MINISTRY OF EDUCTION AND SCIENCE OF UKRAINE
NATIONAL TECHNICAL UNIVERSITY OF UKRAINE
"IGOR SIKORSKY KYIV POLYTECHNIC INSTITUTE"
Chemical Technology Faculty

Guidance

for course, control and laboratory works on discipline
«Technology and Equipment for Drinking and Service Water Treatment»

Kyiv-2017

MINISTRY OF EDUCTION AND SCIENCE OF UKRAINE
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APPROVED

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«Technology and Equipment for Drinking and Service Water Treatment»
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Guidance

for course, control and laboratory works on discipline
«Technology and Equipment for Drinking and Service Water Treatment»
For *masters of science*
in specialty *161 – "Chemical Technologies and Engineering"*
form of study *full time*

Approved by the methodical commission of

The Chemical Technology Faculty

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_____O.V. Sanginova

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CONTENT

INTRODUCTION

No one really questions that water is the life blood of humankind. We all remain amazed that the existence of water separates our planet from every other we have thus far viewed in our universe. We can arguably do without every naturally occurring molecule on the earth except water. Life was clearly formed within water and exists in one way or another on water.

Stocks of local water resources (per capita 1,000 m^3 of water) Ukraine is one of the poorest countries in Europe. Improving water treatment technologies in Ukraine with current international achievements and opportunities is an important task for chemical engineers. The main purpose of discipline - creating the optimum environment-friendly technological schemes for water purification on based knowledge of physical and chemical characteristics of natural water impurities and common methods of water treatment depending on the destination.

Topics of laboratory works reflect some of the main methods of improving the quality of natural water of different origin. After these works students have to be able to choose the right method of analyzing the content of substances such as iron, manganese, aluminum, fluoride and etc., where the residual content of water is regulated for drinking and for various technical purposes.

Adapting guidance from Ukrainian language [1] was made in parts of order laboratory works and questions for self-examination. Theoretical and technological parts are used materials of Water Encyclopedia [2] and analysis methods [3] based primarily on "Standard Methods for the Examination of Water and Wastewater; APHA, AWWA and WEF, 21st Edition, 2005". The material was taken from the English-language sources to provide students and teachers authentic scientific English.

1 The determination of water oxidation

The aim of work – to evaluate the total content in water organic and simply-oxidation inorganic impurities (for example, H_2S, sulfites, iron (II) etc.).

Introduction

Natural organic materials might be present in water supplies, especially from surface water sources. Dissolved organics may cause taste, odor, or color problems in a community's drinking water, resulting in consumer complaints. Sources of SOCs include leaking underground gasoline/storage tanks, agricultural runoff containing herbicides or pesticides, solid waste or hazardous waste landfills, and improperly disposed chemical waste. The technologies most suitable for organic contaminant removal in drinking water systems are granular activated carbon (GAC) and aeration. GAC has been designated by the U.S. Environmental Protection Agency (EPA) as the best available technology (BAT) for synthetic organic chemical removal. Various kinds of GAC are available for removing organics from drinking water. The most frequently used carbon in U.S. treatment plants is coal-based carbon because of its hardness, adsorption capacity, and availability. Some peat and lignite carbons have been used also. Aeration systems that might be suitable for small drinking water systems include packed column aeration, diffused aeration, and multiple-tray aeration. Recent technologies that use aeration for organics removal include mechanical aeration, catenary grid, and Higee aeration [2].

Chemical Oxygen Demand (COD) test determines the oxygen requirement equivalent of organic matter that is susceptible to oxidation with the help of a strong chemical oxidant. It is an important, rapidly measured parameters as a means of measuring organic strength for streams and polluted water bodies. The test can be related empirically to BOD, organic carbon or organic matter in samples from a specific source taking into account its limitations. The test is useful in studying performance evaluation of wastewater treatment plants and monitoring relatively polluted water bodies. COD determination has advantage over BOD determination. COD results can be obtained in 3-4 hrs as compared to 3-5 days required for BOD test. Further, the test is

relatively easy, precise, and is unaffected by interferences as in the BOD test. The intrinsic limitation of the test lies in its inability to differentiate between the biologically oxidisable and biologically inert material and to find out the system rate constant of aerobic biological stabilization [3].

1.1 TECHNOLOGIES FOR ORGANIC REMOVAL IN SMALL SYSTEMS

Some small drinking water systems face contamination of raw water by natural or synthetic organic chemicals (SOCs). Natural organic materials might be present in water supplies, especially from surface water sources. Dissolved organics may cause taste, odor, or color problems in a community's drinking water, resulting in consumer complaints. Sources of SOCs include leaking underground gasoline/storage tanks, agricultural runoff containing herbicides or pesticides, solid waste or hazardous waste landfills, and improperly disposed chemical waste. The technologies most suitable for organic contaminant removal in drinking water systems are granular activated carbon (GAC) and aeration. GAC has been designated by the U.S. Environmental Protection Agency (EPA) as the best available technology (BAT) for synthetic organic chemical removal. Various kinds of GAC are available for removing organics from drinking water. The most frequently used carbon in U.S. treatment plants is coal-based carbon because of its hardness, adsorption capacity, and availability. Some peat and lignite carbons have been used also. Aeration systems that might be suitable for small drinking water systems include packed column aeration, diffused aeration, and multiple-tray aeration. Recent technologies that use aeration for organics removal include mechanical aeration, catenary grid, and Higee aeration. Table 1.1 presents operational conditions for the organics treatment technologies most suitable for small systems.

A. Activated Carbon

Description. Activated carbon is carbon that has been exposed to very high temperatures, creating a vast network of internal pores. Two types of activated carbon, granular and powdered, have been used widely in drinking water treatment. Powdered activated carbon (PAC), which is most often used for taste and odor control, is added directly to the raw water and removed by settling in sedimentation basins. GAC removes many organic contaminants as well as taste and odor from water supplies.

Performance/Advantages. Organics that are readily adsorbed by activated carbon include:

- aromatic solvents (benzene, toluene, nitrobenzenes);
- chlorinated aromatics (PCBs, chlorobenzenes, chloroaphthalene);
- phenol and chlorophenols;
- polynuclear aromatics (acenaphthene, benzopyrenes);
- pesticides and herbicides (DDT, aldrin, chlordane, heptachlor);
- chlorinated aliphatics (carbon tetrachloride, chloroalkyl ethers); and
- high molecular weight hydrocarbons (dyes, gasoline, amines, humics).

Limitations. Organics that are poorly adsorbed by activated carbon include:

- alcohols;
- low molecular weight ketones, acids, and aldehydes;
- sugars and starches;
- very high molecular weight or colloidal organics; and
- low molecular weight aliphatics.

GAC is not effective in removing vinyl chloride from water. In addition, because of the long empty bed contact time (EBCT) required, radon removal at the treatment plant scale is not feasible. However, at the residential scale, GAC systems are cost-effective for radon removal.

Several operational and maintenance factors affect the performance of GAC. Contaminants in the water can occupy GAC adsorption sites, whether they are targeted for removal or not. Also, adsorbed contaminants can be replaced by other contaminants with which GAC has a greater affinity. Therefore, the presence of other contaminants might interfere with the removal of the contaminants of concern.

A significant drop in the contaminant level in influent water will cause a GAC filter to desorb, or slough off, adsorbed contaminants because GAC is an equilibrium

process. As a result, raw water with frequently changing contaminant levels can result in treated water of unpredictable quality.

Bacterial growth on the carbon is another potential problem. Excessive bacterial growth may cause clogging and higher bacterial counts in the treated water. Bacterial levels in the treated water must be closely monitored, and the final disinfection process must be carefully controlled.

Table 1. Organic Treatment Technologies Suitable for Small Systems

Technology	Level of Operational Skill Required	Level of Maintenance Required	Energy Requirements
Granular Activated Carbon (GAC)	Medium	Low	Low
Packed Column Aeration (PCA)	Low	Low	Varies
Diffused Aeration	Low	Low	Varies
Multiple-Tray Aeration	Low	Low	Low
Mechanical Aeration	Low	Low	Low
Catenary Grid	Low	Low	High
Higee Aeration	Low	Medium	High

Source: U.S. Environmental Protection Agency, 1989.

Process. Activated carbon removes contaminants through adsorption, primarily a physical process in which dissolved contaminants adhere to the porous surface of the carbon particles. The adsorption process can be reversed relatively easily. The ease of reversing adsorption is another key factor in activated carbon's usefulness because it facilitates the recycling or reuse of the carbon. GAC can be used as a replacement for existing media (such as sand) in a conventional filter, or it can be used in a separate contactor (a vertical steel pressure vessel used to hold the activated carbon bed).

GAC contactors require monitoring to ensure that they work effectively. A GAC monitoring system should include:

• laboratory analysis of treated water to ensure that the system is removing organic contaminants,

• monitoring of headloss (the amount of energy used by water in moving from one point to another) through the contactors to ensure that backflushing (reversing the flow to remove trapped material) is performed at appropriate times,

• bacteria monitoring of the contactor's effluent (since bacteria can grow rapidly within the activated carbon bed),

• turbidity monitoring of the contactor's effluent (to determine if suspended material is passing through GAC bed).

After a period of months or years, depending on the concentration of contaminants, the surface of the pores in the GAC can no longer adsorb contaminants. The carbon must then be replaced. The GAC vendor will be able to provide guidance concerning when to replace the GAC. Disposing of carbon with contaminants that are classified as hazardous wastes will dramatically increase disposal costs.

Equipment/Design. The typical GAC unit can be similar in design to either gravity or pressure filters. In some communities, the sand in existing filters has been either partially or completely replaced with GAC. Media depth of up to 10 feet is needed to ensure adequate removal of potentially harmful organic contaminants. Activated carbon filters can be designed to treat hydraulic loadings of 2 to 10 gallons per minute per square foot (gpm/ft2). Sufficient detention time in the filter must be provided to achieve the desired level of the organic contaminant removal. The detention time is determined by the volume of the GAC filter divided by the flow rate. This is referred to as the EBCT since the volume of carbon in the bed is not considered. For adequate removal of most organic contaminants to occur, the EBCT should be about 10 minutes. EBCTs less than 7.5 minutes are generally ineffective.

GAC is available in different grades of effectiveness. Low-cost carbon requires a lower initial capital outlay but must be replaced more often, resulting in higher operating costs.

B. Aeration

Description. Aeration, also known as air stripping, mixes air with water to volatilize contaminants (turn them to vapor). The volatilized contaminants are either released directly to the atmosphere or treated and released. Aeration is used to remove volatile organic chemicals and can also remove radon.

Equipment. A small system might be able to use a simple aerator constructed from relatively common materials instead of a specially designed aerator system.

Examples of simple aerators include:

• a system that cascades the water or passes it through a slotted container,

• a system that runs water over a corrugated surface, or

• an airlift pump that introduces oxygen as water is drawn from a well.

Other Aeration Types

Packed Column Aeration. Packed column aeration (PCA) or packed tower aeration (PTA) is a waterfall aeration process that drops water over a medium within a tower to mix the water with air. The medium is designed to break the water into tiny droplets and to maximize its contact with tiny air bubbles for removal of the contaminant. Air is also blown in from underneath the medium to enhance this process (see Fig. 1).

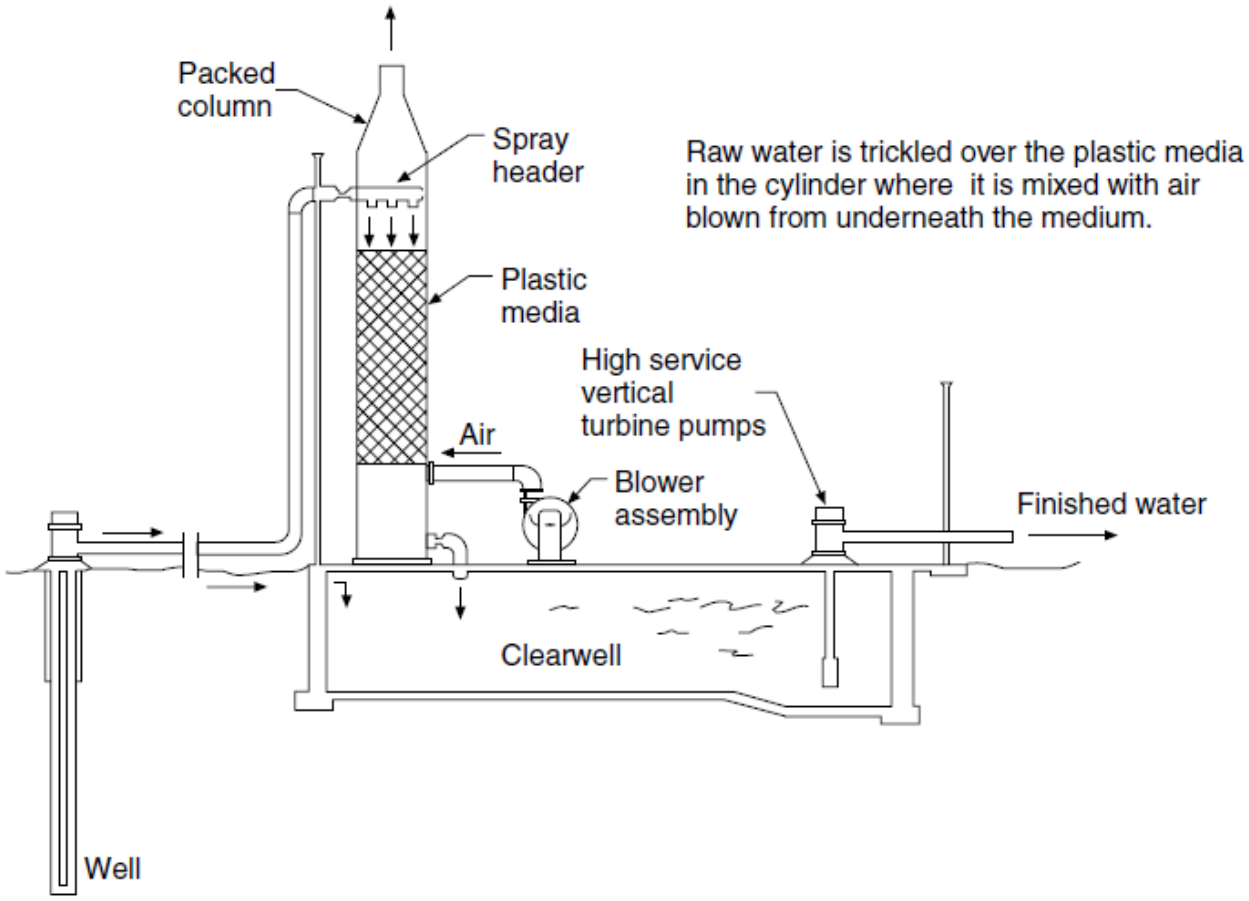

Figure 1. Packed tower aeration

Raw water is trickled over the plastic media in the cylinder where it is mixed with air blown from underneath the medium.

Systems using PCA may need pretreatment to remove iron, solids, and biological growth to prevent clogging of the packing material. Post treatment such as the use of a corrosion inhibitor, may also be needed to reduce corrosive properties in water due to increased dissolved oxygen from the aeration process. Packed columns usually operate automatically and need only daily visits to ensure that the equipment is running satisfactorily. Maintenance requirements include servicing pump and blower motors and replacing air filters on the blower, if necessary. PCA exhaust gas may require treatment to meet air emissions regulations, which can significantly increase the costs of this technology.

Diffused Aeration. In a diffused aeration system, a diffuser bubbles air through a contact chamber for aeration. The diffuser is usually located near the bottom of the chamber. The air introduced through the diffuser, usually under pressure, produces fine bubbles that create water-air mixing turbulence as they rise through the chamber.

The main advantage of diffused aeration systems is that they can be created from existing structures, such as storage tanks. However, they are less effective than packed column aeration, and usually are employed only in systems with adaptable existing structures.

Multiple Tray Aeration. Multiple tray aeration directs water through a series of trays made of slats, perforations, or wire mesh. A blower introduces air from underneath the trays.

Multiple tray aeration units have less surface area than PCA units. This type of aeration is not as effective as PCA and can experience clogging from iron and manganese, biological growth, and corrosion problems. Multiple tray aeration units are readily available from package plant manufacturers.

Mechanical Aeration. Mechanical aeration uses mechanical stirring mechanisms to mix air with the water. These systems can effectively remove volatile organic chemicals (VOCs).

Mechanical aeration units need large amounts of space because they demand long detention times for effective treatment. As a result, they often require openair designs, which can freeze in cold climates. These units also can have high energy requirements.

However, mechanical aeration systems are easy to operate and are less susceptible to clogging from biological growth than PCA systems.

Catenary Grid. Catenary grid systems are a variation of the packed column aeration process. The catenary grid directs water through a series of wire screens mounted within the column. The screens mix the air and water in the same way as packing materials in PCA systems.

These systems can effectively remove VOCs. They have higher energy requirements than PCA systems, but their more compact design lowers their capital cost relative to PCA.

Higee Aeration. Higee aeration is another variation of the PCA process. These systems pump water into the center of a spinning disc of packing material, where the water mixes with air.

Higee units require less packing material than PCA units to achieve the same removal efficiencies. Because of their compact size, they can be used in limited spaces and heights. Current Higee systems are best suited for a temporary application of less than 1 year with capacities up to 380 liters (100 gallons) per minute.

1.3 Analysis of Chemical Oxygen Demand (COD)

1.3.1 Principle

The open reflux method is suitable for a wide range of wastes with a large sample size. The dichromate reflux method is preferred over procedures using other oxidants (e.g. potassium permanganate) because of its superior oxidizing ability, applicability to a wide variety of samples and ease of manipulation. Oxidation of most organic compounds is up to 95-100% of the theoretical value.

The organic matter gets oxidised completely by potassium dichromate ($K_2Cr_2O_7$) with silver sulphate as catalyst in the presence of concentrated H_2SO_4 to produce CO_2 and H_2O. The excess $K_2Cr_2O_7$ remaining after the reaction is titrated with ferrous ammonium sulphate [Fe $(NH_4)_2(SO_4)_2$]. The dichromate consumed gives the oxygen (O_2) required for oxidation of the organic matter. The chemical reactions involved in the method are as under:

a. $2K_2Cr_2O_7 + 8\ H_2SO_4 \rightarrow 2\ K_2\ SO_4 + 2Cr_2(SO_4)3 + 8\ H_2O + 3O$

b. $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$

c. $Cr_2O7^{--} + 6Fe^{++} + 14H^{+} \rightarrow 6Fe^{+++} + 2Cr^{3+} + 7H_2O$

1.3.2 Apparatus and equipment

a. 250 or 500mL Erlenmeyer flask with standard (24/40) tapered glass joints

b. Friedrich's reflux condenser (12 inch) with standard (24/40) tapered glass joints

c. Electric hot plate or six-unit heating shelf

d. Volumetric pipettes (10, 25, and 50mL capacity)

e. Burette, 50mL with 0.1mL accuracy

f. Burette stand and clamp

g. Analytical balance, accuracy 0.001g

h. Spatula

i. Volumetric flasks (1000mL capacity)

j. Boiling beads, glass

k. Magnetic stirrer and stirring bars.

