Celsius scale where the freezing point for water is 0° and boiling point for water is 100°.

There are two types of glass thermometers; the total immersion type and the partial immersion type. The total immersion thermometer must be completely immersed in the solution to obtain an accurate reading. The partial immersion thermometer must be immersed at least to the solid line (water-level indicator) for an accurate reading.

For the proper quality control of temperature, you must calibrate your thermometers with a National Bureau of Standards and Technology (formerly American Bureau of Standards) thermometer at least once a year.

PROCEDURE

Immerse the thermometer to the proper depth.

Never let the thermometer touch the bottom or sides of the container because the container is usually influenced by the temperature of the surrounding air which will result in false readings.

If you are measuring the temperature of well water or water from a large container or body of water, let the water run into a cup (a polystyrene cup is ideal) and continuously overflow while the measurement is taken. Keep the thermometer in the water and wait about a minute or until the reading stabilizes before recording the reading.

CALCULATIONS

The following calculations show the correct way to convert from one temperature scale to the other.

$$°C=\frac{(°F-32)}{1.8} \qquad °F=1.8(°C) + 32$$

CHLORINE RESIDUAL

Chlorine residual is the amount of chlorine left in the water after the demand has been satisfied. There are two types of residuals to be measured.

Free residual chlorine refers to the chlorine contained in the compounds chlorine (Cl_2); hypochlorous acid (HOCl), and the hypochlorite ion (OCl-). (MEASURED)

Combined residual chlorine refers to the chlorine in the compounds resulting from the reaction between ammonia and chlorine. The most important of these compounds are monochloramine (NH_2Cl), dichloramine ($NHC1_2$) and trichloramine ($NC1_3$). (CALCULATED)

Total chlorine residual is the sum of the free chlorine and the combined chlorine residuals. (MEASURED)

The three (3) most common methods of analysis are the amperometric titration method, the color comparator method, and the titration method. The only acceptable method of chlorine analysis is the DPD method. The Orthotolidine method is no longer accepted by the DEQ or by the EPA.

AMPEROMETRIC TITRATION METHOD

This method is the most accurate and the least subject to interferences. However, it requires more operator skill than the other methods and requires relatively expensive equipment. This method will not be outlined in this manual but the method is described in Standard Methods.

COMMERCIAL KITS

This method is quick, simple, inexpensive, and suitable for field use, as well as, laboratory use. There are various manufacturers of DPD kits that measure both the free chlorine and the total chlorine levels. There are slight variations in the instructions and usage of the kits available.

PRECAUTIONS

Analysis must be made immediately after sampling. (Within fifteen (15) minutes.)

Rinse the sample bottle and the viewing containers with the water being tested.

Add the proper chemicals as instructed, **mix well**.

Fill one viewing container with the treated sample, stopper and be sure there are no air bubbles present. Do the same with the untreated sample.

When measuring the residual, always try to use the same light source and intensity when you make your reading. Do not use direct sunlight, but try to use the same source of artificial light.

You should always strive to perform the test at the same temperature each time (preferably at room temperature).

The manufacturer's instructions must be followed exactly to assure the reliability of your results. In general, the method consists of adding various reagents to the sample, visually comparing the color sample, and reading the chlorine residual in mg/L directly from the color disk.

<u>One thing should be made very clear</u> – DPD kits made for swimming pool analysis are NOT acceptable for potable water analysis because they <u>are not accurate</u> enough. Chlorine residual test kits should be accurate at least to the nearest 0.05 mg/L.

DPD TITRAMETRIC METHOD

This method is usually more accurate than the color comparison method and is easier to perform than the amperometric method.

APPARATUS:

graduated cylinder (100 ml)
pipettes (1 & 10 ml)
Erlenmeyer flask (250 ml)
buret (10 ml)
magnetic stirrer and stirring bar
analytical balance

REAGENTS:

H_2SO_4 solution add 10 ml of concentrated sulfuric acid to 30 mL distilled water then cool.

Standard ferrous ammonium sulfate solution (FAS titrant), 0.00282 N dissolve 1.106 gr. of $Fe(NH_4)_2(SO_4)_2$ 6 H_2O in distilled water containing 1.0 ml of the acid solution described above and dilute to 1.0 liter using freshly boiled and cooled distilled water.

Phosphate buffer solution, pH 4.

DPD indicator solution.

Potassium iodide (KI) crystals.

PROCEDURE:

(A) FREE RESIDUAL

1. Place 5 ml of buffer solution and 5 ml of DPD indicator solution in a 250 ml flask and mix.
2. Add 100 ml of sample to the flask and mix.
3. Titrate with standards FAS until red color disappears.
4. Record the volume of FAS used (A). If combined residual is needed, proceed to Step (B).

Ml FAS = mg/L Cl residual

(B) TOTAL RESIDUAL

1. Add about 1 gram of KI crystals to the flask, mix until dissolved and let stand for two (2) minutes.
2. Continue titration with the FAS until the red color again disappears.
3. Record total volume of FAS used (B).

Ml FAS = mg/L Cl residual

COMBINED RESIDUAL

Ml FAS = mg/L Cl residual

A = mg/L free Cl
B = mg/L total Cl
B-A = mg/L combined Cl

PRECAUTIONS:

pH control is essential. The pH of the sample, buffer, and the DPD indicator must be between 6.2 and 6.5.