1.3.3 Reagents and standards

a. Standard potassium dichromate solution, 0.25N (0.04167 M): Dissolve 12.259g $K_2Cr_2O_7$ dried at 103°C for 24h in distilled water and dilute to 1000mL. Add about 120mg sulphamic acid to take care of 6 mg/L NO_2 – N.

b. Sulphuric acid reagent: Add 10g of Ag_2SO_4 to 1000mL concentrated H_2SO_4 and let stand for one to two days for complete dissolution.

c. Standard ferrous ammonium sulphate approx. 0.25N (0.25M): Dissolve 98g $Fe(NH_4)_2(SO_4)_2.6H_2O$ in about 400mL distilled water. Add 20mL concentrated H_2SO_4 and dilute to 1000mL.

d. Ferroin indicator: Dissolve 1.485g 1, 10-phenanthroline monohydrate and 695mg $FeSO_4.7H_2O$ in distilled water and dilute to 100mL.

e. Mercuric Sulphates: $HgSO_4$, crystals, analytical grade

f. Potassium hydrogen phthalate (KHP) Standard: Dissolve 425mg lightly crushed dried potassium hydrogen phthalate (HOOC.C_6H_4.COOK) in distilled water and dilute to 1000mL. This solution has a theoretical COD of 500µg O_2/mL. This solution is stable when refrigerated, up to 3 months in the absence of visible biologi

1.3.4 Sample collection, preservation and storage

Preferably collect samples in glass bottles. Homogenise samples containing settleable solids. If there is delay in collection and analysis, preserve sample by acidification to pH≤2 using concentrated H_2SO_4. Samples can be preserved for maximum 7 days.

1.3.5 Calibration

Since the procedure involves chemical of organic matter by potassium dichromate as oxidizing agent, which is a primary standard, calibration is not applicable. For standardisation of ferrous ammonium sulphate, dilute 10mL standard $K_2Cr_2O_7$ to about 100mL. Add 10mL concentration of H_2SO_4 and allow it to cool. Titrate with ferrous ammonium sulphate (FAS) to be standardized using 2-3 drops of ferroin indicator. Calculate normally.

(mL $K_2Cr_2O_{7)}$ (0.25)

Normality of FAS =

mL FAS required

The deterioration of FAS can be decreased if it is stored in a dark bottle.

1.3.6 Procedure

Sample preparation: All samples high in solids should be blended for 2 minutes at high speed and stirred when an aliquot is taken for analysis. Select the appropriate volume of sample based on expected COD range, e.g. for COD range of 50-500 mg/L take 25-50mL of sample. Sample volume less than 25mL should not be pipetted directly, but serially diluted and then a portion of the diluted sample taken. Dilution factor should be incorporated in calculations.

a. 500mL of sample diluted to 1000mL = 0.5mL sample/mL of diluent, 50mL = 25mL of sample.

b. 100mL of sample diluted to 1,000mL = 0.1mL sample/mL diluent, 50mL of diluent = 5mL of sample.

Reflux of samples:

a. Place 0.4g $HgSO_4$ in a 250mL reflux sample

b. Add 20mL sample or an aliquot of sample diluted to 20mL with distilled water. Mix well.

c. Add clean pumic stones or glass beads.

d. Add 10mL 0.25N (0.04167M) $K_2Cr_2O_7$ solution and mix.

e. Add slowly 30mL concentrated H_2SO_4 containing Ag_2SO_4 mixing thoroughly. This slow addition along with swirling prevents fatty acids to escape due to generation of high temperature. Alternatively attach flask to condenser with water flowing and then add H_2SO_4 slowly through condenser to avoid escape of volatile organic substance due to generation of heat.

f. Mix well. If the colour turns green, either take fresh sample with lesser aliquot or add more potassium dichromate and acid.

g. Connect the flask to condenser. Mix the contents before heating. Improper mixing will result in bumping and blow out of flask content.

h. Reflux for a minimum of 2 hours. Cool and then wash down condenser with distilled water.

i. Disconnect reflux condenser and dilute the mixture to about twice its volume with distilled water. Cool to room temperature and titrate excess $K_2Cr_2O_7$ with0.1M FAS using 2-3 drops of ferroin indicator. The sharp colour change from blue green to reddish brown indicates end-point or completion of the titration. After a small time gap, the blue-green colour may reappear. Use the same quantity of ferroin indicator for all titrations.

j. Reflux blank in the same manner using distilled water instead of sample.

Alternate procedure for low COD samples less than 50mg/L: Follow similar procedure with two exceptions (i) use standard 0.025N (0.004167M) $K_2Cr_2O_7$ and (ii) titrate with

standardize 0.025M FAS. The sample volume should be 5.mL. Exercise extreme care with this procedure because even a trace of organic matter on the glassware or from the atmosphere may cause gross errors. Compute amount of $HgSO_4$ to be added based on chloride concentrations. Carry blank reagent through the same procedure.

1.3.7 Calculations

COD as mg/L = (a –b) x N x 8000 / mL sample

Where, a = mL FAS used for blank

b = mL FAS used for sample

N = normality of FAS

8000 = Milieq. wt. of O_2 x 1000

1.3.8 Precision and Bias

Precision and bias: A set of synthetic samples containing potassium hydrogen phthalate with a COD of 200mg/L was analysed in many labs with standard deviation of 13mg/L in absence of chloride.

Sources of Error:

a. The largest error is caused by using a non-homogeneous sample. Every effort should be made to blend and mix the sample so that solids are never excluded from any aliquot.

b. Use volumetric flasks and volumetric pipettes with a large bore.

c. The $K_2Cr_2O_7$ oxidising agent must be precisely measured. Use a volumetric pipette and use the same one each time if possible.

d. When titrating, be certain that the burette is clean and free of air bubbles.

e. Always read the bottom of the meniscus and position the meniscus of eye level.

Carry distilled water blank through a same procedure to nullify impurities if any. A standard solution of glucose or potassium acid phthalates should be checked for precision and accuracy every fortnight. Duplicate analysis is preferred.

Method Sensitivity:

1. Standard procedure is precise and accurate for COD of 50mg/L or more
2. For low COD more sample volume and the dilute reagents are used
3. Interference by chloride needs to be handles very carefully to get accurate results

1.3.9 Interferences

Fatty acids, straight chain aliphatic compounds, aromatic hydrocarbons, chlorides, nitrite and iron interfere in the estimation. The interference caused by chloride can be eliminated by the addition of mercuric sulphate to the sample prior to the addition of other reagents. About 1.0g of mercuric sulphate is adequate to complex 100mg chloride ions in the sample in the form of poorly ionized soluble mercuric chloride complex. Addition of Ag_2SO_4 to concentrated H_2SO_4 as a catalyst stimulates the oxidation of straight chain aliphatic and aromatic compounds. Nitrite nitrogen exerts a COD of 1.14mg/mg NO_2-N.

Sulphamic acid at the rate of 10mg/mg NO_2-N may be added to $K_2Cr_2O_7$ solution to avoid interference caused by NO_2-N. Aromatic hydrocarbons and pyridine are not oxidised under any circumstances. Volatile organic compounds will react in proportion to their contact with the oxidant. For complete oxidation of organic matter, it is necessary to take volumes of Sulphuric acid and sample plus potassium dichromate in 3:2:1 ratio. However, to maintain the ratio, the volumes and strength of oxidant/sample may suitable be varied.

1.3.10 Safety

In carrying out the procedures, use proper safety measures, including protective clothing, eye protection and a fume hood. Reagents containing heavy metals ($HgSO_4$ and Ag_2SO_4) should be disposed of as toxic wastes. Use of such chemicals can be minimised whenever feasible.

1.3.11 Pollution prevention and waste minimization

Since hazardous chemicals like silver and mercury salts, Sulphuric acid, dichromate are used in the test, the quantity of such chemicals can be minimised by selecting minimum suitable sample size. The liquid waste generated should be treated as hazardous waste. Adequate dilution of such waste before final disposal is essential.

Self-control questions

1. What types of oxidation do you know? Compare, what the method gives more full characteristic of organic component content in water?
2. What organic compounds belong to simply-oxidation, hard-oxidation and non-oxidation?
3. Explain the term «biological oxygen consumption», «chemical oxygen consumption»?
4. For calculating the permanganate and dichromate oxidation well-known formulas are used, explain the origin of everyone component. Are the constants in formulas changed at reagents concentration changing?
5. Write the reactions, flowing at the determination of permanganate water oxidation?
6. Write the reactions, placing at the determination of dichromate water oxidation?

2 The control of water disinfection

The aim of work – familiarization of the main methods of control of water disinfection, by chlorination.

Introduction

Disinfection is an important step in ensuring that water is safe to drink. Water systems add disinfectants to destroy microorganisms that can cause disease in humans. The Surface Water Treatment Rule requires public water systems to disinfect water obtained from surface water supplies or groundwater sources under the influence of surface water.

Primary methods of disinfection are chlorination, chloramines, ozone, and ultraviolet light. Other disinfection methods include chlorine dioxide, potassium permanganate, and nanofiltration. Since certain forms of chlorine react with organic material naturally present in many water sources to form harmful chemical byproducts, the U.S. Environmental Protection Agency has proposed maximum levels for these contaminants [2].

Chlorine applied to water in its molecular or hypochlorite form initially undergoes hydrolysis to form free chlorine consisting of aqueous molecular chlorine, hypochlorous acid and hypochlorite ion. The relative proportion of these free chlorine forms is pH and temperature-dependent. At the pH of most waters, hypochlorous acid and hypochlorite ion will predominate.

Free chlorine reacts readily with ammonia and certain nitrogenous compounds to form combined chlorine. With ammonia, chlorine reacts to form the chloramines: monochloramine, dichloramine and nitrogen trichloride. The presence and concentrations of these combined forms depend chiefly on pH, temperature, initial chlorine-to-nitrogen ratio, absolute chlorine demand and reaction time. Both free and combined chlorine may be present simultaneously. Combined chlorine in water supplies may be formed in the treatment of raw waters containing ammonia or by the addition of ammonia or ammonium salts. Chlorinated wastewater effluents, as well as certain chlorinated industrial effluents, normally contain only combined chlorine. Historically

the principal analytical problem has been to distinguish between free and combined forms of chlorine [3].

2.1 BASICS OF DISINFECTION

Why Disinfect Drinking Water?

Disinfection kills or inactivates disease-causing organisms in a water supply and must provide a 99.9 percent inactivation of *Giardia lamblia* cysts and enteric viruses to protect health and to comply with the U.S. Environmental Protection Agency (EPA) regulations. There are two kinds of disinfection: primary disinfection achieves the desired level of microorganism kill or inactivation, while secondary disinfection maintains a disinfectant residual in the finished water that prevents the regrowth of microorganisms.

What Regulations Govern It?

The EPA Surface Water Treatment Rule (SWTR) requires systems using public water supplies from either surface water or groundwater under the direct influence of surface water to disinfect.

Also, since some disinfectants produce chemical byproducts, the dual objective of disinfection is to provide the required level of organism destruction and remain within the maximum contaminant level (MCL) for the SWTR disinfection set by EPA. At this time, an MCL is set for only Total Trihalomethanes, and proposed for additional disinfection by-products.

How is Disinfection Achieved?

Our natural environment contains numerous microorganisms. Most of these present no concerns. However, some—such as *Giardia lamblia* and various viruses, which can be present in water supplies—are extremely harmful and can cause disease in humans. These diseasecausing organisms are known as pathogens.

Because pathogens can be present in drinking water supplies, disinfection is very important—the EPA requires it for surface water and groundwater under the influence of surface water. Disinfection treatment methods include chlorination, chlorine dioxide, chloramines, ozone, and ultraviolet light.

When combined with conventional treatment, such as coagulation, flocculation, sedimentation, and filtration, good results have been obtained. Direct filtration, slow

sand filtration, and diatomaceous earth filtration, along with disinfection, have been just as successful.

Groundwater systems that disinfect may have to add filtration if the water contains iron and manganese. In fact, insoluble oxides form when chlorine, chlorine dioxide, or ozone are added to these systems. Both ozonation and chlorination may cause flocculation of dissolved organics, thus increasing turbidity and necessitating filtration. The effectiveness of disinfection is judged by analyzing for an indicator organism (total coliform bacteria). This organism is considered harmless, but its presence indicates that pathogens may also have survived.

COMPARING DISINFECTANTS

Chlorination (Gas)

At normal pressures, elemental chlorine is a toxic, yellowgreen gas, and is liquid at high pressures.

Advantages. Chlorine is very effective for removing almost all microbial pathogens and is appropriate as both a primary and secondary disinfectant.

Limitations. Chlorine is a dangerous gas that is lethal at concentrations as low as 0.1 percent air by volume.

Process. Chlorine gas is released from a liquid chlorine cylinder by a pressure reducing and flow control valve operating at a pressure less than atmospheric. The gas is led to an injector in the water supply pipe where highly pressurized water is passed through a venturi orifice creating a vacuum that draws the chlorine into the water stream. Adequate mixing and contact time must be provided after injection to ensure complete disinfection of pathogens. It may be necessary to control the pH of the water.

Equipment. A basic system consists of a chlorine cylinder, a cylinder-mounted chlorine gas vacuum regulator, a chlorine gas injector, and a contact tank or pipe (see Fig. 2). Prudence and/or state regulations would require that a second cylinder and gas regulator be provided with a change-over valve to ensure continuity of disinfection. Additional safety and control features may be required.

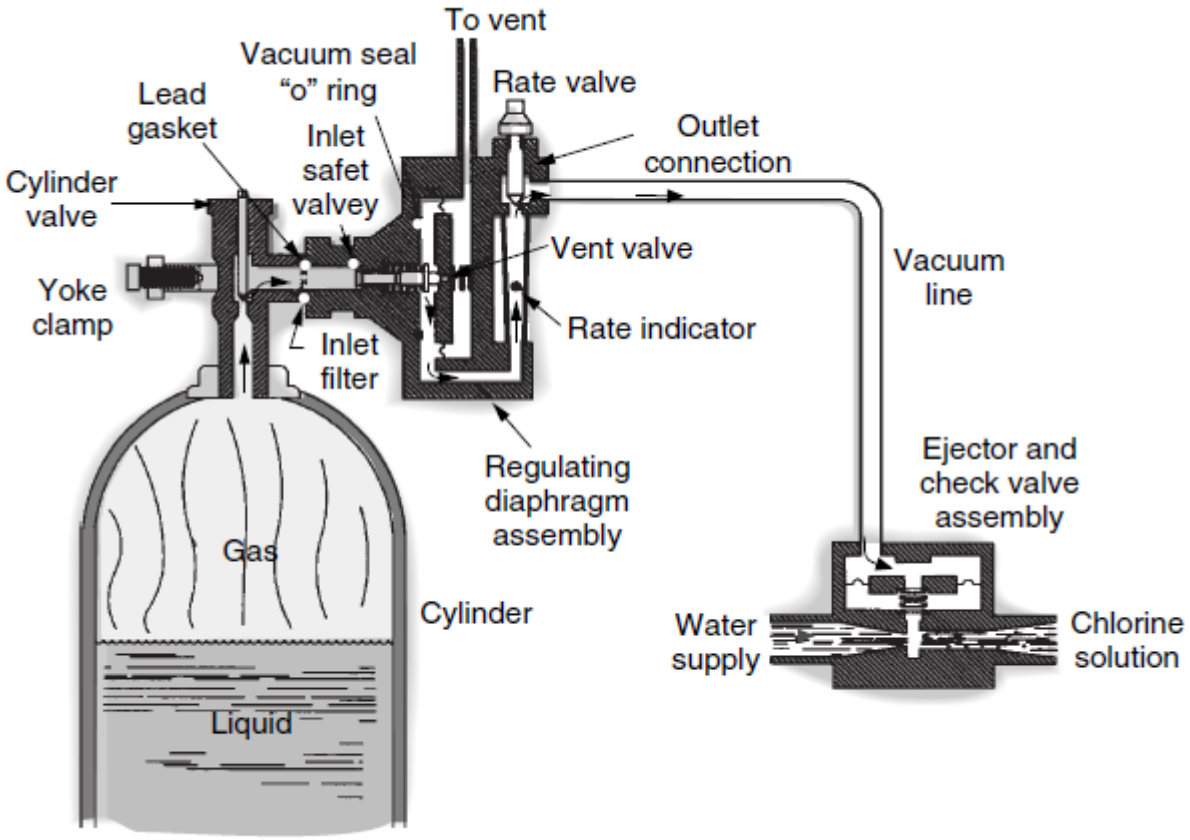

Figure 2. Cylinder-mounted chlorinator. Reprinted with permission from Capital Controls Company, Inc.

A gas chlorinator should be installed in a room or chamber with direct emergency access to outside air and fitted with an exhaust fan ventilation system. Federal and state safety regulations must be observed. If not onsite, self-contained breathing apparatus and a chlorine cylinder repair kit should be available within a reasonable time frame and/or distance. **Chemicals.** Chlorine gas is supplied as liquid in high pressure cylinders.

Chlorination (Sodium Hypochlorite Solution)

Sodium hypochlorite is available as a solution in concentrations of 5 to 15 percent chlorine, but is more expensive than chlorine gas (as available chlorine).

Advantages. Sodium hypochlorite is easier to handle than gaseous chlorine or calcium hypochlorite.

Limitations. Sodium hypochlorite is very corrosive and should be stored with care and kept away from equipment that can be damaged by corrosion. Hypochlorite

solutions decompose and should not be stored for more than one month. It must be stored in a cool, dark, dry area.

Process. Sodium hypochlorite solution is diluted with water in a mixing/holding tank. The diluted solution is injected by a chemical pump into the water supply pipe at a controlled rate. Adequate mixing and contact time must be provided.

Equipment. A basic liquid chlorination system, or hypochlorinator, includes two metering pumps (one serving as a standby), a solution tank, a diffuser (to inject the solution into the water), and tubing.

Chemicals. Sodium hypochlorite solution is readily available.

Sodium hypochlorite can also be generated onsite by electrolysis of sodium chloride solution in specialized proprietary equipment. The only supplies required are common salt and electricity. Hydrogen is given off as a by-product and must be safely dispersed.

Chlorination (Solid Calcium Hypochlorite)

Calcium hypochlorite is a white solid that contains 65 percent available chlorine and dissolves easily in water.

Advantages. When packaged, calcium hypochlorite is very stable, allowing a year's supply to be bought at one time.

Limitations. Calcium hypochlorite is a corrosive material with a strong odor that requires proper handling. It must be kept away from organic materials such as wood, cloth, and petroleum products. Reactions between calcium hypochlorite and organic material can generate enough heat to cause a fire or explosion. Calcium hypochlorite readily absorbs moisture, forming chlorine gas. Therefore, shipping containers must be emptied completely or carefully resealed.

Process. Calcium hypochlorite may be dissolved in a mixing/holding tank and injected in the same manner as sodium hypochlorite. Alternatively, where the pressure can be lowered to atmospheric, such as at a storage tank, tablets of hypochlorite can be directly dissolved in the free flowing water by a proprietary device that provides flowproportional chlorination with gravity feed of the tablets.

Equipment. The equipment used to mix the solution and inject it into the water is the same as that for sodium hypochlorite. Solutions of 1 or 2 percent available chlorine

can be delivered by a diaphragm-type, chemical feed/metering pump or by tablet chlorinator.

Chemicals. Calcium hypochlorite can be purchased in granular, powdered, or tablet form.

Chloramine

Chloramines are formed when water containing ammonia is chlorinated or when ammonia is added to water containing chlorine (hypochlorite or hypochlorous acid).

Advantages. An effective bactericide that produces fewer disinfection by-products, chloramine is generated onsite. Usually, chloramine-forming reactions are 99 percent complete within a few minutes.

Limitations. Chloramine is a weak disinfectant. It is much less effective against viruses or protozoa than free chlorine. Chloramine is appropriate for use as a secondary disinfectant to prevent bacterial regrowth in a distribution system. Nitrogen trichloride appears to be the only detrimental reaction. It may be harmful to humans and imparts a disagreeable taste and odor to the water. The use of the proper amounts of each chemical reactant will avoid its production.

Process. Chlorine (gaseous solution or sodium hypochlorite) is injected into the supply main followed immediately by injection of ammonia (gaseous solution or as ammonium hydroxide). As before, adequate mixing and contact time must be provided. The mix of products produced when water, chlorine, and ammonia are combined depends on the ratio of chlorine to ammonia and the pH of the water. Chlorine-to-ammonia ratios of 5:1 should not be exceeded. If the pH drops below 5, some nitrogen trichloride may be formed.

Equipment. The generation of chloramines requires the same equipment as chlorination (gaseous or aqueous hypochlorination), plus equipment for adding ammonia (gaseous or aqueous).

All chlorine added to drinking water must meet American National Standards Institute (ANSI), and NSF *International*, formerly the National Sanitation Foundation (NSF) standards. *ANSI/NSF Standard 60: Drinking Water Chemicals—Health Effects* covers water treatment chemicals.

Chemicals. Chemicals used to generate chloramine from ammonia and chlorine gas depend on the ammoniabased chemical used. Anhydrous ammonia is the least expensive, while ammonium sulfate is the most expensive.

Ozonation

Ozone, an allotrope of oxygen having 3 atoms to each molecule, is a powerful oxidizing and disinfecting agent. It is formed by passing dry air through a system of high voltage electrodes.

Advantages. Requiring shorter contact time and dosage than chlorine, ozone is widely used as a primary disinfectant in many parts of the world—but is relatively new to the U.S. Ozone does not directly produce halogenated organic materials unless a bromide ion is present.

Limitations. Ozone gas is unstable and must be generated onsite. A secondary disinfectant, usually chlorine, is required because ozone does not maintain an adequate residual in water.

Process. The five major elements of an ozonation system are:

• air preparation or oxygen feed;

• electrical power supply;

• ozone generation—usually using a corona discharge

cell consisting of two electrodes;

• ozone contact chamber; and

• ozone exhaust gas destruction.

Equipment. Ozonation equipment includes air preparation equipment; an ozone generator, contactor, destruction unit; and instrumentation and controls. The capital costs of ozonation systems are relatively high. Operation and maintenance are relatively complex. Electricity represents 26 to 43 percent of total operating and maintenance costs for small systems.

Chemicals. For many applications, pure oxygen is a more attractive ozone feed gas than air because:

• it has a higher production density,

• it requires lower energy consumption,

• it doubles the amount of ozone that can be generated

per unit, and

• it requires smaller gas volumes for the same ozone

output, thus lowering costs for ancillary equipment.

Ultraviolet Light (UV)

Ultraviolet (UV) radiation is generated by a special lamp. When it penetrates the cell wall of an organism, the cell's genetic material is disrupted and the cell is unable to reproduce.

Advantages. UV radiation effectively destroys bacteria and viruses. As with ozone, a secondary disinfectant must be used to prevent regrowth of micro-organisms. UV radiation can be attractive as a primary disinfectant for small systems because:

• it is readily available,

• it produces no known toxic residuals,

• it requires short contact times, and

• the equipment is easy to operate and maintain.

Limitations. UV radiation may not inactivate *Giardia lamblia* or *Cryptosporidium* cysts, and should be used only by groundwater systems not directly influenced by surface water—where there is virtually no risk of protozoan cyst contamination. UV radiation is unsuitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter. These materials can react with or absorb the UV radiation, reducing the disinfection performance.

Process. The effectiveness of UV radiation disinfection depends on the energy dose absorbed by the organism, measured as the product of the lamp's intensity (the rate at which photons are delivered to the target) and the time of exposure. If the energy dosage is not high enough, the organism's genetic material might only be damaged instead of destroyed. To provide a safety factor, the dosage should be higher than needed to meet disinfection requirements.

Equipment. UV lamps and a reactor (see Fig. 3).

Chemicals. No chemical oxidant required; therefore, microorganisms can be killed without generating byproducts of chemical oxidation or halogenation.

HOW DO YOU CONTROL DISINFECTION BYPRODUCTS?

A number of factors can affect the formation of disinfection byproducts. These include the types and concentrations of organic materials present when chlorine is added, the dosage of chlorine, the temperature and pH of the water, and the reaction time.

To control the formation of halogenated byproducts (compounds formed by the reaction of a disinfectant, such as chlorine with organic material in the water supply) during chlorination, EPA has identified these three strategies:

1. Remove the byproducts after they are formed, which can be difficult and costly.

2. Use alternative disinfectants that do not produce undesirable byproducts, which is often the most cost-effective strategy.

3. Reduce the concentration of organics in the water before oxidation or chlorination to minimize the formation of byproducts. This will provide the highest quality finished water.

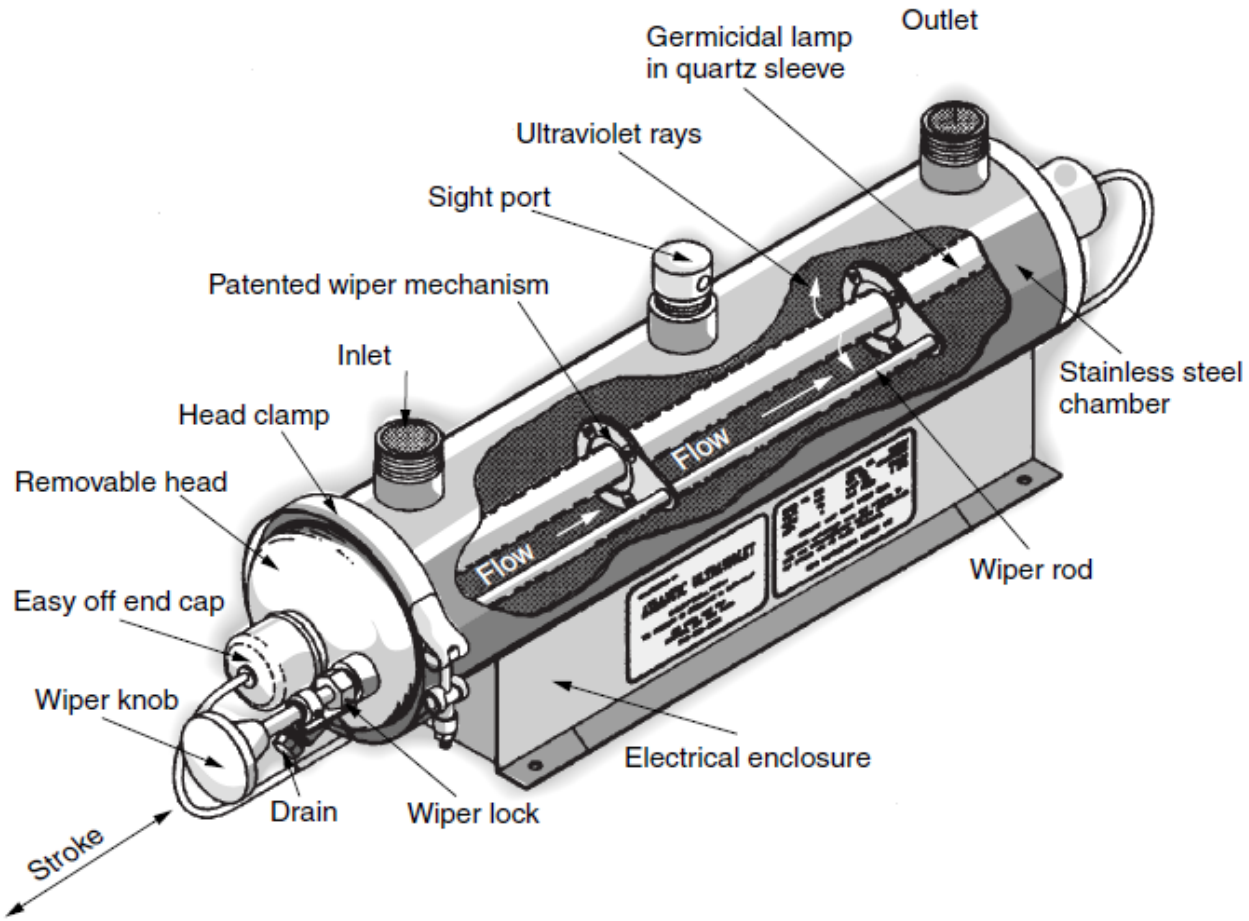

Figure 3. Ultraviolet water purifier.

2.2 Choosing of chlorine dose and determination of the indicator of water chlorination

The optimal dose at normal chlorination is the quantity of inputting chlorine (mg/L), providing the residual concentration of chlorine 0,5 mg/L after 30 min. contact of chlorine with water. The dose is determined by test source water chlorination.

The water treatment

Reactants

Chlorine water, containing 1 mg chlorine in 1 ml (titer is established as 0,1 (0,05) mole-eq./L by solution $Na_2S_2O_3$); $Na_2S_2O_3$ (0,005 mole-eq./L solution); KI (10 % solution); acetate buffer mixture, starch (1 % solution).

The investigated water (100 ml) is measured into eight conic bulbs (250 ml). Then in interval 2 min. the chlorine water (1,0; 1,5; 2; 2,5; 3; 4; 5; 10 $см^3$) is added into everyone bulb (1 ml of chlorine water responds the dose of chlorine 1 mg/L). Bulbs are closed by stoppers, the content of it is mixed and left on 30 min. After 30-min. contact of chlorine with water sample, the content of residual chlorine in everyone sample is determined by the scheme, presented earlier.

By the data of work, the concentration of residual chlorine in everyone sample is calculated. To build the graph «chlorine dose – residual chlorine», to delay on the horizontal axis the dose of entered chlorine (mg/L), on the vertical axis – the concentration of residual chlorine (mg/L). To determine the optimal chlorine dose.

To calculate the indicator of water chlorination by the following formula:

$$O(Cl) = \frac{1}{D},$$

where D – the dose of chlorine (mg/L), responding the content of residual chlorine 0,5 mg/L.

2.3 Analysis of Chlorine

Chlorine will liberate free iodine from potassium iodine (Kl) solutions at pH 8 or less. The liberated iodine is titrated with a standard solution of sodium thiosulphate ($Na_2S_2O_3$) with starch as the indicator. The liberated iodine is directly proportional to

the concentration of chlorine present in sample. Titrate at pH 3 to 4 because the reaction is not stoichiometric at neutral pH due to partial oxidation of thiosulphate to sulphate.

Select a sample volume that will require not more than 20mL 0.01N sodium thiosulphate. For residual chlorine concentration of 1 mg/L or less, 100mL sample for chlorine range 1-10 mg/L, 500mL for chlorine above 10mg/L and proportionally less as per chlorine concentration.

The iodometric method is suitable for measuring total chlorine concentrations greater than 1 mg/L. All acidic iodometric methods suffer from interferences, generally in proportion to the quantity of potassium iodine (Kl) and H^+ added.

2.3.1 Reagents and standards

a. Acetic acid, conc. (glacial)

b. Potassium iodide, Kl, crystals

c. Standard sodium thiosulphate, 0.1N: Dissolve 25g $Na_2S_2O_3.5H_2O$ in 1L freshly boiled distilled water and standardise against Potassium bi-iodate or potassium dichromate after at least 2 weeks storage. This initial storage is necessary to allow oxidation of any sulphate ion present. Use boiled distilled water and add a few mLs chloroform ($CHCl_3$) to minimise bacterial decomposition.

d. Starch indicator solution: To 5g Starch (potato, arrowroot, or soluble), add a little cold water and grind in a mortar to a thin paste. Pour into 1L of boiling distilled water, stir, and let settle overnight. Use clear supernate. Preserve with 1.25g salicylic acid, 4g zinc chloride, or a combination of 4g sodium proportionate and 2g sodium azide/L starch solution. Some commercial starch substitutes are satisfactory.

e. Standard iodine, 0.1N: Dissolve 40g Kl in 25mL distilled water. Add 13g resublimed iodine and stir until dissolved. Transfer to a 1L volumetric flask and dilute to make volume up to mark.

f. Dilute standard iodine, 0.0282N: Dissolve 25g Kl in a little distilled water in a volumetric flask, and add to correct amount of 0.1N iodine solution to get 0.0282N solution; standardise this solution daily.

2.3.2 Sample collection, preservation and storage

Chlorine in aqueous solution is not stable, and the chlorine content of samples or solutions, particularly weak solutions, will decrease rapidly. Exposure to sunlight or other strong light or agitation will accelerate the reduction of chlorine. Therefore, chlorine determination should be done immediately after sampling, avoiding excessive light and agitation. The sample should not be stored for analyses of residual chlorine.

2.3.3 Calibration

Standardise 0.1N $Na_2S_2O_3$ by one of the following.

a. Iodate method – Dissolve 3.249g anhydrous potassium bi-iodate. $KH(IO_3)_2$, primary standard quality; or 3.567g KlO_3 dried at 103 ± 2°C for 1h, in distilled water and dilute to 1000mL to yield a 0.1N solution. Store in a glass-stoppered bottle.

b. To 80mL distilled water, add, with constant stirring, 1mL conc. H_2SO_4, 10.0mL 0.1N $KH(lO_3)_2$, and 1g Kl. Titrate immediately with 0.1N $Na_2S_2O_3$ titrant until the yellow colour of the liberated iodine almost is discharged. Add 1mL starch indicator solution and continue titrating until the blue colour disappears.

c. Dichromate method – Dissolve 4.904g anhydrous potassium dichromate, $K_2Cr_2O_7$, of primary standard quality, in distilled water and dilute to 1000mL to yield a 0.1N solution. Store in a glass-stoppere

d. Proceed as in the iodate method with the following exceptions: substitute 10.00mL 0.1N $K_2Cr_2O_7$ for iodate and let reaction mixture stand 6min in the dark before titrating with 0.1N $Na_2S_2O_3$ titrant.

$$\text{Normality } Na_2S_2O_3 = 1 / \text{mL } Na_2S_2O_3 \text{ consumed}$$

e. Standard sodium thiosulfate titrant, 0.01N or 0.025N: Improve the stability of 0.01N or 0.025N by $Na_2S_2O_3$ diluting an aged 0.1N solution, made as directed above, with freshly boiled distilled water. Add 4g sodium borate and 10mg mercuric iodide/L solution. For accurate work, standardise this solution daily in accordance with the directions given above, using 0.01N or 0.025N iodate or $K_2Cr_2O_7$. Use sufficient

volumes of these standard solutions so that their final dilution is not greater than 1+4. To speed up operations where many samples are to be titrated, use an automatic burette of a type in which rubber does not come in contact with the solution. Standard titrants, 0.01N and 0.025N, are equivalent, respectively to 354.5 µg and 886.3 µg Cl as Cl_2/mL.

2.3.4 Procedure

a. Volume of sample: Select volume that will require not more than 20mL 0.01N $Na_2S_2O_3$ and not less than 0.2mL for the starch-iodide end point. For a chlorine range of 1 to 10mg/L., use a 500mL sample: above 10mg/L, use proportionately less sample. Use smaller samples and volumes of titrant with the amperometric end point.

b. Preparation for titration: Place 5ml acetic acid, or enough to reduce the pH between 3.0 and 4.0, in a flask or white porcelain casserole. Add about 1g Kl estimated on a spatula. Pour sample in and mix with a stirring rod.

c. Titration: Titrate away from direct sunlight. Add 0.025N or 0.01N $Na_2S_2O_3$ from a burette until the yellow colour of the liberated iodine almost id discharged. Add 1mL starch solution and titrate $Na_2S_2O_3$ instead of 0.01N, then, with a 1L sample, 1drop is equivalent to about 50g/L. It is not possible to discern the end point with greater

2.3.5 Calculation

For standardizing chlorine solution for temporary standards:

mg Cl as Cl_2/mL = (A ± B) x N x 35.45 / mL sample

For determining total available residual chlorine in a water sample:

mg Cl as Cl_2/mL = (A ± B) x N x 35450 / mL sample

where: A = mL titration for sample.

B = mL titration for blank (positive or negative), and

N = normality of $Na_2S_2O_3$

2.3.6 Precision and Bias

Correct result of sample titration by determining blank contributed by oxidising or reducing agent impurities. The blank also compensates for the concentration of iodine bound to starch at the end point.

Take a volume of distilled water corresponding to the sample used for titration, Add 5mL acetic acid, 1g Kl, and 1mL starch solution. Perform blank titration as given in a and b below, whichever applies.

a. If a blue colour develops, titrate with 0.01N or 0.025N $Na_2S_2O_3$ to disappearance of blue colour and record result. B is negative.

b. If no blue colour occurs, titrate with 0.0282N iodine solution until a blue colour appears. Back-titrate with 0.01N 0.025N $Na_2S_2O_3$ and record the difference. B is positive.

Before calculating the chlorine concentration, subtract the blank titration of a from the sample titration; or, if necessary, add the net equivalent value of the blank titration of B.

c. Analyse the sample in duplicate.

2.3.7 Interferences

Oxidised forms of manganese and other oxidising agents interfere. Reducing agents such as organic sulphides also interfere. Although the neutral titration minimises the interfering effect of ferric and nitrite ions, the acid titration is preferred because some forms of combined chlorine do not react at pH 7. Use only acetic acid for the acid titration; sulphuric acid (H_2SO_4) will increase interferences; never use hydrochloric acid (HCl).