If oxidized manganese is present in the sample, add 5 ml of buffer solution and 0.5 ml of sodium arsenite to the titration flask.

Higher temperatures lead to false positive results and increase color fading.

Copper (Cu) interferences up to about 10 mg/L is overcome by the addition of EDTA.

Chromate above 2 mg/L will interfere with the end point determination – add barium chloride to mask this interference.

The analysis of chlorine residual must be made as soon as possible after sampling. You cannot store chlorine samples to be analyzed at a later time because the chlorine will dissipate from the sample.

TOTAL ALKALINITY

Alkalinity is a measure of the water's capacity to neutralize acids. Many of the chemicals used in water treatment, such as alum, chlorine, and lime causes changes in alkalinity concentration. Alkalinity concentration is important in determining chemical dosages for coagulation, softening, and stability.

The alkalinity of water is the capacity of that water to accept protons. Alkalinity is usually imparted by the bicarbonate, carbonate, and hydroxide components of a natural or treated water supply. It is determined by titration with a standard solution of a strong mineral acid to the successive bicarbonate and carbonic acid equivalence points indicated electromagnetically or by means of color. Phenolphthalein indicator enables the measurement of that alkalinity fraction contributed by the hydroxide and half of the carbonate. Indicators responding in the pH range 4-5 are used to measure the alkalinity contributed by hydroxide, carbonate, and bicarbonate. The phenolphthalein alkalinity and total-alkalinity titrations are useful for the calculation of chemical dosages required in the treatment of natural water supplies. The stoichiometric relationships between hydroxide, carbonate, and bicarbonate are valid only in the absence of significant concentrations of weak acid radicals other than hydroxyl, carbonate, or bicarbonate.

COMMERCIAL KITS

There are various commercial kits available for the analysis of total alkalinity and it is most important that the manufacturer's instructions are followed exactly.

PRECAUTIONS:

Rinse the sample container with the water being tested.

Fill the sample container to the fill line or with the proper volume.

After adding the reagent, **mix well.**

When adding the indicator, **mix by swirling the bottle after each drop.**

Keep an accurate count of the drops of indicator added.

PHENOLPHTHALEIN

Add the required amount of sample to a beaker or flask. Then add the required amount of indicator to the sample and mix well by swirling.

If no pink color appears, the "P" alkalinity is 0 and the pH is less than 8.3.

If color appears, add the acid reagent as instructed, slowly, drop by drop, until the color changes to clear. That point is the endpoint. **Be sure to count the drops accurately.** Calculate the "P" alkalinity according to the manufacturer's instructions.

TOTAL

To the same sample, add the required amount of the indicator for the total analysis. Swirl to mix.

Add the proper number of drops of the proper indicator.

If the color appears (green), titrate with the acid as instructed, slowly drop by drop, until the color turns rose red (Purplish), **counting the drops accurately**. Calculate the total alkalinity as the instructions indicate.

pH METER AND TITRATION METHOD

TOTAL AND PHENOLPHTHALEIN ALKALINITY

1. Add 100 ml of sample to a beaker (or a volume that will give you less than 50 ml of acid titrant).
2. Put the electrodes of the pH meter into the beaker and slowly stir the sample.
3. Check the pH of the sample. If the pH is 8.3 or lower, there is no "P" alkalinity. Go to step 5.
4. If the pH is greater than 8.3, titrate very carefully and slowly with 0.02 N sulfuric acid (H_2SO_4) until the meter reads pH 8.3. Record the amount of acid used in ml to reach pH 8.3.
5. amount of acid used in steps four (4) and five (5).
6. Calculate the total and "P" alkalinities as shown by the example below.

CALCULATIONS:

The results of titrations for alkalinity on a water sample were:

Sample size		100 ml
Titrant used to pH 8.3	A=	0.5 ml
Total titrant used to pH 4.5	B=	6.8 ml
Sulfuric acid (H_2SO_4) normality		0.02 N

"P" Alkalinity in mg/L as calcium carbonate ($CaCO_3$)

$$= \frac{A \times N \times 50{,}000}{\text{ml of sample}}$$

$$= \frac{(0.5 \text{ ml}) \times (0.02 \text{ N}) \times 50{,}000}{} = 5 \text{mg/L}$$

100 ml

Total Alkalinity in mg/L as calcium carbonate ($CaCO_3$)

$$= \frac{B \times N \times 50{,}000}{\text{Ml of sample}}$$

$$= \frac{(6.8 \text{ ml}) \times (0.02 \text{ N}) \times 50{,}000}{100 \text{ ml}} = 68 \text{ mg/L}$$

CALCIUM CARBONATE STABILITY (MARBLE TEST)

Although most modern waterworks practice some form of corrosion control for the water mains, it is still essential that treated waters be as non-corrosive as possible. This is especially true concerning the plumbing in private and public buildings when considering the regulations for lead and copper concentrations. Corrosive water will attack the lead and copper in plumbing fixtures, joints, and piping resulting in concentration above the limits allowed by state and federal regulations.

Calcium carbonate is an excellent material for the protection of mains and pipes against corrosion. It is chemically inert to most waters, and can be made to form a strong, smooth, and tightly adhering film on the inside surfaces of most mains and pipes (with the exception of plastic material). This is the principle behind controlling corrosion by adjusting the chemical characteristics of the water.

The objective is to control the composition of the water so that a very thin film of calcium carbonate will be deposited on the surfaces which have contact with the water. On the other hand, it is undesirable for the film to be too thick because of the reduction of the inside diameter of the pipes. This increases the possibility of producing a rough inside surface of the pipe, reduces water pressure, and lowers water volume delivered.

The nature and amounts of the substances dissolved in water determine its chemical "balance". Some waters are known to be "aggressive", which means that they will have a tendency to attack and corrode many mains and plumbing. Others with different chemical balances will tend to deposit layers of calcium carbonate scale on the walls of the mains and plumbing; these are known as "scale forming". In between these two (2) conditions are waters which are "in balance" and exhibit little tendency towards corrosion or scale deposition but instead result in a very thin layer of calcium carbonate which protects the surface from serious corrosion.

APPARATUS:

BOD bottle, 300 ml
funnel
filter paper

REAGENTS:

Powdered calcium carbonate

PROCEDURE:

1. Determine the total alkalinity.
2. Collect 300 ml of the sample in a 300 ml BOD bottle.

3. Add about 0.3 to 0.4 grams (about ½ teaspoon) of calcium carbonate ($CaCO_3$) to the sample.
4. Replace the stopper so that the bottle is completely full and no air bubbles are trapped in the bottle.
5. Shake vigorously every fifteen (15) minutes for at least three (3) hours.
6. Allow the sample to set for at least three (3) hours (preferably overnight) without any movement or vibration.
7. Carefully withdraw 200 ml of supernatant off the top.
8. Filter through a funnel and filter paper.
9. Determine the total alkalinity.

INTERPRETATION:

If the first alkalinity reading is less than the second reading (marble alkalinity), you have a negative value and the water is under-saturated and may be corrosive.

($Alkalinity_1$) – ($Alkalinity_2$) < 0 = Corrosive

If the first alkalinity reading is greater than the second reading (marble alkalinity), you have a positive value and the water is super-saturated and may cause scale deposition.

($Alkalinity_1$) – ($Alkalinity_2$) > 0 = Scaling

If both alkalinity readings are equal or very near equal, the water is considered stable.

($Alkalinity_1$) – ($Alkalinity_2$) = 0 = Stable

Record the 2nd reading in the stability column of your MOR.

pH—METER METHOD

The measurement of pH is another important and misunderstood measurement in water chemistry. Almost every phase of water treatment chemistry from prechlorination through coagulation to final treatment is pH dependent. pH is used in many measurements, such as alkalinity, carbon dioxide, dissolved oxygen, stability, and many more measurements of acid-base equilibrium. The hydrogen ion activity or pH is the intensity of the acid-base relationship at any given temperature. pH is defined as the logarithm (base 10) of the reciprocal of the hydrogen ion activity or – log (H^+). Because the pH is based on the logarithm expression, pH cannot be averaged.

The pH scale is from 0 to 14. The neutral point is pH 7, above pH 7 is basic and below pH 7 is acidic.

As the pH decreases from neutral (pH 7) toward a pH of 0, the H^+ activity increases at a logarithmic rate and the hydroxyl (OH^-) activity decreases as the solution becomes more acidic. When the pH increases from pH 7 towards pH 14, the effect is opposite from that above and the solution becomes more basic.

It cannot be stressed enough how important pH measurement is in controlling chemical reactions, the rates of chemical processes, and the accuracy of laboratory analysis.

APPARATUS:

pH meter and probe
small beaker

REAGENTS:

pH standards of pH 4, 7, and 10.

PROCEDURE:

Plug in the meter and let it warm up for five to ten minutes. Standardize the meter using the pH 7.0 and either the pH 4.0 or the pH 10.0 standards. The actual sample pH should fall between pH 7.0 and the other standard used. Usually with ground water the two standards will be pH 7.0 and pH 10.0. The standards must be purchased from a supply house instead of making up the standards in the lab. In either case, pour enough of each standard into a small beaker to immerse about the lower one inch of the pH probe. Using each standard, follow the manufacturer's instructions for standardizing the meter.

Place the sample in a beaker or flask and swirl to mix, or use a magnetic stirrer.

The pH is read directly from the meter, no conversions are necessary.

After shutdown, follow the manufacturer's instructions for the proper care of the probe.

PRECAUTIONS:

Even though the meter will automatically compensate for the temperature changes, temperature differences will cause a change in the pH. Therefore, always bring the standards and the sample to the same temperature before measurement (preferably room temperature).

Rinse the probe with distilled water after each and every reading.

At the end of the day or when you are finished using the meter, do not pour the used standards back into the bottle. **THROW AWAY THE USED STANDARD.** This prevents you from contaminating the unused portion of the standard in the bottle.

Never use indicators such as methyl orange or other organic indicators to calibrate the pH meter. The end points are not accurate enough because of the individual interpretation of the end point and the many interferences that may change the end point.

FLUORIDE

The recommended concentration range of fluoride for drinking water in Oklahoma is 0.8 mg/L to 1.3 mg/L. Most natural water in Oklahoma is within or below this range. However, there are a few isolated pockets of groundwater that the fluoride levels may be around 10.0 mg/L.