Minimum detectable concentration: The minimum detectable concentration approximates 40g Cl as Cl_2/L if 0.01N $Na_2S_2O_3$ is used with a 1000mL sample. Concentrations below 1mg/L cannot be determined accurately by the starch-iodine end point in this method.

2.3.8 Pollution prevention and waste management

The chemicals and reagent are used in very dilute form. During washing further dilution will take place. It may not pose any problem of disposal.

Self-control questions

1. What disinfection methods are known, compare their affectivity.
2. What concentration of residual chlorine is allowed in water-line water?
3. What way is water disinfection carried by chlorine compounds by?
4. Uncover the mechanism of post-chlorination.
5. Give the chemical scheme of water disinfection by ozonation.
6. Give the chemical scheme of water disinfection by photocatalytic methods.
7. Give the examples of disinfection reagents action and products of its degradation to human and water purification system.
8. Compare the affectivity of using different disinfection systems in water purification technology of Ukraine, Russia, England, Japan and USA.

3 The iron removing by the aeration

The aim of work – familiarization with methods of iron removing from natural waters and exploration some standard methods of evaluation of iron ions concentration in water.

Introduction

Iron and manganese are common in groundwater supplies used by many small water systems. Exceeding the suggested maximum contaminant levels (MCL) usually results in discolored water, laundry, and plumbing fixtures. This, in turn, results in consumer complaints and a general dissatisfaction with the water utility. There are secondary standards set for iron and manganese, but these are not health related and are not enforceable. The secondary (aesthetic) MCLs for iron and manganese are 0.3 milligrams per liter (mg/L) and 0.05 mg/L, respectively. Small water plants may choose to either sequestrate or remove iron and manganese. Sequestration only works for combined iron and manganese concentrations up to 1.0 mg/L and only in cases where the treatment is not permanent. Removal is usually achieved through ion exchange or oxidation/filtration. There are a number of chemical oxidants and filtration media available that can be used in various combinations [2].

Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1, 10-phenanthroline at pH 3.2 to 3.3. Three molecules of Phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The coloured solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid colour development in the presence of an excess of Phenanthroline. Colour standards are stable for at least 6 months [3].

3.1 Theoretical and technological part

Small amounts of iron are often found in water because of the large amount of iron present in the soil and because corrosive water will pick up iron from pipes. Clothing washed in water containing excessive iron may become stained a brownish

color. The taste of beverages, such as tea and coffee, may also be affected by iron. Manganese produces a brownish color in laundered clothing, leaves black particles on fixtures, and—as with iron—affects the taste of beverages, including coffee and tea.

Well water from the faucet or tap is usually clear and colorless. However, when water containing colorless, dissolved iron is allowed to stand in a cooking container or comes in contact with a sink or bathtub, the iron combines with oxygen from the air to form reddish-brown particles (commonly called rust). Manganese forms brownish-black particles. These impurities can give a metallic taste to water or to food.

The rusty or brown stains on plumbing fixtures, fabrics, dishes, and utensils cannot be removed by soaps or detergents. Bleaches and alkaline builders (often sodium phosphate) can make the stains worse. Over time, iron deposits can build up in pressure tanks, water heaters, and pipelines, reducing the quantity and pressure of the water supply.

Iron and/or manganese in water creates problems common to many water supply systems. When both are present beyond recommended levels, special attention should be paid to the problem. How iron and manganese are removed depends on the type and concentration and this helps determine the best procedure and (possible) equipment to use.

WHAT IS THE CHEMISTRY OF IRON AND MANGANESE IN WATER SYSTEMS?

Iron (Fe) and manganese (Mn) can be present in water in one of three basic forms:

1. Dissolved: ferrous (Fe^{2+}) and manganous (Mn^{2+})
2. Particulate: ferric (Fe^{3+}) and manganic (Mn^{4+}) states
3. Colloidal: very small particles (difficult to settle and filter).

The predominance of one form over another is dependent on the pH, Eh (redox potential), and temperature of the water. Knowledge of the forms or states of iron and manganese can help finetune a given treatment practice for these metals.

WHAT ARE THE MOST COMMON TREATMENT PROCESSES?

The majority of iron and manganese treatment systems employ the processes of oxidation/filtration. The oxidant chemically oxidizes the iron or manganese (forming a particle), and kills iron bacteria and any other diseasecausing bacteria that may be present. The filter then removes the iron or manganese particles (Fig. 4). Oxidation followed by filtration is a relatively simple process. The source water must be monitored to determine proper oxidant dosage, and the treated water should be monitored to determine if the oxidation process was successful.

Oxidation

Before iron and manganese can be filtered, they need to be oxidized to a state in which they can form insoluble complexes. Oxidation involves the transfer of electrons from the iron, manganese, or other chemicals being treated to the oxidizing agent. Ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which readily forms the insoluble iron hydroxide complex $Fe(OH)_3$. Reduced manganese (Mn^{2+}) is oxidized to (Mn^{4+}), which forms insoluble (MnO_2).

The most common chemical oxidants in water treatment are chlorine, chlorine dioxide, potassium permanganate, and ozone. Oxidation using chlorine or potassium permanganate is frequently applied in small groundwater systems. The dosing is relatively easy, requires simple equipment, and is fairly inexpensive.

Chlorination is widely used for oxidation of divalent iron and manganese. However, the formation of trihalomethanes (THMs) in highly colored waters may be a problem. Chlorine feed rates and contact time requirements can be determined by simple jar tests.

As an oxidant, potassium permanganate ($KMnO_4$) is normally more expensive than chlorine and ozone, but for iron and manganese removal, it has been reported to be as efficient and it requires considerably less equipment and capital investment. The dose of potassium permanganate, however, must be carefully controlled. Too little permanganate will not oxidize all the iron and manganese, and too much will allow permanganate to enter the distribution system and cause a pink color. Permanganate can also form precipitates that cause mudball formations on filters. These are difficult to remove and compromise filter performance.

Ozone may be used for iron and manganese oxidation. Ozone may not be effective for oxidation in the presence of humic or fulvic materials. If not dosed carefully, ozone can oxidize reduced manganese to permanganate and result in pink water formation as well. Manganese dioxide particles, also formed by oxidation of reduced manganese, must be carefully coagulated to ensure their removal.

A low-cost method of providing oxidation is to use the oxygen in air as the oxidizing agent in a tray aerator. Water is simply passed down a series of porous trays to provide contact between air and water. No chemical dosing is required, which allows for unattended operation. This method is not effective for water in which the iron is complexed with humic materials or other large organic molecules. Oxygen is not a strong enough oxidizing agent to break the strong complexes formed between iron and manganese and large organic molecules. Furthermore, the rate of reaction between oxygen and manganese is very slow below pH values of 9.5.

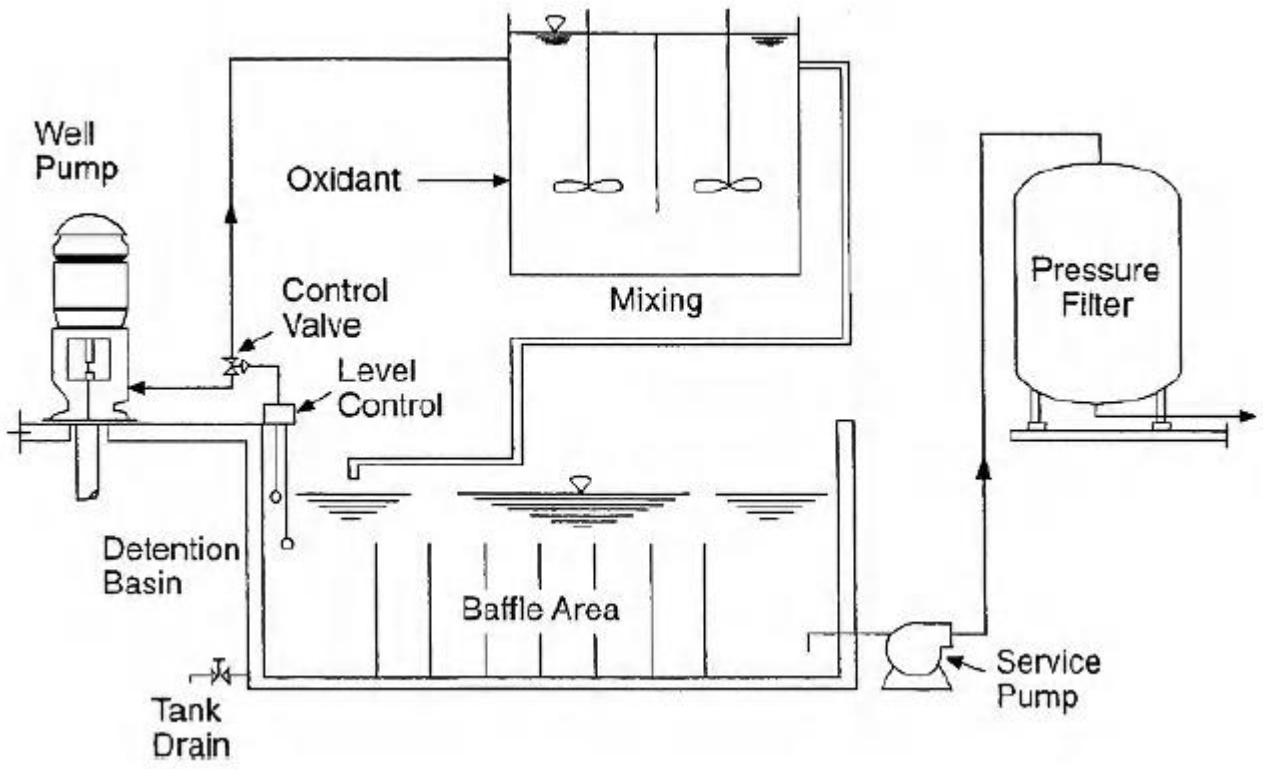

Figure 4. Chlorination, detention, and filtration (iron and manganese removal)

The presence of other oxidizable species in water hinders oxidation of the desired reduced compounds. Volatile organic chemicals, other organic compounds, or taste- and odor-causing compounds may result in an oxidant demand. This additional oxidant demand must be accounted for when dosing the oxidant. The expense of operation derives from the chemical use in most cases, and therefore is directly related to the source water quality.

Filtration

In general, manganese oxidation is more difficult than iron oxidation because the reaction rate is slower. A longer detention time (10 to 30 minutes) following chemical addition is needed prior to filtration to allow the reaction to take place.

There are different filtration media for the removal of iron and manganese, including manganese greensand, anthra/sand or iron-man sand, electromedia, and ceramic. Manganese greensand is by far the most common medium in use for removal of iron and manganese through pressure filtration. Greensand is a processed material consisting of nodular grains of the zeolitemineral glauconite. The material is coated with manganese oxide. The ion exchange properties of the glauconite facilitates the bonding of the coating. This treatment gives the media a catalytic effect in the chemical oxidation-reduction reactions necessary for iron and manganese removal. This coating is maintained through either continuous or intermittent feed of potassium permanganate. Anthra/sand (also iron-man sand) are other types of media available for removal of iron and manganese. They consist of select anthracite and sand with a chemically bonded manganese oxide coating. Unlike manganese greensand, these media are conditioned in the filter after media installation.

Electromedia provides a slightly different option from the manganese oxide coated media. This is a proprietary multi-media formulation which uses a naturally occurring zeolite and does not require potassium permanganate regeneration.

Finally, macrolite, unlike the other media discussed so far, is not a naturally occurring material which then undergoes processing for iron and manganese removal purposes. It is a manufactured ceramic material with a spherical shape and a rough, textured surface. The principal removal mechanism is physical straining rather than contact oxidation or adsorption.

Each medium has its advantages and disadvantages. Selection of a medium and oxidant should be based on pilot testing in which all necessary design criteria can be determined. Pressure filtration systemmanufacturers who offer the indicated media also offer fully automated systems.

ARE THERE ALTERNATIVE TREATMENTS?

Sequestration

Sequestration is the addition of chemicals to groundwater aimed at controlling problems caused by iron and manganese without removing them. These chemicals are added to groundwater at the well head or at the pump intake before the water has a chance to come in contact with air or chlorine. This ensures that the iron and manganese stays in a soluble form.

If the water contains less than 1.0 mg/L iron and less than 0.3 mg/L manganese, using polyphosphates followed by chlorination can be an effective and inexpensive method for mitigating iron and manganese problems. No sludge is generated in this method. Below these concentrations, the polyphosphates combine with the iron and manganese preventing them from being oxidized. Any of the three polyphosphates (pyrophosphate, tripolyphosphate, or metaphosphate) can be used.

To determine the best polyphosphate to use and the correct dosage, a series of samples at different concentrations may be prepared. Chlorine is added, and the samples are observed daily against a white background. The right polyphosphate dose is the lowest dose that does not noticeably discolor the water samples for four days.

Applying sodium silicate and chlorine simultaneously has also been used to sequester iron and manganese. However, while this technique is reliable in the case of iron treatment, it has not been found to be effective in manganese control.

Ion Exchange

Ion exchange should be considered only for the removal of small quantities of iron and manganese because there is a risk of rapid clogging. Ion exchange involves the use of synthetic resins where a pre-saturant ion on the solid phase (the “adsorbent,” usually sodium) is exchanged for the unwanted ions in the water (see Ion Exchange and Demineralization Tech Brief #DWBLPE56). One of the major difficulties in using this method for controlling iron and manganese is that if any oxidation occurs during the

process, the resulting precipitate can coat and foul the media. Cleaning would then be required using acid or sodium bisulfate.

Other

Systems that have a lime-soda ash softening plant do not need a separate iron and manganese removal plant. The high pH during softening allows rapid oxidation and precipitation of the iron and manganese as well as incorporation in the calcium and magnesium precipitates. Similarly, surface water treatment plants using coagulation, flocculation, sedimentation, and filtration also will remove iron and manganese as long as they make certain the iron and manganese get oxidized. Oxidation is sometimes a problem because of the presence of organic matter. Finally, biological treatment methods are being pilot tested at different locations. Biological treatment methods are used extensively in European countries, such as the Netherlands, France, and Germany, and are advantageous primarily when water simultaneously contains iron, manganese, and ammonia.

HOW CAN IRON AND MANGANESE PROBLEMS BE MINIMIZED IN DISTRIBUTION MAINS?

Problems due to iron and manganese in distributionmains may be minimized by:

- prior removal by appropriate treatment,
- protecting iron/steel mains with bituminous linings,

or using noncorrosive materials,

- avoiding dead-end mains,
- avoiding disturbances in the water flow, and
- flushing periodically.

3.2 Analysis of Iron

Iron occurs in the minerals as hematite, taconite and pyrite. It is widely used in steel and other alloys. Elevated iron levels in water can cause stains in plumbing, laundry and cooking utensils and can impart objectionable taste and colour to foods. The United Nations FAO recommended level for irrigation water is 5mg/L. The US EPA secondary drinking water standard MCL is 0.3mg/L. The BIS standard desirable limit is 0.3mg/L.
Methods for analysis:

A. Inductively coupled plasma (ICP) method/AAS

B. Phenanthroline method

Phenanthroline method

Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1, 10-phenanthroline at pH 3.2 to 3.3. Three molecules of Phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The coloured solution obeys Beer's law; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid colour development in the presence of an excess of Phenanthroline. Colour standards are stable for at least 6 months.

Interference: Among the interfering substances are strong oxidising agents, cyanide, nitrite, and phosphates (polyphosphates more so than orthophosphate), chromium, zinc in concentrations exceeding 10 times that of iron, cobalt and copper in excess of 5mg/L, and nickel in excess of 2mg/L. Bismuth, cadmium, mercury, molybdate, and silver precipitate Phenanthroline. The initial boiling with acid converts polyphosphates to orthophosphate and removes cyanide and nitrite that otherwise would interfere. Adding excess hydroxylamine eliminates errors caused by excessive concentrations of strong oxidising reagents. In the presence of interfering metal ions, use a larger excess of Phenanthroline to replace that complexed by the interfering metals. Where excessive concentrations of interfering metal ions are present, the extraction method may be used. If noticeable amounts of colour or organic matter are present, it may be necessary to evaporate the sample, gently ash residue, and redissolve in acid. Ashing may be carried out in silica, porcelain crucibles that have been boiled for several hours in 1+1 HCl. The presence of excessive amounts of organic matter may necessitate digestion before use of the extraction procedure.

Minimum detectable concentration: Dissolved or total concentrations of iron as low as 10µg/L can be determined with a spectrophotometer using cells with a 5 cm or longer light path. Carry a blank through the entire procedure to allow for correction.

3.2.3 Apparatus and equipment

i. Spectrophotometer: use a 510nm, providing a light path of 1cm or longer.

ii. Acid-washed glassware: wash al glassware with conc. hydrochloric acid (HCl) and rinse with distilled water before use to remove deposits of iron oxide.

iii. Separatory funnels: 125mL, squibb from, with ground glass or TFE stopcocks and stoppers.

3.2.4 Reagents and standards

Use reagents and distilled water free from iron contamination

i. Hydrochloric acid, HCl, conc. containing less than 0.5 ppm iron.

ii. Hydroxylamine solution: Dissolve 10g $NH_2OH.HCl$ in 100mL water.

iii. Ammonium acetate buffer solution: Dissolve 250g $NH_4C_2H_3O_2$ in 150mL water. Add 70mL conc. (glacial) acetic acid. Because even a good grade of $NH_4C_2H_3O_2$ contains a significant amount of iron, prepare new reference standards with each buffer preparation.

iv. Sodium acetate solution: Dissolve 200g $NaC_2H_3O_2.3H_2O$ in 800 mL water.

v. Phenanthroline solution: Dissolve 100mg 1, 10-phenanthroline monohydrate, $C_{12}H_8N_2.H_2O$, in 100mL water by stirring and heating to 80°C. Do not boil. Discard the solution if it darkens. Heating is unnecessary if 2 drops of conc. HCl are added to the water (note: One milliliter of this reagent is sufficient for no more than 100µg Fe).

vi. Stock iron solution: Use metal (1) or salt (2) for preparing the stock solution.

i. Use electrolytic iron wire, or “iron wire for standardizing” to prepare the solution. If necessary, clean wire with fine sandpaper to remove any oxide coating and to produce a bright surface. Weigh 200mg wire and place in a 1000mL volumetric flask. Dissolve in 20mL 6N sulphuric acid (H_2SO_4) and dilute to mark with water; 1mL = 200µg Fe.

ii. If ferrous ammonium sulphate is preferred, slowly add 20mL conc.H_2SO_4 to 50mL water and dissolve 1.404g Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$.Add 0.02M potassium permanganate (KMnO4) drop-wise until a faint pink colour persists. Dilute to 1000mL with water and mix; 1mL = 200µg Fe.

Standard iron solutions: Prepare daily for use.

Pipette 50mL stock solution into a 1000 mL volumetric flask and dilute to mark with water; 1mL = 10µg Fe.

Pipette 5mL stock solution into a 1000 mL volumetric flask and dilute to mark with water; 1 mL =1µg Fe.

vii. Disopropyl or isopropyl ether.

Cautions: Ethers may form explosive peroxides; test before using.

3.2.5 Procedure

Total iron: Mix sample thoroughly and measure 50mL into a 125mL Erlenmeyer flask. If this sample volume contains more than 200 µg iron, use a smaller accurately measured portion and dilute to 50mL. Add 2mL conc. HCl and 1mL $NH_2OH{\cdot}HCl$ solution. Add a few glass beads and heat to boiling. To insure dissolution of all the iron, continue boiling until volume is reduced to 15 to 20mL. (If the sample is ashed, take up residue in 2mL conc. HCl and 5mL water). Cool to room temperature and transfer to a 50 or 100 mL volumetric flask or nessler tube. Add 10mL $NH_4C_2H_3O_2$ buffer solution and 4mL Phenanthroline solution and dilute to mark with water. Mix thoroughly and allow at least 10 to 15 min to maximum colour development.

Dissolved iron: Immediately after collection filter sample through a 0.45µg membrane filter into a vacuum flask containing 11mL conc. HCl/ferrous iron. Calculate suspended iron by subtracting dissolved from total iron.

Ferrous iron: Determine ferrous iron at sampling site because of the possibility of change in the ferrous-ferric ration with time in acid solutions. To determine ferrous iron only, acidify a separate sample with 2mL conc. HCl/100mL sample at the time of collection. Fill bottle directly from sampling source and stopper. Immediately withdraw a 50mL portion of acidified sample and add 20mL Phenanthroline solution and 10mL $NH_4C_2H_3O_2$ solution with vigorous stirring. Dilute to 100mL and measure colour intensity within 5 to 10 min. Do not expose to sunlight. (Colour development is rapid in the presence of exc Phenanthroline. The Phenanthroline volume given is suitable for less than 50µg total iron, if larger amounts are present, use a correspondingly larger volume of Phenanthroline or a more concentrated

reagent. Excess Phenanthroline is required because of kinetics of the complexing process). Calculate ferric iron by subtracting ferrous from total iron.

Colour measurement: Prepare a series of standards by accurately pipetting calculated volumes of standard iron solutions (use weaker solution to measure 1 to 10µg portions) into 125mL Erlenmeyer flasks, diluting to 50mL by adding measured volumes of water.

For photometric measurement, use light path at 510nm. Read standards against distilled water set at zero absorbance and plot a calibration curve, including a blank.

If samples are coloured or turbid, carry a second set of samples through all steps of the procedure without adding Phenanthroline.

Samples containing organic interferences: Digest samples containing substantial amounts of organic substances.

a. From the digested sample, pipette 10.0 mL or other suitable portion containing 20 to 500µg Fe into a 125mL separatory funnel. If the volume taken is less than 10mL, add distilled water to make up to 10mL. To the separatory funnel add 15 mL conc. HCl for a 10mL aqueous volume; or, if the portion taken was greater than 10mL. Add 1.5mL conc. HCl/mL of sample. Mix, cool.

b. To prepare a sample solely for determining iron, measure a suitable volume containing 20 to 500µg Fe. However, use only 5mL of H_2SO_4 or $HClO_4$ and omit H_2O_2. When digestion is complete, cool, dilute with 10mL of water, heat almost to boiling to dissolve slowly soluble salts and, if the sample is still cloudy, filter through a glass fibre, sintered-glass or porcelain filter, washing with 2 to 3 mL water. Quantitatively transfer filtrates or clear solution to a 25mL volumetric flask and make up to 25mL with water. Empty flask into a 125mL separatory funnel, rinse with 5mL conc. HCl that is added to the funnel and add 25mL conc. HCl measured with the same graduated or flask. Mix and cool to room temperature.

c. Extracts iron from the HCl solution in the separatory funnel by shaking for 30s with 25mL isopropyl ether (caution). Draw off lower acid layer into a second separatory funnel. Extract acid solution again with 25mL isopropyl ether, drain acid layer into a suitable clean vessel and combine the two portions of isopropyl ether. Pour acid layer back into second separatory funnel and re-extract with 25 mL isopropyl ether. Withdraw

and discard acid layer and add ether layer to original funnel. Persistance of a yellow colour in the HCl solution after three extractions does not signify incomplete separation of iron because copper, which is not extracted, gives a similar yellow colour. Shake combined ether extracts with 25mL water to return iron to aqueous phase and transfer lower aqueous extract. Discard ether layer.

d. Add 1mL $NH_2OH.HCl$ solution, 10mL Phenanthroline solution and 10mL $NaC_2H_3O_2$ solution. Dilute to 100mL with water, mix thoroughly and let stand for 10 min. Measure absorbance at 510 nm using a 5cm absorption cell for amounts of iron less than 100 µg or 1cm cell for quantities form 100 to 500µg. As reference, use either distilled water or a sample blank prepared by carrying the specified quantities of acids through the entire analytical procedure. If distilled water is used as reference, correct sample absorbance by subtracting absorbance of a sample blank. Determine micrograms of iron in the sample from the absorbance (corrected, if necessary) by reference to the calibration curve prepared by using a suitable range of iron standards containing the same amounts of Phenanthroline, hydroxylamine and sodium acetate as the sample.

3.2.6 Calculation

mg Fe/L = µg Fe (in 100mL final volume) / mL sample

OR for digested samples

Mg Fe/L = {µg Fe (in 100mL final volume) / mL sample} x {100 / mL portion}

Report details of sample collection, storage and pre-treatment, if they are pertinent to interpretation of results.

3.3 Iron removing from water by the aeration

Iron removing from water by the aeration in laboratory is carried at experimental installation (fig. 5).

The air is pumped by compressor 1 and come in Drexel glass 2, where water sample is aerated, the time of aeration is given by teacher. After aeration water is filtered for iron hydroxide precipitation removing.

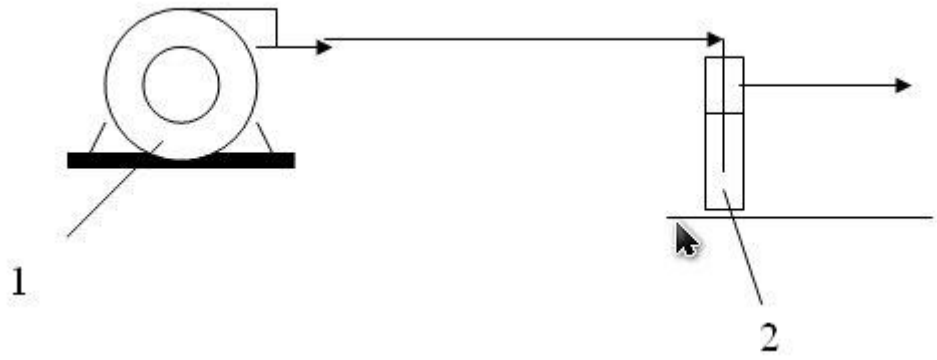

Figure 5. The scheme of aeration installation: 1 – compressor; 2 – Drexel glass.

Iron content water analysis

For determining iron in analyzed solution, the aliquot of this solution is transferred to volumetric flask (50 ml). The same operations and in the same sequence are charged with solution, as at its preparation, for constructing calibration graph, and then filtered relatively water. The content of iron is determined by calibration graph.

The processing of results

Iron content is determined by the formula, mg/L:

$$C_{Fe} = \frac{C_к \cdot 1000}{V},$$

where C_k – the concentration of Fe, determined by calibration graph, mg;

V – the volume of water sample, ml.

The degree of iron removing for whole water samples is determined by the formula, %:

$$\alpha = \frac{C_{Fe}^0 - C_{Fe}}{C_{Fe}^0} \cdot 100,$$

where C_{Fe}^0 – iron content in input water, mg/L;

C_{Fe} – iron content in water after purification, mg/L.

Self-control questions

1. What the sense of iron MCL in drinking water?
2. What the harmful of iron excess in drinking and technical water?
3. What methods are for iron removing from water? What is its essence?
4. What cases are advisable for using one or another method of iron removing?
5. In what form do iron compounds present in natural water (surface, underground origin)?
6. Write the reactions, placing at iron removing from water by the aeration.
7. Give the reactions, placing at iron removing from water by liming.
8. What substances are used as catalysts at iron removing from water?
9. Write the ion exchange reaction among iron (II) sulfate and Ca-cation exchanger.

4 The magnesium removing from water

The aim of work – familiarization with methods of manganese compounds removing from water and exploration the standard method of the determination of magnesium ion concentration in natural and drinking water, choosing of parameters at process of manganese compounds removing.

Introduction

The majority of iron and manganese treatment systems employ the processes of oxidation/filtration. The oxidant chemically oxidizes the iron or manganese (forming a particle), and kills iron bacteria and any other disease-causing bacteria that may be present. The filter then removes the iron or manganese particles. Oxidation followed by filtration is a relatively simple process. The source water must be monitored to determine proper oxidant dosage, and the treated water should be monitored to determine if the oxidation process was successful. In details see 3.1.

4.1 Analysis of manganese

Manganese is associated with iron minerals and occurs in nodules in ocean, fresh water and soils. The common ores are pyrolusite and psilomelane. Manganese is used in steel alloys, batteries and food additives. The FAO-recommended maximum level for manganese in standard is 50μg/L. BIS desirable limit is 0.1 mg/L [3].

Methods for analysis:

A. Inductively coupled plasma method

B. Persulphate Method

Sampling and storage

Manganese may exist in a soluble form in neutral water when first collected, but it oxidises to a higher oxidation state and precipitates or becomes absorbed on the container walls. Determine very soon after sample collection. When delay is unavoidable, total manganese can be determined if the sample is acidified at the first time of collection with HNO_3 to pH <2.

4.1.2 Summary of the method

Principle: Persulphate oxidation of soluble manganous compounds to form permanganate is carried out in the presence of silver nitrate. The resulting colour is stable for at least 24h if excess Persulphate is present and organic matter is absent.

Interferences: As much as 0.1g chloride (Cl) in a 50-mL sample can be prevented from interfering by adding 1g mercuric sulphate ($HgSO_4$) to form slightly dissociated complexes. Bromide and iodine still will interfere and only trace amounts may be present. The Persulphate procedure can be used for potable water with trace to small amounts of organic matter, if the period of heating is increased after more Persulphate has been added.

For wastewater containing organic matter, use preliminary digestion with nitric and sulphuric acids (HNO_3 and H_2SO_4). If large amounts of Cl^- interfering traces of Cl^- in the special reagent.

Coloured solutions from other inorganic ions are compensated for in the final colorimetric step. Samples that have been exposed to air may give low results due to precipitation of manganese dioxide (MnO_2). Add 1 drop of 30% hydrogen peroxide (H_2O_2) to the sample, after adding the special reagent, to redissolve precipitated mang

Minimum detectable concentration:

The molar absoptivity of permanganate ion is about 2300 Lg^{-1} cm^{-1}. This corresponds to a minimum detectable concentration (98% transmittance) of 210µg Mn/L when a 1cm cell is used or 42µg Mn/L when a 5cm cell is used.

4.1.3 Apparatus and equipment

i. Colorimetric equipment: One of the following is required: Spectrophotometer: for use at 525nm, providing a light path of 21cm or longer.

Filter photometer: providing a light path of 1cm or longer and equipped with a green filter having maximum transmittance near 525nm.

ii. Nessler tubes: matched, 100mL, tall form.

4.1.4 Reagents and standards

Use reagents and distilled water free from manganese contamination.

i. Special reagent: Dissolve 75g $HgSO_4$ in 400mL conc. HNO_3 and 200mL distilled water. Add 200mL 85% phosphoric acid (H_3PO_4) and 35mg silver nitrate ($AgNO_3$). Dilute the cooled solution to 1L.

ii. Ammonium Persulphate: $(NH_4)_2S_2O_8$ solid.

iii. Standard manganese solution: Prepare a 0.1N potassium permanganate ($KMnO_4$) solution by dissolving 3.2g $KMnO_4$ in distilled water and making up to 1L. Age for several weeks in sunlight or heat for several hours near the boiling point, then filter through a fine fritted-glass filter crucible and standardise against sodium oxalate as follows:

> Weigh several 100 to 200mg samples of $Na_2C_2O_4$ to 0.1mg and transfer to 400mL beakers. To each beaker, add 100mL distilled water and stir to dissolve. Add 10mL of (1+1) H_2SO_4 and heat rapidly to 90 to 95°C. Titrate rapidly with the $KMnO_4$ solution to be standardised, while stirring, to a slight pink endpoint colour that persists for at least 1 min. Do not let temperature fall below 85°C. If necessary, warm beaker contents during titration; 100mg $Na_2C_2O_4$ will consume about 15mL, permanganate solution. Run a blank on distilled water a

Normality of $KMnO_4$ = g $Na_2C_2O_4$ / (A –B) x 0.067 01

Where:

A = mL titrant for sample and

B = mL titrant for blank

Average results of several titrations; calculate volume of this solution necessary to prepare 1L of solution so that 1.00mL = 50µg Mn as follows:

mL $KMnO_4$ = 4.55 / Normality, $KMnO_4$

To this volume, add 2 to 3 mL conc. H_2SO_4 and $NaHSO_3$ solution drop wise, with stirring, until the permanganate colour disappears. Boil to remove excess SO_2, cool and dilute to 100mL with distilled water. Dilute this solution further to measure small amounts of manganese.

iv. Standard manganese solution (alternate): Dissolve 1g manganese metal (99.8% min) in 10mL redistilled HNO_3. Dilute to 1000mL with 1% (v/v) HCl; 1mL = 1mg Mn. Dilute 10mL to 200mL with distilled water; 1mL = 0.05mg Mn. Prepare dilute solution daily.

v. Hydrogen peroxide: H_2O_2, 30%

vi. Nitric acid: HNO_3, conc.

vii. Sulphuric acid: H_2SO_4, conc.

viii. Sodium nitrite solution: Dissolve 5g $NaNO_2$ in 95mL distilled water.

ix. Sodium oxalate: $Na_2C_2O_4$, primary standard

x. Sodium bisulphate: Dissolve 10g $NaHSO_3$ in 100mL distilled water.

4.1.5 Procedure

Treatment of sample: If a digested sample has been prepared according to directions for reducing organic matter and/or excessive chlorides, pipette a portion containing 0.05 to 2mg Mn into a 250mL conical flask. Add distilled water, if necessary, to 90mL and proceed.

To a suitable sample portion add 5mL special reagent and 1 drop H_2O_2. Concentrate to 90mL by boiling or dilute to 90mL. Add 1g $(NH_4)_2S_2O_8$, bring to a boil and boil for 1min.Do not heat on a water bath. Remove from heat source, let stand 1 min and then cool under the tap (boiling too long results in decomposition of excess Persulphate and subsequent loss of permanganate colour; cooling too slowly has the same effect). Dilute to 100mL with distilled water free from reducing substances and mix. Prepare standards containing 0, 5, to 1500µg Mn by treating various amounts of standard Mn solution in the same way.

Photometric determination:

Use a series of standards from 0 to 1500µg Mn/100 ml. final volume. Make photometric measurements against a distilled water blank. The following table shows light path length appropriate for various amounts of manganese in 100ml. final volume:

Mn Range	Light Path
µg	cm
5-200	15
20-400	5
50-1000	2
100+1500	1

Prepare a calibration curve of manganese concentration vs. absorbance from the standards and elements and determine Mn in the samples from the curve.

Correction for turbidity or interfering colour:

Avoid filtration because of possible retention of some permanganate on the filter paper. If visual comparison is used, the effect of turbidity only can be estimated and no correction can be made for interfering coloured ions. When photometric measurements are made, use the following 'bleaching' method, which also corrects for interfering colour. As soon as the photometer reading has been made, add 0.05mL H_2O_2 solution permanganate colour has faded completely and no bubbles remain, absorbance to obtain absorbance due to Mn.

4.1.6 Calculation

i. When the entire original sample is taken for analysis:

Mn, mg/L = {µg Mn (in 100mL final volume) / mL sample} x {100 / mL portion}

ii. When a portion of the digested sample (100mL final volume) is taken for analysis:

Mn, mg/L = µg Mn / 100mL / mL sample

4.2 Magnesium removing from water

Water sample (100 ml) is diluted in 2 times and passed through the column, completing «black sand». The time of passing is 45 min. After the process finishing, the residual manganese content is determining in water sample by photometric method by the same way the analysis of initial water sample. Nitrate acid (3 ml) is added to 20 ml of sample and heating to boiling, 50 mg of $(NH_4)_2S_2O_8$ are added, then 2 drops of

$AgNO_3$ solution. The mixture is boiled 5 min. After cooling it is transferred quantitatively to the volumetric flask (200 ml), diluted by 200 ml of distilled water to the mark, then optical density is measured at λ=525 nm. Manganese content is determined by the calibration graph, including dilution.

Self-control questions

1. Name the compounds, in which manganese is present in different origins of water.
2. What the harmful of manganese compounds presence in drinking water?
3. Name the methods of manganese removing from water. What is their essence?
4. In what cases is one or another one methods group used?
5. What reagents are the most often used for manganese removing from water? Describe the features of using «black sand».
6. Write down the reaction of manganese removing from water by ozone.
7. Write down the reaction of manganese removing from water by anion exchanger.
8. What MCL of manganese in drinking water?

5 The determination of fluorine and its removing by sorption methods

The aim of work – familiarization with main methods of fluorine removing from water and exploration the standard method of fluorine ions concentration evaluation in water.

Introduction

Fluoridation of water supplies has been a controversial subject for more than 60 years. Much of the debate is concerned with questions of safety, but recently questions have been also raised about the efficacy of fluoridation. More than 35,000 papers on fluoridation have been published in the years since fluoride supplementation was first proposed as a safe and effective way of decreasing tooth decay. The overwhelming conclusion is that fluoride is safe and cost-effective [2].

It has never been shown that fluoride intake at 1 ppm has any negative effect on disease or death rates. Numerous studies performed before and after supplemental fluoridation have shown no changes in death rates from cancer, heart disease, intracranial lesions, nephritis, cirrhosis, or from any other cause. In addition, the normal disease and death rates of more than 7 million Americans who have lived for generations where the natural fluoride concentration was 2 to 10 mg/L (1 mg/L is the recommended dose), is compelling evidence of fluoridation's safety. Two extensive studies have established that there is no link between fluoridation and Down's syndrome, cleft palate, heart abnormalities, clubfoot, and other common birth defects.

Fluoride is a very active element, it forms compounds with most elements. Widespread of soluble fluorine-containing compounds in the rocks and soils determines the presence of fluoride in natural waters used for drinking water.