Water from these isolated pockets should be defluoridated or new sources obtained. Accurate measurement of fluoride has increased in importance since many water facilities add fluoride to maintain the optimum level (about 1.0 mg/L) in their drinking water.

The presence of the optimum level of fluoride has been proven in many studies to significantly reduce dental cavities in young people without any harmful effects.

SPADNS METHOD

This colorimetric method is based on the reaction of fluoride and zirconium-dye lake producing a color complex. As the amount of fluoride increases, the color produced becomes lighter. The reaction rate is greatly influenced by the acidity. The higher the acidity, the faster the reaction rate.

INTERFERENCES:

CHLORINE

Dechlorinate using 1 drop (0.05 m/l) sodium arsenite ($NaAsO_2$) solution for every 0.1 mg of chlorine residual.

Do not use sodium thiosulfate because sodium thiosulfate may produce turbidity which may give false readings.

TURBIDITY & COLOR

Remove by distillation as described in Standard Methods.

ALKALINITY

Remove by the addition of HCl or HNO_3 if this is the only interference.

APPARATUS:

Spectrophotometer for use at 570 nm and providing a light path of at least 1 cm.

REAGENTS:

For instructions and preparation see Standard Methods.

Standard fluoride solution
SPADNS solution, Zirconyl-acid reagent, or
Acid zirconyl-SPADNS reagent
Reference solution
Sodium Arsenite solution

PROCEDURE:

1. Add 50 ml of sample to a 125 ml Erlenmeyer flask, dechlorinate if necessary.
2. Add 5 ml each of SPADNS solution and zirconyl-acid reagent or 10 ml of acid zirconyl-SPADNS reagent.
3. Adjust spectrophotometer to 0.730 absorbance with the reference solution of 0.0 mg/L of fluoride.
4. Read absorbance and determine the amount of fluoride from standard curve.
5. Construction of a standard calibration curve.
    a. Prepare the standard fluoride solutions at concentrations of 0.5, 0.75, 1.0, and 1.25 mg/L.
    b. Obtain the absorbance for each of the above standard concentrations of fluoride.
    c. Construct the curve by plotting the absorbance obtained against the fluoride concentration in mg/L on standard graph paper.

ION-SELECTIVE PROBE METHOD

The fluoride electrode can be used with a standard calomel reference electrode and almost any modern pH meter having an expanded millivolt scale.

The fluoride electrode measures the activity of fluoride in solution rather than concentration.

This method is suitable for fluoride concentrations from 0.1 to more than 10.0 mg/L. Adding the prescribed fluoride buffer frees the electrode method from most interferences that affect the SPADNS method and usually eliminates the need for distillation.

INTERFERENCES:

Aluminum concentrations up to 3.0 mg/L are complexed by the fluoride buffer at a pH of five (5) or above. Greater concentrations should be removed by distillation.

If the total dissolved solids concentration is above 10,000 mg/L, the sample must be distilled.

APPARATUS:

Expanded-scale or digital pH meter or ion-selective meter
Sleeve type selective electrode (do not use fiber-tip electrodes)
Fluoride electrode
Magnetic stirrer with stirring bar
Timer

REAGENTS:

Same reagents used in the SPADNS method (see Standard Methods)

PROCEDURE:

1. Instrument Calibration
    a. Normally, no major adjustments are required for any instrument when using electrodes that are in the range of 0.2 to 2.0 mg F-/L.
    b. For instruments with zero at the center scale adjust the calibration control so that the 1.0 mg F-/L standard reads at the center zero (100mV) when the meter is in the expanded scale position.
    c. When using the selective-ion meter, follow the manufacturer's instructions.
2. Fluoride Standards Preparation
    a. Prepare F- standards as outlined in Standard Methods equivalent to 0.5, 1.0, and 2.0 mg F-/L.
3. Standards and Sample Treatment
    a. With the volumetric pipet, add 10.0 to 25.0 ml of standard or sample to a beaker.
    b. Bring standard and sample to the same temperature (preferably room temperature).
    c. Add an equal amount of fluoride buffer to the beaker. The total volume should be enough to permit the immersion of the electrode over the stirring bar.

4. Electrode Measurements

   a. Immerse the electrode before stirring action is started. If stirring is started before the immersing of the electrodes, this may cause entrapment of air bubbles around the crystal and give false readings or needle fluctuations.

   b. Leave electrode immersed in the solution at least three (3) minutes or until the reading becomes constant.

   c. A thin layer of insulating material between the stirring bar and the beaker will minimize solution heating.

   d. Withdraw electrode, rinse with distilled water, and blot dry (blot gently or you might contaminate the electrode).

   e. If using the expanded scale pH meter or the selective-ion meter, recalibrate frequently using the 1.00 mg F-/L standard.

   f. Always follow the manufacturer's recommendations.

DISTILLATION

The following interferences must be removed by distillation when the indicated concentrations are exceeded. For distillation procedure, see Standard Methods.