Low concentrations of fluoride are found in most surface water sources - rivers, lakes, reservoirs. The concentration of fluoride in water from artesian wells is more or less constant and reaches values that exceed the maximum permissible concentration (1.5 mg / dm3). Groundwater sources in some parts of Ukraine are characterized by high fluorine content - 4 - 5 mg /dm3, sometimes up to 9 mg /dm3.

Excess fluoride in drinking water (more than 1.5 mg /dm3) by prolonged its consumption causes fluorosis - the disease known as "hypoplasia" or mottling of tooth enamel. The optimum concentration of fluoride is considered to be about 1 mg / dm3, because the lack of fluoride is harmful to human health.

Removing fluoride from water carried by reagents, filtration methods, which are based on chemical sorption processes. As a result of these processes, fluoride binds to nonsoluble compounds and falls together with sorbent as a precipitate (reagent methods) or adsorbed by filters (filtration methods). Filtration methods are more effective at removing fluoride from groundwater that do not require other kinds of treatment.

Reagent methods useful for fluoride removing from surface waters when simultaneously needs a discoloration of water.

Ion selective electrode method [3] can be used to determine the concentration of ionic species in water and is known as direct potentiometry. The electrode whose potential depends upon the concentration of the ions to be determined is termed as the indicator electrode. The electrodes are used with a reference electrode and for this purpose a silver-silver chloride electrode is usually prepared. A double junction reference electrode is used for measurement of pH. The glass membrane of the electrode when replaced by other materials such as a single crystal or solid ion exchange material, it gives electrode, capable of measuring the concentration available for determination of pH, sodium, potassium, calcium, nitrate, chlorite, silver, lead, cadmium, copper, fluoride, bromide, iodide, cyanide, thiocyanide and Sulphide. The fluoride-sensitive electrode is of the solid state type, consisting of a lanthanum fluoride crystal; in use it forms a cell in combination with a reference electrode, normally the calomel electrode. The crystal contacts the sample solution at one face and an internal reference solution at the other.

5.1 Basis of fluoridation

HISTORY OF WATER FLUORIDATION

In 1892, Sir Crichton-Browne advocated augmenting the common diet of his era with fluoride to reduce decay. Not until the 1950s, however, did years of research pay off, and it was unequivocally determined that when water contains approximately 1 part of fluoride per million parts of water (1 ppm) which is equivalent to 1 milligram of

fluoride per liter of water (1 mg/L), decay rates are reduced by up to 60%. In the 1940s, there was substantial resistance to adding fluoride to community water supplies, even though people had been drinking naturally occurring fluoridated water containing several times the 1-ppm level of fluoride for a lifetime without any negative side effects.

The most famous study of the effects of fluoridation was done in the 1940s in Newburgh and Kingston, New York. These cities are located 35 miles apart near the Hudson River; both had populations of about 30,000 and were also similar in their demographics. Newburgh's water supply was fluoridated, and Kingston's was not. After 10 years, the study found that there were no medical differences between the two groups except for the fact that Newburgh's children had almost 60% fewer cavities. Many studies have confirmed these findings in the years since.

FLUORIDE

Fluoride is one of the earth's most common elements and is therefore present in variable amounts in all water supplies. It is also found in most plants and animals that we eat. The fluoride concentrations in water supplies within the United States vary from 0.1 to 10 mg/L. Ocean water also contains fluoride at concentrations of 1.0 to 1.5 mg/L. This causes a fairly uniform level of fluoride in all seafood.

Fluoride is classified by the National Academy of Sciences as an essential nutrient. Unlike many other essential elements that are found in food, water consumption is the most practical, consistent and effective method of fluoride application to the teeth. In growing children, fluoride will be incorporated throughout the entire hard structure (enamel and dentin) of the teeth. This continues until around age 50 when it appears that the spaces available to fluoride in the tooth's structure will be filled. In adults, fluoride will continue to be absorbed by the enamel surface, lending the teeth temporary but substantial resistance to decay. Fluoride is easily absorbed into the blood stream from the gastrointestinal tract and reaches a peak concentration within 20–60 minutes. This level declines rapidly due to the uptake of fluoride by the hard tissues and the removal of fluoride by the kidneys. Approximately 50% of the fluoride that is absorbed is incorporated in the body's teeth and bones within 24 hours.

The amount of decay reduction caused by fluoridation of local water supplies has decreased during the last 40 years probably because of improved dental hygiene and widespread use of fluoride toothpaste. This increase in fluoride availability has led to a reduction in the dose of fluoride supplementation recommended for children living in non-optimally fluoridated communities (Table 2). In 1991, it was found that fluoride reduces the incidence of cavities 20% to 40% in children and 15% to 35% in adults (5).

Table 2. Supplemental Fluoride Dosage (Milligrams of Fluoride per Day)

	Concentration of Fluoride in Water (parts/million)		
Age (years)	0.0 to 0.3	0.3 to 0.6	Over 0.6
Birth to six months	None	None	None
Six months to three years	0.25	None	None
Three to six years	0.50	0.25	None
Six to sixteen years	1.0	0.50	None

THE SAFETY OF FLUORIDE

In 1970, the World Health Organization (WHO) issued a report, "Fluorides and Human Health," that had taken years of research to compile. The WHO wanted to evaluate impartially the vast number of scientific studies of fluoridation that had been published. These papers included population studies, experimental research, animal studies, human autopsy studies, clinical trials, and X-ray research. The WHO expert panel concluded that there was no reliable evidence that drinking water fluoridated at the recommended levels caused any ill health effects. In 1975, the WHO stated, "The only sign of physiological or pathological change in life-long users of optimally fluoridated water supplies . . . . is that they suffer less from tooth decay" (3).

Fluoride ingested through community water systems has a large margin of safety. It has never been shown that fluoride intake at 1 ppm has any negative effect on disease or death rates. Numerous studies performed before and after supplemental fluoridation have shown no changes in death rates from cancer, heart disease, intracranial lesions, nephritis, cirrhosis, or from any other cause. In addition, the normal disease and death rates of more than 7 million Americans who have lived for generations where the natural fluoride concentration was 2 to 10 mg/L (1 mg/L is the recommended dose), is compelling evidence of fluoridation's safety. Two extensive studies have established

that there is no link between fluoridation and Down's syndrome, cleft palate, heart abnormalities, clubfoot, and other common birth defects.

Antifluoridationists have long claimed that fluoride use leads to an increase in cancer rates. Consumer's Union characterized this accusation as ‘‘absurd.’’ It has been shown that fluoride has no mutagenic effect in studies of cattle or mice. This makes sense because fluoride is not in the class of electrophilic compounds that can interact with DNA, nor is it likely that the small tissue levels of fluoride present due to fluoridated water supplies could interfere with DNA replication. It has also been proven that fluoride does not cause allergic reactions. The executive committee of the American Academy of Allergy has stated, ‘‘There is no evidence of allergy or intolerance to fluorides as used in fluoridation of community water supplies.’’

The effect of fluoridated water on kidney function has been thoroughly investigated, and here again no ill effects have been shown. No kidney changes were detected in a population exposed for a lifetime to water supplies that have fluoride levels of 8 mg/L.

Opponents of fluoridation also routinely claim that it causes coronary artery disease. They use data on heart disease rates from Antigo, Wisconsin, to support this claim. Antigo did show increased death rates from heart disease in the period since fluoride was introduced to its water supply in 1949. But, in that same period, the percentage of elderly people living in Antigo doubled, due to longer life spans. Actually, the segment of the population 75 years old or older increased 106% (2). The higher death rates from heart disease amongst the elderly were never factored into the interpretation of the Antigo death-rate data. When this factor is taken into account, the alleged deleterious effect of fluoride disappears. Unfortunately, the population of Antigo believed the scare tactics and false claims of the antifluoridationist movement and voted to end the fluoridation of their water supply. After only 4 years, the decay rates in permanent teeth of second graders rose 183%. A year later, Antigo voted to reinstate fluoridation.

FLUORIDE SAFETY MARGINS

Food and water account for 1.2 to 2.6 mg of fluoride ingestion per day. Urban air usually contains less than 1 μg/m3, an insignificant amount. The margin of safety for fluoride is very large, and toxic effects have not been demonstrated at levels far higher than one could receive in a lifetime of exposure to drinking water containing 8 times the recommended level of 1 ppm. The acute lethal dose for a 150 lb. (70 kg) man is 5 to 10 g of sodium fluoride or 2.3 to 4.5 g of fluoride. Chronic overexposure to fluoride at levels over 1 ppm before age 8 can lead to discoloration of the enamel, ranging from barely detectable white flecks to large brown areas. Known as enamel fluorosis, this solely cosmetic problem can be achieved only by ingesting high amounts of fluoride, not by topical application.

THE COST OF FLUORIDATING WATER SYSTEMS

Fluoride protection obtained through community water treatment costs approximately 50 cents per person per year. This saves an estimated $75 in dental treatment costs. The National Preventive Demonstration Program monitored nearly 30,000 children, ages 5 to 14, for 4 years and found that the most cost-effective method of decay prevention was to drink fluoridated water from birth and have sealants applied as needed (12).

THE ANTIFLUORIDATIONIST MOVEMENT

The water supply of the developed world is slowly becoming entirely fluoridated, although overcoming the misinformation promoted by those opposed to fluoridation is a long and difficult process. The resistance to this overwhelmingly endorsed public health benefit tells us a great deal about the psychology of fear, the strength of rumor, and the loss of trust in government and industry. William T. Jarvis, Ph.D., the Executive Director of the National Council Against Health Fraud, has stated. These charges seem to grow out of a mentality of distrust. Antifluoridation groups are led by many of the same people who oppose immunization, pasteurization, sex education, mental health programs, and other public health advances. Most are closely connected with sellers of alternatives to medically accepted products and services. The so-called ‘‘health food’’ industry justifies its existence by declaring that our conventional sources of food, water, and health care are misguided.

No studies will satisfy those who are opposed to fluoridation. A vociferous minority, made up mostly of food faddists, cultists, chiropractors, and people who misunderstand what fluoridation is, has developed effective ways of stopping fluoride from being adjusted to optimum levels in water. "Lifesavers Guide to Fluoridation," a pamphlet by John Yiamouyiannis, Ph.D., is often distributed in communities that are considering fluoridation. It cites 250 references as proof that fluoride is dangerous. However, in 1988, experts from the Ohio Department of Health published "Abuse of the Scientific Literature in an Antifluoridation Pamphlet." This review traced the references and found that almost half had no relevance to community water fluoridation and that many others actually supported fluoridation but were selectively misquoted and misrepresented.

In 1990, an article in *Newsweek* magazine implied that fluoridation was ineffective and unsafe. The article was a response to the unauthorized and premature release of data from an experiment at the National Institute of Environmental Health Science. The experiment exposed rats and mice to high doses of fluoride. A thorough review of the experiments by a U.S. Public Health Service expert panel concluded that the data were insignificant and that fluoridation posed no risk of cancer or any other disease. Dr. Stephen Barrett, a leading consumer health advocate, called the *Newsweek* article "the most irresponsible analysis of a public health topic ever published by a major national news outlet."

Fluoride has been a favorite target of those who want to frighten the public into believing that our health system is dangerous and uncaring. They continue to undermine the significant health advances that have been made by public health measures, modern agriculture, and industry. The simple truth is that there's no "scientific controversy" over the safety of fluoridation. The practice is safe, economical, and beneficial. The survival of this fake controversy represents one of the major triumphs of quackery over science in our generation.

FLUORIDATION RATES AROUND THE WORLD

Tooth decay, or caries, is the most prevalent disease of all humanity, more common than the common cold. The cost of tooth decay in human suffering as well as economic expenditures is also enormous, accounting for many billions of dollars. Yet,

as we enter the twentyfirst century, only a small percentage of the world's population can easily drink fluoridated water. In addition, the majority of bottled water is not fluoridated, and many types of home water filtering devices actually remove the fluoride that may be in the water.

In the United States, 62.2% of the population has access to public water supplies that are optimally fluoridated. More than 360 million people worldwide in approximately 60 countries also drink fluoridatedwater. Dr. C. Everett Kopp, the former Surgeon General of the United States has stated, ‘‘Fluoridation is the single most important commitment that a community can make to the oral health of its citizens.’’ It is imperative to continue to fluoridate water systems throughout the world.

5.2 Analysis of Fluoride

When the fluoride electrode is dipped in sample whose concentration is to be measured, a potential is established by the presence of fluoride ions by any modern pH meter having an expanded millivolt scale.

The fluoride ion selective electrode can be used to measure the activity or concentration of fluoride in aqueous sample by use of an appropriate calibration curve. However, fluoride activity depends on the total ionic strength of the sample. The electrode does not respond to bound or complexed fluoride. Addition of a buffer solution of high total ionic strength containing a chelate to complex aluminium preferentiality overcomes these difficulties.

5.2.1 Apparatus and equipment

a. Ion meter (field/laboratory mode) or pH/mV meter for precision laboratory measurements

b. Reference electrode (calomel electrode)

c. Fluoride-sensitive electrodes

d. Magnetic stirrer

e. Plastic lab ware (samples and standards should always be stored in plastic containers as fluoride reacts with glass).

5.2.2 Reagents and standards

a. Stock fluoride solution: dissolve 221mg anhydrous NaF and dilute to 1000mL. 1mL = 100µgF^-

b. Standard fluoride solution: Dilute stock solution 10 times with distilled water to obtain 1mL = 10µg F^-

c. Total Ionic Strength Adjustment Buffer (TISAB): place approximately 500mL distilled water in a 1L beaker, add 57mL glacial acetic acid, 58g, NaCl and 4g 1, 2-cyclohexylenediamine tetraacetic acid. Stir to dissolve. Place beaker in a cool water bath and add slowly 6N NaOH (about 125mL) with stirring, until pH is between 5 to 5.5. Transfer to a 1L volumetric flask and make up the volume to the mark.

5.2.3 Sample collection, preservation and storage

Polyethylene bottles are preferred for collecting and storing samples for fluoride analysis. Glass bottles are satisfactory, provided that they have not previously contained high-fluoride solutions. Always rinse the bottle with a portion of the sample. Sodium thiosulphate in excess of 100mg/L will interfere by producing a precipitate.

5.2.4 Calibration

Take 50mL of each 1ppm and 10ppm fluoride standard. Add 50mL TISAB (or 5mL if conc. TISAB is used) and calibrate the instrument.

5.2.5 Procedure

a. For connecting the electrodes to meter and for further operation of the instrument follow the instruction manual supplied by the manufacturer.

b. Check the electrode slope with the ion meter (59.16mV for mono valent ions and 29.58mV for divalent ions at 25°C).

c. Transfer 50 to 100mL of sample to a 150mL plastic beaker. Add TISAB.

d. Rinse electrode, blot dry and place in the sample. Stir thoroughly and note down the steady reading on the meter.

e. Recalibrate every 1 or 2 hours.

f. Direct measurement is a simple procedure for measuring a large number of samples. The temperature of samples and standard should be the same and the ionic strength of standard and samples should be made the same by addition of TISAB to all solutions.

g. Direct measurement results can be verified by a known addition procedure. The known addition procedure involves adding a standard of known concentration to a sample solution. From the change in electrode potential before and after addition, the original sample concentration is determined.

5.2.6 Calculation

The concentration in mg/L is obtained directly from the specific ion meter.

5.2.7 Precision and Bias

When using an expanded-scale pH meter or selective-ion meter, recalibrate the electrode frequently by checking the potential reading of the 1mg/L F standard and adjust the calibration control, if necessary, until the meter reads as before. Confirm the calibration after each unknown and also after reading each standard when preparing the standard curve. Use the recovery of known addition as part of regular analytical protocol.

5.2.8 Interferences

Polyvalent cations such as AI (III) and Si (IV) will complex fluoride ions. However, the addition of CDTA (cyclohexylene diamine tetra acetic acid) preferentially will complex concentrations of aluminium up to 5mg/L. Hydrogen ion forms a complex with fluoride while hydroxide ion interferes with electrode response. By adjusting the pH between 5 and 8 no interference occurs.

5.2.9 Pollution prevention and waste management

The chemicals are used in micro quantities. No health-hazardous chemicals are used. There is little need for waste management as no large volumes of solvents or hazardous chemicals are used. The laboratory waste management practices be followed so that the protection of water and land by minimizing and controlling all releases from bench operations will be possible.

5.3 Fluorine removing from water by sorption

Water sample (100 ml) is placed into conic bulb, 1g of crushed mordenite is added (or other sorbent, given by teacher) and strongly shaken during 30 min. (by the apparatus for shaking). The sample is filtered after shaking.

Self-control questions

4. What the sense of fluorine MCL in drinking water?
5. What the harmful and lack of fluorine in drinking water?
6. What 2 groups are the fluorine removing methods divided into? What is its essence?
7. What cases of using one or another one group of methods?
8. What reagents are the most wide used at fluorine removing from water? Name the features of its using.
9. What sorbents are used as backfilling of fluorine removing filters? What the features of its using?
10. Write the reaction of F-ion removing from water by hydroxide apatite.
11. Write the reaction of F-ion removing from water by anion exchanger.
12. Give the possible ways of wasted sorbents utilization.
13. The optimal concentration of fluorine in drinking water is 1 mg/L, but in countries with heat climate it can be 0,8 mg/L and even 0,5 mg/L. What the explanation?

6 The removing of aluminium by coagulation

The aim of work – familiarization with the methods of aluminium compounds removing from water; exploration the standard method of alumina ions concentration evaluation in drinking and natural water; the determination of the removal degree of aluminium from water by coagulation.

Introduction (to coagulation block)

Particulate matter in natural water varies in size, concentration, and surface chemistry. The particle size may range from a few tens of nanometers to a few hundred micrometers. Discrete particles less than one micron in size are called colloidal. Colloidal particles have significantly higher external surface area per unit area and move in a random diffusional motion known as Brownian motion. In colloidal suspension, surface phenomena dominate over mass phenomena. The most important surface property is the accumulation of electrical charges at the particle surface. Loss of atoms due to abrasion, molecular arrangement within the crystal, and imperfections within the molecular structure may result in surfaces being charged. The colloidal particles in most surface water are negatively charged. Because of hydration and/or electrostatic surface charges, colloidal particles repel other material and thereby remain suspended. Surface waters that are turbid due to colloidal particles cannot be clarified without special treatment. Coagulation is a process for enhancing the tendency of particulate matter in aqueous suspension to attach to one another and/or to attach to collector surfaces [2].

Aluminium is the third most abundant element on the earth’s crust. The presence of aluminium in all natural water is in the form of soluble salt, a colloid, or an insoluble compound. Soluble, colloidal, and insoluble aluminium may be present in treated water in residual form of coagulation with aluminium-containing material. The USEPA water standard for Al is 0.05mg/L max. BIS desirable limit is 0.03mg Al/L.

6.1 Particulate matter removal by coagulation

Coagulation promotes destabilization of surface charges on colloidal particles. Destabilization and aggregation of particulate matter and precipitation or adsorption of NOM in subsequent solid–liquid separation processes are the primary functions of the coagulation process. The coagulation process involves two steps: (1) the addition of chemical coagulants to destabilize particulate matter and react with NOM and (2) the physical transport of collisions among particulate matter, resulting in aggregation or floc formation. In the water treatment literature, coagulation refers to all reactions and mechanisms that result in aggregation, and the physical transport step of producing interparticle aggregation is called flocculation. In a water treatment plant, coagulation is achieved by rapid or flash mixing of coagulants followed by flocculation.

The two most common types of coagulants are metallic salts and polymers; the most common metallic salt coagulants are aluminum sulfate (alum) and ferric chloride. The selection of a particular coagulant depends on the required level of effectiveness. A standard jar test is a recommended method for determining the relative effectiveness of coagulants for a particular raw water supply. The factors that are considered normally in selecting a coagulant include cost, availability, overall safety, ease of storage, handling, and application. Alum is the most widely used coagulant because of its availability, low cost, ease of use, and ease of storage. Ferric chloride, other metallic salts, and polymers are less widely used. Alum’s performance, however, is greatly affected by the pH of the influent. The commonly used dosage of alum ranges from 5 to 150 mg/L, but the problem of sludge disposal increases at higher alum dosages. Due to special raw water characteristics and because of health concerns about aluminum, some water utilities use ferric chloride. Although ferric chloride is not always as effective as alum in reducing trihalomethane formation potential (THMFP) and total organic carbon (TOC), it is more effective than alum for water that has high dissolved color, low turbidity, and a moderate pH.

Polymers are effective coagulants, coagulant aids, and filter aids. They consist of monomers and are classified according to their charge or lack of charge. A polymer that has a charge is an ionized polymer, or a polyelectrolyte. Polymers can be cationic, anionic, or nonionic. In applications where polymers are effective, dosages are generally

lower than alum dosages for the same effect. Typical polymer dosages range from 1.5 to 10 mg/L. Consequently, polymer coagulants produce less residual sludge than alum.

Coagulant aids are added to the influent after or simultaneously with the primary coagulants to improve particle capture efficiency during flocculation, sedimentation, and filtration. Nonionic and anionic polymers are commonly used as coagulant aids. The ratio of alum to coagulant aid dosages ranges from 100:1 to 50:1. Standard jar tests are required to determine precise coagulant aid dosages.

There are four coagulation mechanisms that, it is thought, occur in destabilizing colloidal particles: double layer compression, surface charge neutralization, sweep coagulation, adsorption and interparticle bridging. The double layer model is used to understand the ionic environment near a charged colloid particle. The surface charge on the colloid attracts ions of opposite charge and forms a dense layer adjacent to the particle known as the Stern layer. Excess positive ions are still attracted by the negatively charged colloids but are repelled by the Stern layer. This dynamic equilibrium results in creating a diffuse layer of counterions. The Stern and the diffuse layer in the interfacial region around colloidal particles are referred to collectively as the double layer. The electrical potential at the junction of the Stern layer and the diffuse layer, called the zeta potential, can be measured experimentally. It correlates with colloid particle stability. Highly stable colloidal systems are characterized by a high zeta potential, whereas lower zeta potentials reflect less stable systems. The DLVO theory (named after Derjaguin, Landau, Verwey, and Overbeek) governs the net interactive force between colloidal particles by combining the van der Waals attractive force and the electrostatic repulsion force. The double layer can be compressed by adding a coagulant that has a positive charge (to counteract negatively charged colloids). In water treatment practice, destabilization by double layer compression is not a dominant mechanism because it requires an extremely high salt concentration. This is an important destabilization mechanism in natural systems, for instance, delta formation in estuaries.

Destabilization by surface charge neutralization involves reducing the net charge of colloidal particles in the suspension. The net surface charge can be reduced by adjusting the solution chemistry. In other cases, colloidal particles can be destabilized

by neutralizing using counterions of coagulants. In water treatment practice, a similar type of surface charge destabilization occurs that is called heterocoagulation. The distribution of charges on a colloidal surface is not uniform. Large particles that have high negative surface charges may come in contact with smaller particles that bear relatively low positive charges. These particles may be destabilized by simple electrostatic interaction.

Sweep coagulation or sweep-floc coagulation is also known as enmeshment in a precipitate. At higher coagulant doses, excess metal salts hydrolyze into metallic hydroxides. These hydroxides are extremely insoluble in water, amorphous, heavier than water, and gelatinous. As the hydroxide precipitate forms and accumulates, the colloidal particles are enmeshed or entrapped in the hydroxide floc. This destabilization mechanism is called sweep coagulation.

Interparticle bridging destabilization occurs when highmolecular- weight polymers are used as coagulants or coagulant aids. These polymers are highly surface-active, and their surface structure may be linear or branched. The polymers destabilize particles by first adsorbing at one or more sites on the colloidal particle surface and then extending the chain length into solution and attaching to other particles. This results in forming an interparticle bridge. Sometimes an excessive dosage of polymer may cause restabilization due to surface saturation or sterical stabilization.

6.2 Analysis for aluminum in water

With Eriochrome Cyanine R dye, dilute aluminium solutions buffered to a pH 6.0 produce a red to pink complex that exhibits maximum absorption at 535 nm. The aluminium concentration, reaction time, temperature, pH, alkalinity, and concentration of other ions in the sample influence the intensity of the complex. To compensate for colour and turbidity, the aluminium is one portion of sample is complexed with EDTA to provide a blank. Adding ascorbic acid eliminates the interference of iron and manganese. The optimum range lies between 20 and 30μg/L but can be extracted by sample dilution [3].

Interference:

Both fluoride and polyphosphates cause negative errors. When the fluoride concentration is constant, the percentage error decrease with increasing amount of aluminium. Because the fluoride concentration often is known or can be determined readily, fairly accurate results can be obtained by adding the known amount of fluoride to a set of standards. Orthophosphate in concentrations under 10mg/L does not interfere. The interference caused by even small amount of alkalinity is removed by acidifying the sample just beyond the neutralization point of methyl orange. Sulphate does not interfere up to a concentration of 2000mg/L.

Minimum detectable concentration:

The minimum aluminium concentration detectable by this method in the absence of fluorides and complex phosphates is approximately 6µg/L.

6.2.1 Apparatus and equipment

i. Spectrophotometer, wavelength at 535nm, with a light path of 1cm.

ii. Glassware: Treat all glassware with warm 1+1 HCl and rinse with aluminium free distilled water to avoid errors due to materials absorbed on the glass. Rinse sufficiently to remove all acid.

6.2.2 Reagents and standards

Use reagents and distilled water free from aluminium contamination.

i. Stock aluminium solution: Use either the metal (1) or soluble salt (2) for preparing stock solution; 1mL = 500µg Al: 1) Dissolve 500mg aluminium metal in 10mL conc. HCl by heating gently. Dilute to 1000mL with distilled water, 2) Dissolve 8.791g aluminium potassium sulfate, $AlK(SO_4)_2.12H_2O$, in water and dilute to 1000mL. Correct this weight by dividing by the decimal fraction of analysed $AlK(SO_4)_2.12H_2O$ in the reagent used.

ii. Standard aluminium solution: Dilute 10.0mL stock aluminium to 1000mL with water; 1mL = 5.00µg Al. Prepare fresh stock.

iii. Sulphuric acid, H_2SO_4, 0.02N and 6N.

iv. Ascorbic acid solution: Dissolve 0.1-g ascorbic acid in water and make up to 100mL in volumetric flask. Prepare fresh daily.

v. Buffer reagent: Dissolve 136g sodium acetate, $NaC_2H_3O_2.3H_2O$, in water, add 40mL 1N acetic acid, and dilute to 1L.

vi. Stock dye solution: Eriochrome cyanine: R: Dissolve 100mg in water and dilute to 100mL in volumetric flask. This solution should have a pH of about 9 to 2.9. Stock solutions have excellent stability and can be kept for at least a year.

vii. Working dye solution: Dilute 10mL of selected stock dye solution to 100mL in volumetric flask with water. Working solutions are stable for at least 6 months.

viii. Methyl orange indicator solution (or) bromocresol green indicator solution: as in alkalinity test

ix. EDTA (sodium salt of ethylenediamine-tetraacetic acid dehydrate): 0.01M: Dissolve 3.7g in water, and dilute to 1L.

x. Sodium hydroxide: NaOH, 1N and 0.1N.

6.2.3 Procedure

Preparation of calibration curve: Prepare a series of aluminium standards from 0 to 7μg (0 to 280μg/L) based on a 25mL sample by accurately measuring the calculated volumes of standard aluminium solution into 50mL of volumetric flasks or Nessler tubes. Add water to a total volume of approximately 25mL.

Add 1mL of 0.02N H_2SO_4 to each standard and mix. Add 1mL ascorbic acid solution and mix. Add 10mL buffer solution and mix. With a volumetric pipette, add 5.00mL working dye reagent and mix. Immediately make up to 50mL with distilled water. Mix and let it stand for 5 to 10 min. The colour begins to fade after 15min. Read transmittance or absorbance on a spectrophotometer, using a wavelength of 535nm. Adjust instruments to zero absorbance with the standard containing no aluminium. Plot concentration of Al (micrograms Al in 50mL final volume) against absorbance.

Sample treatment in absence of fluorides and complex phosphate:

Place 25mL sample, or a portion diluted to 25mL, in a porcelain dish or flask, add a few drops of methyl orange indicator, and titrate with 0.02N H_2SO_4 to faint pink colour. Record reading and discard sample. To two similar samples at room temperature add the same amount of 0.02N H_2SO_4 used in the titration and 1mL in excess.

To one sample add 1mL EDTA solution. This will serve as a blank by complexing any aluminium present and compensating for colour and turbidity. To both samples add 1mL ascorbic acid, 10mL buffer reagent and 5mL working dye reagent.

Set instrument to zero absorbance or 100% transmittance using the EDTA blank.

After 5 to 10 minutes contact time, read transmittance or absorbance and determine aluminium concentration from the calibration curve previously prepared.

Removal of phosphate interference:

Add 1.7mL 6H2SO4 to 100mL sample in a 200mL Erlenmeyer flask. Heat on a hot plate for at least 90 min, keeping solution temperature just below the boiling point. At the end of the heating period the solution volume should be about 25mL. Add water if necessary to keep it at or above that volume.

After cooling, neutralize to a pH of 4.3 to 4.5 with NaOH, using 1N NaOH at the start and 0.1N for the final time adjustment. Monitor with a pH meter. Make up to 100mL with water, mix and use a 25mL portion for the aluminium test.

Run a blank in the same manner, using 100mL distilled water and 1.7mL $6H_2SO_4$.

Subtract blank reading from sample reading or use it to set instrument to zero absorbance before reading the sample.

Correction for samples containing fluoride

Add the same amount of fluoride as in the sample to each aluminium standard, and draw calibration curve for aluminium standard

6.2.4 Calculation

Mg Al/L = μg Al (in 50mL final volume) / mL sample

6.3 The removing of alumina from water by coagulation

Water purification from alumina is carried by several methods: ion exchange, reverse osmosis and distillation, coagulation treatment.

Water purification from alumina by ion exchange is in using ion exchangeable resins, insoluble compounds with functional non-ionic groups, entering to exchange reactions with ions of a solution. Water purification from alumina by ion exchange consists of two stages: treatment through

H^+ - cation and OH^- - anion filter.

Water purification from alumina by reverse osmosis is in using half-permeable membranes, partitions, separating the filtrate from solution, containing alumina. The

process is carried out by pressure from the membrane, higher, than osmotic pressure, for water passing through the partition.

The thermal method of water purification is distillation. The essence is in solution separation into liquid and condensate with different chemical composition, because the treated system is freed from some substances.

By coagulation method, the removing of alumina is charged by its transferring into hydroxide. Iron salts (chlorides or sulfates) are used as a coagulant. The time of process – 30 min., pH 8 – 9. The removing of alumina from water sample is carried after determination of alumina compound in analyzed sample.

The example of determining the dose of coagulant

The quantity of $FeSO_4$ or other is calculated by the task of the teacher. It's necessary to know for this: the dose of coagulant D_{FeSO4} mg/L, the concentration of coagulant C_{FeSO4} mg/L and the volume of water sample V, L.

The dose of coagulant depends on input characteristics of water volume, especially, from alumina content in investigated facility.

The necessary volume of the coagulant is calculated by the formula, ml,

$$V_{FeSO4} = D^{опт}_{FeSO4} * V(sample) / C_{FeSO4},$$

where V_{FeSO4}- the necessary volume of the coagulant, ml;

D^{opt}_{FeSO4} – the optimal dose of coagulant in recalculation into anhydrous iron sulfate (II), mg/L;

V(sample) – the volume of sample for coagulation, ml;

C_{FeSO4} – the concentration of coagulant, mg/L.

Coagulation purification with separation of precipitate from treated water by filtration and alumina content analysis of purified water are charged after making the calculated quantity of coagulant into the water sample.

Analysis (simplified)

The sample (25 ml) is placed into a volumetric flask (50 ml), 25 – 30 g of ascorbate acid and 1 ml of ammonia sulfate solution are added, the mixture is mixed and then 2 ml of aluminum solution is added. The solution is mixed, 10 ml of acetate buffer is added after every 3 – 5 min, and solution volume is reached to mark by

distilled water. The optic density is measured every 20 min. at λ = 525 – 540 nm in cuvette (3 cm) relatively idle test. The quantity of alumina in the sample is found from calibration schedule (μg).

The content of residual alumina C_{res}, μg/ml,

$$C_{res}(Al) = C_c / V_{al},$$

де C_c – the concentration of Al, determined by calibration schedule, μg;

V_{al} –the volume of the water sample, ml, including dilution.

The degree of aluminum removal, %,

$$\alpha = \frac{C_{res}(Al)}{C(Al)} \cdot 100 .$$

Self-control questions

1. What the sense of MCL of alumina in drinking water?
2. Name origins of alumina sources hit into water and what is its harmful excess of its compounds in drinking water?
3. Name the analytic methods, using for alumina determination in water?
4. What reagents are used for colorimetric determination of alumina compounds in water?
5. In what form does alumina present in alkaline solutions? Hover the characteristic reactions.
6. What forms of alumina compounds existing in weak-alkaline and neutral solutions? Hover the characteristic reactions.
7. What forms of alumina compounds existing in acid solutions? Hover the characteristic reactions.
8. The comparison characterization of the methods of alumina compounds removing from water.

7 The determination of silicon and its removing by reagent methods

The aim of work – familiarization of the basic methods of silicon determination in water samples and its removing by reagent methods.

7.1 Determination of Silicon and Silicates

Several methods have been employed for quantitative determination of silica in different water samples. This involves spectrophotometry, titrimetry, gravimetry, electroanalytical, or chromatography techniques. The demand for routine rapid analysis resulted in the introduction of the flow injection analysis (FIA) technique. FIA has proven to be adding a lot to the development of water analysis at large. The determination of silica in water samples is considered very important in the industry because silica deposits on stream turbine blades at high pressure and temperature. This lowers the efficiency of heat transfer, leading to costly downtime for cleaning and may result in total failure of the boiler system. Phosphate is usually added to the boiler feed water to ensure that it is in the alkaline range, and this serves as an anticorrosion measure. Phosphates react similarly with reagents used for silica determination to give the same colored product; this poses a serious interference problem for the colorimetric determination of silica in the presence of phosphate. This interference problem is especially challenging when analyzing very low concentration of silica.

Spectrophotometric methods for the determination of silicates in water samples resemble the majority of the methods so far reported as it is cheaper and easier to apply for routine work. The technique has been heavily utilized with modifications that lead to automation and robustness and the introduction of the FIA methodology and application. All the methods reported involve the complexation reaction of the molybdate with silica, a method that has been applied and subjected to different modifications to adapt the different water media and contents. All these modifications are mentioned in the following paragraph with focus and details of the standard and FIA methods.

American Public Health Association, APHA Standard Method [4].

The method is based on the reaction of ammonium molybdate with silica and any phosphate present at pH 1.2 to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid but not the molybdosilicate acid. Even if phosphate is known to be absent, the addition of oxalic acid is highly desirable and is a mandatory step. The intensity of the yellow color is proportional to the concentration of ‘‘molybdatereactive’’ silica. In at least one of its forms, silica does not react with molybdate. It is not known to what extent such ‘‘unreactive’’ silica occurs in waters. Terms such as ‘‘colloidal,’’ ‘‘crystalloidal,’’ and ‘‘ionic’’ have been used to distinguish among various forms of silica but such terminology cannot be substantiated. ‘‘Molybdate-unreactive’’ silica can be converted to the ‘‘molybdate-reactive’’ form by heating or fusing with alkali. Molybdate-reactive or unreactive silica does not imply reactivity, or lack of it, toward other reagents or processes.

7.1.1 Interference

Because both apparatus and reagents may contribute silica, avoid using glassware as much as possible and use reagents low in silica. Also, make a blank determination to correct for silica so introduced. In this method, tannin, large amounts of iron, color, turbidity, sulfide, and phosphate interfere. Treatment with oxalic acid eliminates interference from phosphate and decreases interference from tannin. If necessary, use photometric compensation to cancel interference from color or turbidity.

7.1.2 Minimum Detectable Concentration

Approximately 1 mg SiO2=L can be detected in 50 mL Nessler tubes.

7.1.3 Apparatus

i. Platinum dishes, 100 mL

ii. Colorimetric equipment: One of the following is required:

– Spectrophotometer, for use at 410 nm, providing a light path of 1 cm or longer

– Filter photometer, providing a light path of 1 cm or longer and equipped with a violet filter having maximum transmittance near 410 nm

– Nessler tubes, matched, 50 mL, tall form

7.1.4 Reagents

For best results, use batches of chemicals low in silica. Store all reagents in plastic containers to guard against high blanks.

i. Sodium bicarbonate, $NaHCO_3$, powder.

ii. Sulfuric acid, H_2SO_4, 1 N.

iii. Hydrochloric acid, HCl, I N.

iv. Ammonium molybdate reagent: Dissolve 10 g$(NH_4)_6Mo_7O_2 \cdot 4H_2O$ in distilled water, with stirring and gentle warming and dilute to 100 mL. Filter if necessary. Adjust to pH 7 to 8 with silica-free NH_4OH or NaOH and store in a polyethylene bottle to stabilize. If the pH is not adjusted, a precipitate gradually forms. If the solution is stored in glass, silica may leach out and cause high blanks. If necessary, prepare silica-free NH_4OH by passing gaseous NH_3 into distilled water contained in a plastic bottle.

v. Oxalic acid solution: Dissolve 7.5 g $H_2C_2O_4 \cdot H_2O$ in distilled water and dilute to 100 mL.

vi. Stock silica solution: Dissolve 4.73 g sodium metasilicate nonahydrate, Na_2SiO_3 $9H_2O$, in distilled water and dilute to 1000 mL. Analyze 100.0 mL portions to determine concentration. Store in a tightly stoppered plastic bottle.

vii. Standard silica solution: Dilute 10.00 mL stock solution to 1000 mL with distilled water; 1:00 mL j 10:0 mg SiO_2. Calculate exact concentration from concentration of stock silica solution. Store in a tightly stoppered plastic bottle.

viii. Permanent color solutions:

i. Potassium chromate solution: Dissolve 630 mg K_2CrO_4 in distilled water and dilute to 1 L.

ii. Borax solution: Dissolve 10 g sodium borate decahydrate, $Na_2B_2O_7 \cdot 10H2O$, in distilled water and dilute to 1 L.