	SPADNS mg/L	**ELECTRODE** mg/L
Aluminum (Al_3)	0.1	3.0
Chloride (Cl^-)	7,000	20,000
Iron (Fe)	10	200
Hexametaphosphate [$(NaPO_3)_6$]	1.0	50,000
Phosphate (PO_4)	16	50,000
Sulfate (SO_4)	200	50,000

HARDNESS

Hardness is caused mainly by the calcium and magnesium ions commonly found in water. Hardness may also be caused by iron, manganese, aluminum, strontium, and zinc if these ions are present in significant amounts. Because only the calcium and magnesium ions are present in significant concentrations, total hardness is defined as the sum of the calcium and magnesium concentrations both expressed as calcium carbonate in mg/L.

There are two types of hardness: carbonate and non-carbonate. Carbonate hardness is due to calcium and magnesium bicarbonates and carbonates. Non-carbonate hardness is due primarily to calcium and magnesium sulfates, chlorides, and nitrates.

The type of hardness and its compounds are explained below.

If total hardness is greater than the sum of carbonate + bicarbonate alkalinity, then the amount of hardness equal to the total alkalinity is called "carbonate harness". The amount of hardness in excess of the carbonate hardness above is called "non-carbonate hardness".

If the total hardness is equal to or less than the sum of carbonate + bicarbonate alkalinity, then all the hardness is "carbonate" hardness.

HARDNESS BY CALCULATION

The **preferred method** for determining hardness is to compute it from results of separate determinations of calcium and magnesium concentrations by the atomic absorption method (see Standard Methods).

Hardness, mg/L as $CaCO_3$ = 2.497 (Ca, mg/L) + 4.118 (Mg, mg/L)

For the specific procedures in determining the concentrations of Ca and Mg refer to Standard Methods.

TOTAL HARDNESS – EDTA TITRIMETRIC METHOD

APPARATUS:

Buret 25 ml with stand
Graduated cylinder 100 ml
Beaker 250 ml
Magnetic stirrer and stirring bar

REAGENTS:

Buffer Solution

Standard EDTA titrant solution – 0.01 M. Dissolve 3.723 g of EDTA salt in distilled water and dilute to 1000 ml – using this solution (1.0 mg of $CaCO_3$ = 1.0 ml EDTA).

Indicator Solution

Eriochrome Black T
Calmagite

PROCEDURE:

1. Dilute 25 ml of sample to 50 ml with distilled water.
2. Add 2 ml of buffer solution.
3. Add two (2) drops of indicator solution and the color should change from red to purple.
4. While stirring with the magnetic stirrer, titrate with the standard EDTA solution until the last reddish tinge disappears from the mixture. At the endpoint it is pure blue.
5. Record the ml of EDTA used (A).
6. Calculate the hardness.

$$\text{Total hardness, mg/L as } CaCO_3 = \frac{A \times B \times 1{,}000}{\text{ml sample}}$$

A = ml of titrant used for the sample
B = mg of $CaCO_3$ equivalent to 1.0 ml of EDTA titrant.

CALCIUM HARDNESS – EDTA TITRATION

With the addition of EDTA to the sample, the EDTA combines first with the calcium. Calcium content can be determined directly if the pH is high enough to precipitate the magnesium as the hydroxide. Then the indicator combines with the calcium only. Several indicators will give a color change when all the calcium has been complexed by the EDTA at a pH of 12 to 13.

REAGENTS:

Indicators

Murexide (ammonium purpurate) or Eriochrome Black R
Sodium Hydroxide, NaOH, 1.0 N
EDTA Titrant, 0.01 M (400.8 g Ca/1.0 ml of titrant)

INTERFERENCES:

Orthophosphate precipitates calcium at this pH.

Strontium and Barium gives a + interference.

Alkalinity in excess of 300 mg/L may cause an indistinct endpoint.

PROCEDURE:

1. Add 50 ml of the sample to a 250 ml beaker.
2. Add 2.0 ml of NaOH (or enough to reach a pH of 12 to 13) to the sample.
3. Add 0.1 or 0.2 g of indicator (1 or 2 drops of solution is used).
4. Titrate with EDTA solution and record the amount in ml.

CALCULATIONS:

$$\text{Mg Ca/L} = \frac{\text{A x B x 400.8}}{\text{ml of sample}}$$

$$\text{Ca hardness as mg } CaCO_3\text{/L} = \frac{\text{A x B x 1000}}{\text{ml of sample}}$$

A = ml titrant for sample.
B = ml $CaCO_3$ equivalent to 1.0 ml EDTA (0.01 M) titrant.

TURBIDITY

The clarity of natural waters is a very important factor in almost all phases of commercial and industrial usage. Clarity is even more important in the potable water for human consumption because of the health standpoint.

Turbidity in water is caused by suspended or colloidal particles such as clay, silt, finely divided particles of organic and inorganic matter, and microorganisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than be transmitted with no change in direction through the sample.

Most turbidimeters designed to measure low turbidities give good results with the light scattered and measured 90° to the incident light. Turbidimeters with scattered light detectors located at 90° to the incident beam are called nephelometers. Nephelometers are affected only slightly by differences in design and, therefore, are specified as the only instrument accepted by the EPA and the state of Oklahoma. Measurements are reported as nephelometric turbidity units (NTUs). Because of discrepancies between different types of particulate matter suspensions used as calibration standards, the EPA designates user-prepared formazin, commercial stock formazin suspensions, and commercial styrene-divinylbenzene suspensions as "**primary standards**".

Calibration suspensions made from other particulates that are instrument specific, that is furnished by the instrument manufacturer for calibration, may be used only for calibration checks to determine when to calibrate the instrument with the "primary standard". These instrument specific standards are usually referred to as "**secondary standards**".

APPARATUS:

Nephelometer having the minimum design characteristics of:

a. Light source: Tungsten-filament lamp operating at a color temperature between 2200°K and 3000°K.

b. Light distance: The total distance transversed by incident light and scattered light within the sample tube not to exceed 10 cm.

c. Angle of light: The angle of light acceptance by the detector must be centered at 90° to the incident light path and not to exceed +/- 30° from 90°. The detector and filter system, if used, shall have a spectral peak response between 400 and 600 nm.

REAGENTS:

Dilution water nominal value of 0.02 NTU.

Calibration standards

1. Primary See Standard Methods for makeup procedure.
2. Secondary See manufacturer's instructions.

INTERFERENCES:

1. Floating debris – false low readings.
2. Rapid settling coarse sediment – false low readings.
3. Dirty glassware – false high readings.
4. Air bubbles – false high readings.
5. "True color" – false low readings.
6. Scratched sample cells – false low readings.

PRECAUTIONS:

1. Sample
    a. Floating debris – check sampling site and technique – or remove by skimming or decanting.
    b. Rapidly settling coarse sedimentation – check sampling site and technique or agitate and read at once.

c. Air bubbles – degas by placing in ultra-sonic bath for one (1) to two (2) seconds or by vacuum degassing.

d. "True color" – filter sample and prepare standard curve for dissolved material.

2. Sample cells

   a. Discard scratched or etched cells.

   b. Never handle cells where the light beam strikes them, handle on top or at the corners.

   c. Keep cells as clean as possible by thorough washing and multiple rinsing with distilled or deionized water. Let cells air dry.

   d. Use only a matched pair of cells or the same cell for both standardization and sample measurement.

3. Dilution water

   a. Should be nominal value of 0.02 NTU.

   b. If filtered, filter should remove particles more than 0.1 μm, membrane filter for bacteriological tests is <u>not</u> satisfactory.

   c. Check turbidity of all bottled distilled water to see if it is good enough.

4. Standards

   a. Check standards periodically with fresh standard.

   b. Follow manufacturer's recommendations concerning the correct standards and the shelf life of commercial purchased standards.

PROCEDURE:

<u>Follow the instrument manufacturer's instructions exactly.</u>

JAR TEST

One of the most important variables in the operation of a water treatment plant is the coagulant dosage. The correct dosage of the coagulation chemical will result in good removal of turbidity, color, and algae. The correct dosages of many of the chemicals used in water treatment can be evaluated by the jar test.

In the jar test, an attempt is made to simulate, on a small scale, the coagulation, flocculation, and sedimentation processes that occur in plant operations. Always remember, plant operations cannot be exactly duplicated on a laboratory scale. This is why the jar test is considered to be an estimate of the correct dosage. The test is very important because the results give the operator a dosage level from which to start

evaluations. The jar test is an estimation of results and not a precise analytical analysis, and because of this, the test is not listed in the Standard Methods.

The use of 1,000 ml beakers is chosen in the manual only for the simplicity of calculations, any size containers may be used if the correct calculations are made.

APPARATUS:

A six position jar testing machine with six stirring paddles capable of variable speeds from 0 to 100 rpm.
Six 1,000 ml beakers
Pipettes (10 ml)
Volumetric flask (1,000 ml)
Analytical balance

REAGENTS:

Stock coagulant solution

Dry alum, $Al_2(SO_4)_3 \cdot 14.3H_2O$. Dissolve 10.0 grams of dry alum (17%) in a volumetric flask containing 600 ml of distilled water then fill to the 1,000 ml mark. This solution is now 10,000 mg/L or 10 mg/ml.

If you are making a stock solution of 20 mg/ml, then add 20 grams of dry alum and fill to 1,000 ml with water.

Liquid Alum, $Al_2(SO_4)_3 \cdot 49.6H_2O$. Liquid alum strength should be verified by the operator. Liquid alum is usually from 8.0 to 8.5% which contains about 5.36 lbs/gallon. This translates into about 624,336 mg/L. Therefore, add 15.6 ml of liquid alum to a 1,000 ml volumetric flask, fill it to the mark and this will give you a solution of 10,000 mg/L or 10 mg/ml.

If you are making a stock solution of 20 mg/ml, then add 31.2 ml of liquid alum and fill to 1,000 ml with water.

PROCEDURE:

1. Collect about two (2) gallons of raw water to be tested.

   If any treatment or chemical additions are made to the water before the water reaches the flash mixing basin, be sure that the sample is taken at the influent of the flash mix. This will insure that the sample is a true sample of the water being treated in the coagulation basin.

2. Perform the following analysis on the raw water sample.

   Alkalinity – pH – Turbidity

3. Place 1,000 ml of the raw water in each of the six 1,000 ml beakers and place on the stirring apparatus.

4. Using a measuring pipet, quickly add to each beaker an increasing amount of the coagulant solution. Select a series of dosages that the first beaker will be underdosed and the last beaker will be overdosed.

   Selecting the correct dosage range is something that will be gained through experience in your treatment plant and your raw water source.

5. Lower the stirring paddles into the beakers and stir for one (1) minute at a speed of about 80 rpm. This duplicates the flash mix.

   Reduce the stirring speed to about 20 rpm for the next thirty (30) minutes. This duplicates the coagulation phase in your treatment plant.

   Remember, it is almost impossible to duplicate exactly the mixing speeds and the stirring times that occur in your treatment plant. The best you can do is try to set the speeds and times (if you know them) to match your plant.

6. Stop the stirring apparatus, raise the paddles from the water, and allow the floc to settle for about thirty (30) minutes.

   It is very important that this test is done in a place where there are no vibrations or movement of the beakers.

   At regular intervals, observe the settling characteristics such as floc size, settleability, and supernatant clarity. Record these results as poor, fair, good, or excellent. Remember, these are subjective judgments and different operators will probably make different evaluations.

   At the end of the settling period (around thirty (30) minutes), run the analysis for alkalinity, pH, and turbidity on the supernatant in each beaker. Record these values as well as the observations on a chart similar to the one below.

   The decision made regarding the best concentration of coagulant depends upon judgments based on the information you provide. Maybe the next higher concentration gives slightly better results, but is this very small advantage worth extra chemical cost?

   The information you provide in a chart like the one shown below is invaluable to the operator in making process control decisions.

   If the best results are obtained within the jar with the highest concentration of coagulant, then run another test with concentration of jar #6 as the middle concentration in the new test.

JAR TEST EVALUATION CHART

OBSERVATIONS & RESULTS	JAR #1	JAR #2	JAR #3	JAR #4	JAR #5	JAR #6
FLOC Size						
Settleability						
Clarity						
Turbidity						
Alkalinity						
pH						
mg/L of Coagulant						
Comments						

IRON

In filtered samples of surface waters, iron concentrations seldom reach 1.0 mg/L. However, some ground waters contain considerably more iron. Iron in water may cause staining of laundry and porcelain fixtures. Some people detect a bittersweet astringent taste when iron levels are above 1.0 mg/L.

Under reduced conditions, iron exists in the ferrous state and on exposure to air or with the addition of oxidants, ferrous iron is oxidized to the ferric state and may hydrolyze to form insoluble hydrated ferric oxide. In water samples iron may occur in true solution, in a colloidal state or in relatively coarse suspended particles. It may be either ferrous or ferric, dissolved or suspended.

Iron may be found in acid soluble forms in silt at the bottom of lakes, in groundwater and in rusting metal distribution lines.

The complexing agents used in the colorimetric method are specific to ferrous iron. Because of the instability of ferrous iron, which is changed easily to the ferric state in solutions in contact with air, the determination of ferrous iron requires special precautions and may need to be done in the field at the time of sampling.

SAMPLING AND STORAGE

Plan ahead your methods of collection, storage, and pretreatment of the sample.

Use glass sample containers, clean with HCl and rinse with iron free distilled water.

If dissolved iron is to be measured immediately, equipment for membrane filtering must be on hand. Dissolved iron is considered to be that passing through a 0.45-um membrane filter, but some colloidal iron may be included.

Iron from water wells and tap samples may vary in concentration and form because of the time and volume of flushing before and during sample collection.

If total iron is to be determined, collect a separate sample and treat with acid at the time of sampling.

PHENANTHROLINE METHOD

Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at a pH of 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The solutions color intensity is independent of pH from pH 3.5 to 9, but a pH of 2.9 to 3.5 insures a rapid color development in the presence of an excess of phenanthroline.

The minimum detectable concentration of dissolved or total iron is 10 ug/L. Carry a blank through the entire procedure to allow for correction.

INTERFERENCES:

Strong oxidizing agents – cyanide, nitrate, and phosphates (polyphosphates more than any other phosphates).

Acid boiling removes the cyanide and nitrates and converts polyphosphates to orthophospates.

Chromium and zinc in concentrations of 10 X that of iron.

Cobalt and copper in concentrations in excess of 5 mg/L.

Nickel in excess of 2 mg/L.

Adding an excess amount of hydroxylamine eliminates errors caused by excessive concentrations of strong oxidizing reagents.

In the presence of interfering metal ions, use a larger excess of phenanthroline to replace that complexed by the metal ions.

APPARATUS:

Spectrophotometer, use at 510 nm with a light path at least 1 cm long.

Acid washed glassware, wash all glassware with concentrated hydrochloric acid (HCl) and rinse with iron free distilled water.

REAGENTS:

Use reagents low in iron. Use iron-free distilled water. Store reagents in glass stoppered bottles. The hydrochloric acid and ammonium acetate solutions are stable indefinitely if tightly stoppered. The hydroxylamine, phenanthroline, and stock iron solutions are stable for several months. The standard iron solutions are not stable and must be made fresh each time by diluting the stock solution. The visual standards in Nessler tubes are stable for several months if sealed and protected from light.

Hydrochloric acid, concentrated, containing less than 0.00005% Fe

Hydroxylamine solution, see Standard Methods

Sodium acetate solution, see Standard Methods

Phenanthroline solution, see Standard Methods

Stock iron solutions 1.0 ml = 0.200 mg/L Fe

Standard iron solutions, prepare daily, see Standard Methods

PROCEDURE:

Total Iron

1. Put 50 ml of well mixed sample into a 125 ml Erlenmeyer flask.
2. Add 2 ml of concentrated HCl and 1 ml of hydroxylamine solution.
3. Boil sample until the volume is reduced to about 20 ml. Cool to room temperature.
4. Transfer to 100 ml volumetric flask.
5. Add 10 ml of acetate buffer solution and 2 ml of phenanthroline solution.
6. Dilute sample to the 100 ml mark with Fe-free distilled water and mix thoroughly.
7. Wait fifteen (15) minutes and then measure the absorbance at 510 nm and determine the iron concentration from the standard curve.

CONSTRUCTION OF A STANDARD CALIBRATION CURVE

1. Using the standard solution, prepare the following standards in 100 ml volumetric flasks.

ml of Fe Sol. in 100 ml Vol. Flask	**Fe Conc. Mg/L**
0.0	0.00
1.0	0.10
2.5	0.25
5.0	0.50
7.5	0.75
10.0	1.00

2. Dilute all flasks to 100 ml with iron free distilled water.
3. Transfer 50 ml to 100 ml volumetric flask.
4. Add 1 ml hydroxylamine solution and 1 ml of acetate solution to each flask.
5. Dilute to about 75 ml, add 10 ml of phenanthroline solution, dilute to the 100 ml mark and mix thoroughly.
6. Measure the absorbance at 510 nm against the reference bank.
7. Make corrections for each concentration against the reference blank and plot the curve with Fe concentration on the horizontal axis against the absorbance on the vertical axis.

FERROUS IRON

1. Acidify a separate sample with 2 ml of concentrated HCl/ 100 ml sample at the time of collection.
2. Immediately withdraw a 50 ml portion of the acidified sample and add 20 ml phenanthroline solution and 10 ml of ammonium acetate buffer solution and stir vigorously.
3. Dilute to 100 ml and measure the color intensity within five (5) to ten (10) minutes.
4. Construct a standard calibration curve the same as for total Fe.
5. Calculate ferric iron by subtracting ferrous iron from total iron.

DR-4000 FERROVER METHOD

Set the instrument on an absorbance of 510 for ferrous or total iron and follow the instruments manufacturer instructions exactly. There are no short-cuts in this procedure.

MANGANESE – PERSULFATE METHOD

Manganese is not as abundant in the earth's crust as iron but it is one of the more common elements found. In ground water, manganese is usually found in the soluble or divalent form because of the lack of oxygen. The determination of the manganese concentration does not differentiate between the divalent, trivalent, quadrivalent, or the heptavalent forms. Although rarely present in excess of 1 mg/L, manganese imparts objectionable and tenacious stains to laundry and plumbing fixtures.

Manganese may exist in a soluble form in neutral water when first collected, but oxidizes quickly, precipitates out, and can be absorbed on the container walls. Analysis should be made very soon after sample collection or the sample should be acidified with nitric acid to pH < 2.

Persulfate oxidation of soluble manganese compounds to form permanganate is carried out in the presence of silver nitrate. The resulting color is stable for at least twenty-four (24) hours if excess persulfate is present and organic matter is absent.

INTERFERENCES:

As much as 0.1 g of Chloride (Cl^-) in a 50 ml sample can be prevented from interfering with the addition of 1 g of mercuric sulfate. Trace amounts of chloride are eliminated by the mercuric sulfate in the special reagent.

Samples that have been exposed to air may give low results due to precipitation of manganese dioxide. Add one (1) drop of 30% hydrogen peroxide (H_2O_2) to the sample after adding the special reagent. This re-dissolves the precipitated manganese.

APPARATUS:

Spectrophotometer for use at 525 nm providing a light path of at least 1 cm long.

REAGENTS:

Special reagent, see Standard Methods
Ammonium persulfate $(NH_4)_2S_2O_8$
Standard Manganese Solution, see Standard Methods

PROCEDURE:

1. Place 100 ml of well mixed sample in a 250 ml Erlenmeyer flask which has been marked at the 90 ml level.
2. Add 5 ml of the special reagent and one (1) drop of H_2O_2.
3. Concentrate sample to 90 ml by boiling. Add one (1) gram of ammonium persulfate. Cool immediately under tap water.
4. Dilute to 100 ml.
5. Measure the absorbance at 525 nm and determine the concentration from the standard curve.

CONSTRUCTION OF THE CALIBRATION CURVE

1. Using the standard manganese solution, prepare the following standards in 100 ml volumetric flasks.

ml of Mn Sol. in 100 ml Vol. Flask	**Fe Conc. Mg/L**
0.0	0.00
1.0	0.10
2.0	0.20
3.0	0.30
4.0	0.40
5.0	0.50

2. Dilute all flasks to 100 ml.
3. Transfer to 250 ml Erlenmeyer flasks.
4. Determine amount of manganese as previously outlined.
5. Construct a standard curve by plotting the mg/L manganese on the horizontal axis vs. the absorbance on the vertical axis.

DR-4000 PERIODATE METHOD

Set the instrument absorbance at 525 nm and follow the manufacturer instructions exactly. There are no short-cuts in this procedure.

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