7.1.5 Procedure

1. Color development: To 50.0mLsample add in rapid succession 1.0 mL 1.0 HCl and 2.0 mL ammonium molybdate reagent. Mix by inverting at least six times and let stand for 5 to 10 min. Add 2.0 mL oxalic acid solution and mix thoroughly. Read color after 2 min but before 15 min, measuring time from addition of oxalic acid. Because the yellow color obeys Beer’s law, measure photometrically or visually.

2. To detect the presence of molybdate-unreactive silica, digest sample with $NaHCO_3$ before color development. This digestion is not necessarily sufficient to convert all molybdate-unreactive silica to the molybdate-reactive form. Complex silicates and higher silica polymers may require extended fusion with alkali at high temperatures or digestion under pressure for complete conversion. Omit digestion if all the silica is known to react with molybdate.

3. Prepare a clear sample by filtration if necessary. Place 50.0 mL, or a smaller portion diluted to 50 mL, in a 100 mL platinum dish. Add 200 mg silica-free $NaHCO_3$ and digest on a steam bath for 1 h. Cool and add slowly, with stirring, 2.4 mL in H_2SO_4. Do not interrupt analysis but proceed at once with remaining steps. Transfer quantitatively to a 50 mL Nessler tube and make up to mark with distilled water. (Tall-form 50 mL Nessler tubes are convenient for mixing even if the solution subsequently is transferred to an absorption cell for photometric measurement.)

4. Preparation of standards: If $NaHCO_3$ pretreatment is used, add to the standards (approximately 45 mL total volume) 200 mg $NaHCO_3$ and 2.4 mL of 1 N H_2SO_4 to compensate both for the slight amount of silica introduced by the reagents and for the effect of the salt on color intensity. Dilute to 50.0 mL.

5. Correction for color or turbidity: Prepare a special blank for every sample that needs such correction. Carry two identical portions of each such sample through the procedure, including $NaHCO_3$ treatment if this is used. To one portion add all reagents. To the other portion add HCl and oxalic acid but no molybdate. Adjust photometer to zero absorbance with the blank containing no molybdate before reading absorbance of molybdate-treated sample.

6. Photometric measurement: Prepare a calibration curve from a series of approximately six standards to cover the optimum concentration ranges using standard silica solution diluted to 50.0 mL in Nessler tubes. Set photometer at zero absorbance with distilled water and read all standards, including a reagent blank, against distilled water. Plot micrograms silica in the final 55 mL developed solution against photometer readings. Run a reagent blank and at least one standard with each group of samples to confirm that the calibration curve previously established has not shifted.

7. Calculation

mg SiO_2/L = mg SiO_2 (in 55 mL final volume) / mL sample.

7.2 The removing of silicon from water by iron salts

At adding iron (II) salts to water the sorption of silicon acid, dissolved in water, by hydroxide is happened and also mutual coagulation of iron hydroxide and silicon acid colloids. For successful flowing of the process pH is supported in interval 7,8 – 8,3.

Equipment

Conic bulbs (from 300 to 500 ml); pipettes; conic bulbs (250 ml) – 6 ones; universal indicator; filtration funnels and filters «blue ribbon».

Reactants

Sodium silicate $Na_2SiO_3 \cdot 9H_2O$ for samples preparation, crystal-like: iron (II, III) salts, 1% solution HCl, 1% solution NaOH.

The analysis of sample

200 – 300 ml of investigated water are poured into 7 conic bulbs. The quantities of iron (II) and iron (III) salts are calculated for getting following doses: 50, 100, 150, 200, 300, 400, 500 mg/ L. The necessary quantity of reactants is measured and made into bulbs. Then they are mixed. By the acid or the alkaline pH is proved to 7 – 8 and mixed intensively during 1 minute. They are creamed during 25 minutes. At creaming the silicon acid content investigations of input water is charged by known method. The volume of aliquot is necessary to choose depending on water model, but it's better to begin from 10 ml of investigated sample.

After creaming, water is filtered through the filter and the content of silicon acid is determined. The degree of silicon removing X is calculated by the formula:

$$X = \frac{C_{\text{□}} - C_{\text{fin}}}{C_{\text{□}}} 100 \text{ ,}$$

where C_{in} – the initial concentration of silicon acid in water, mg/L;

C_{fin} – the final concentration of silicon acid in water, mg/L.

A graph of the dependence «silicon removal degree – coagulant dose» is built. The same way the investigations for other iron salts are charged by the task of teacher. By data, got experimentally, the conclusion about coagulants effectivity for silicon acid removing from solutions is made.

The initial concentration of silicon acid: _____ mg/L.

The results of research

Coagulant dose, mg/L	Residual concentration, mg/L	Silicon removal degree, %
Coagulant:		
50		
100		
150		
…		
500		

Self-control questions

1. Name the origins of silicon compounds incoming to natural and technical water.

2. Explain the mechanism of sorption removing of silicon compounds from water.

3.What the harmful or helpful of silicon compounds in water for drinking and technical (cooling) waters?

4. Name the methods of silicon acid removing from water.

5. What the aim of increasing silicon content in water?

6. What the concentration of silicon acid is allowed in water, submitting for water systems cooling?

7. What forms of silicon existing in water?

8. Uncover the chemical scheme of silicon compounds removing by iron, calcium and magnesium salts.

9. Give the chemical scheme of silicon compounds removing by coagulation.

10. Uncover the chemical scheme of silicon compounds removing by ion exchange.

8 The determination of optimal coagulant dose at the dynamic mode of precipitation

***The aim of work*:** determination of optimal coagulant dose and exploration of the method of water purification from suspended particles and color by coagulation with mixing.

8.1 Analysis for Total Solids in water

The term ‘solid’ refers to the matter either filtrable or non-filtrable that remains as residue upon evaporation and subsequent drying at a defined temperature. Further categorisation depends upon depends upon the temperature employed for drying and ignition. Different forms of solids are defined on the basis of method applied for their determination. Solids may affect water or effluent quality adversely in number of ways. Water with high dissolved solids may include an unfavourable physiological reaction in the transient consumer and generally are of inferior palatability. Highly mineralized waters are unsuitable for many industrial applications. High suspended solids in waters may be aesthetically unsatisfactory for such purposes as bathing. Analysis of total solids are important to decide upon the various unit operations and processes in physical and biological wastewater treatment and to asses its performance evaluation. For assessing compliance with regulatory agency, wastewater effluent limitations for various forms of solids act as indicating parameters [3].

8.1.1 Principle

Residue left after the evaporation and subsequent drying in oven at specific temperature 103-105°C of a known volume of sample are total solids. Total solids include “Total suspected solids” (TSS) and “Total dissolved solids” (TDS). Whereas loss in weight on ignition of the same sample at 500°C, 50°C, in which organic matter is converted to CO_2 volatilisation of inorganic matter as much as consistent with complete oxidation of organic matter, are volatile solids.

8.1.2 Apparatus and equipment

a. Electrically heated temperature controlled oven

b. Monopan balance

c. Evaporating dish (200mL)

d. Pipettes

e. Measuring cylinder (100mL)

8.1.3 Sample collection, preservation and storage

The water samples may be collected in resistant glass or plastic bottle. Water has considerable solvent property. There is possibility of increase in mineral content of sample, if water is collected and stored in non-resistant glass bottle. The effect is pronounced with alkaline water. Exclude particles such as leaves, sticks, fish and lump of faecal matter in the sample. Begin analysis as soon as possible due to impracticality of preservation of sample.

8.1.4 Calibration

The oven thermometer and balance need to be properly calibrated regularly.

8.1.5 Procedure

a. Take a known volume of a well-mixed sample in a tarred dish ignited to constant weight (W_1)

b. Evaporate the sample to dryness at 103-105°C for 24hrs.

c. Cool in desiccator, weigh and record the reading (W_2)

d. Ignite the dish for 15-20 minutes in a muffle furnace maintained at 550±50°C.

e. Cool the dish partially in air until most of heat has been dissipated, and then transfer to a desiccator for final cooling in a dry atmosphere and record final weight (W_3).

f. The concentration is to be calculated in percent by weight.

8.1.6 Calculation

The total and the volatiles solids are expressed as:

Total solids, mg/L = $(W_2 - W_1)$ x 1000 / mL of sample

and

$(W_2 - W_3)$ x 1000 / mL of sample

Where W_1, W_2 and W_3 are recorded in mg.

8.1.7 Precision and Bias

The precision of the method is about ± 5%.

The result for total, volatile and fixed residues are subject to considerable error because of volatile compounds during evaporation of carbon dioxide and volatile during ignition, an also because of the presence of calcium oxide in the ash. Results for residues high in oil or grease content may be of questionable value because of the difficulty of drying to constant weight in a reasonable time. By definition, results will not include materials that are volatile under the conditions of the procedure.

In the interpretation of results, these possible sources of error must be recognized. The temperature at which the residue is dried has an important bearing on the results, because weight losses due to volatilisation of organic matter, mechanically occluded water, water of crystallization and gases fro, heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on the temperature and the period of heating. A choice of drying temperatures is provided and the analyst should be familiar with the probable effects of each. The analysis should be performed in duplicate to check the precision of method. Single laboratory duplicate analysis of 41 samples of water and wastewater showed standard deviation of difference of 6 mg/L.

8.2 Total dissolved solids

The filterable residue is the material that passes through a standard glass filter disk and remains after evaporation and drying at 180°C.

8.2.1 Apparatus and equipment

Evaporatory dish (porcelain) – 100/200mL

Drying oven – equipped with thermostatic control capable of maintaining the temperature within 2°C range.

Desiccator – provided with desiccants

Analytical balance – 200mg capacity of weighing to 0.1mg

Filter holder – Gooch crucible adapter or membrane filters

Suction flask – 500mL capacity

8.2.2 Sample collection, preservation and storage

Refer section 16.3. Begin analysis as soon as possible due to impractically of preservation of sample.

8.2.3 Procedure

Filter the well-mixed sample under vacuum through membrane filter or Gooch Crucible.

Transfer 100mL or more, depending upon the concentration of dissolved solids, in a weighed evaporating dish.

Evaporate to dryness on steam bath. Dry the evaporated sample for at least 1 hour in an oven at 180±2°C. Cool in a desiccator and weigh. Repeat the drying until constant weigh is obtained or weight loss is less than 0.5mg.

8.2.4 Calculation

mg/L total filtrable residue at 180°C = (A –B) x 1000 / C

Where:

A = weight of dried residue + dish

B = weight of dish

C = mL of filtrate used

8.2.5 Precision and Bias

The analysis should be performed in duplicate to check the precision of method. A synthetic unknown sample with 134 mg/L filterable residue analysed at different laboratories at the temperature of 103-105°C showed standard deviation of ± 13mg/L.

8.3 The water treatment

Coagulation in dynamic mode is carried at the experimental installation (fig. 6), consisting of switchers 1, 2, four mixers 3 and four containers for coagulation 4.

Two experiments are charged by using two different coagulants:

Experiment 1. Coagulation in dynamic mode by coagulant solution $FeCl_3$.

Experiment 2. Coagulation in dynamic mode by coagulant solution $AlCl_3$.

1. Connect the system to the power source.

2. To fill containers 4 by analyzed water (2 L of models per everyone).

3. To add into everyone container the solution of coagulant $FeCl_3$ with concentration 25 g/L. Into the 1^{st} – 2 ml, into the 2^{nd} – 4 ml, into the 3^{rd} – 8 ml, into the

4^{th} – 16 ml. To calculate the dose depending on volume and concentration of introduced coagulant.

4. To switch on the mixer (maximal rotation) during 2 min. (switcher is established 24 – 25 V).

5. To switch the mixer to ≈35 min^{-1} (switcher is established 14 V) and to leave for 20–30 min.

6. To switch the mixer to ≈25 min^{-1} (switcher is established 12 V) and to leave for 10 min.

7. To switch off mixers, carefully drain the layer of purified water from everyone container (not touching precipitate) into single bulbs and the hard dispersion particle and color analyses of purified water are charged in everyone bulb (the method will have been listed below).

8. Compared receiver data, the conclusion about the optimal coagulant dose is made.

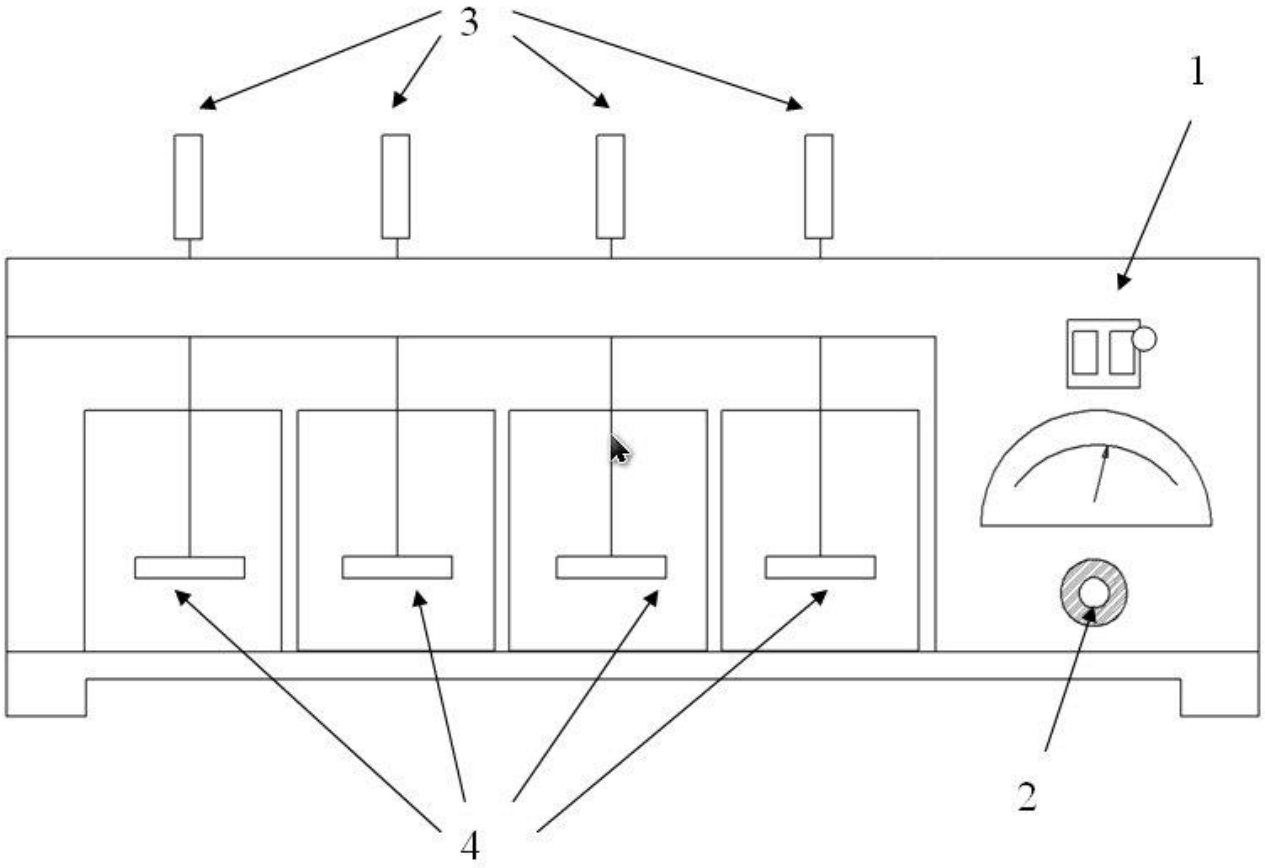

Figure 6. – The installation for coagulation in dynamic mode:

1, 2 – switchers; 3 – mixers; 4 – containers for coagulation.

Self-control questions:

1. Give the parameters, affecting on the efficiency of coagulation.
2. Characterize the influence of the hydrodynamic mode on formation the precipitate of water purification.
3. Name the origins of forming pollutions of colloidal dispersion in industrial waste waters and its characterization.
4. The kinds of coagulations, stages of formation and micelle structure.
5. Give the characterization of coagulants, using at water preparation.
6. What parameters does the choose of coagulant type depend on in water preparation technology from?
7. Explain the chemical scheme of coagulation.
8. Give the stages of coagulation purification of water facilities.

9 The research of influence of the main parameters on the affectivity of flowing coagulation

The aim of work: identification of patterns of the contact environment formation at the process of coagulation purification of water and determination of the optimal coagulant dose.

9.1. Analysis for Alkalinity

Alkalinity of sample can be estimated by titrating with standard sulphuric acid [3] at room temperature using phenolphthalein and methyl orange indicator. Titration to decolourisation of phenolphthalein indicator will indicate complete neutralization of OH^- and S of $CO3^{--}$, while sharp change from yellow to orange of methyl orange indicator will indicate total alkalinity (complete neutralisation of OH^-, CO_3^{--}, HCO_3^-).

9.1.2 Apparatus

a. Beakers: The size and form will depend upon the electrode and the size of the sample to be used for determination of alkalinity.

b. Pipettes (volumetric)

c. Flasks (volumetric): 1000mL, 200mL, 100mL

9.1.3 Reagents and standards

a. Standard H_2SO_4, 0.02 N: Prepare 0.1N H_2SO_4 by diluting 3mL conc. H_2SO_4 to 1000mL. Standardise it against standard 0.1N Na_2CO_3 solution. Dilute appropriate volume of H2SO4 to 1000mL to obtain standard 0.02 H_2SO

b. Phenolphthalein indicator: Dissolved 0.5g in 500mL 95% ethyl alcohol. Add 500mL distilled water. Add dropwise 0.02N NaOH till faint pink colour appears (pH 8.3).

c. Methyl orange indicator: Dissolve 0.5g and dilute to 1000mL with CO_2 free distilled water (pH 4.3-4.5).

OR

Bromo-cresol green indicator: Dissolve 0.1g bramocresol green, sodium salt, in 100mL distilled water (pH 4.5).

9.1.4 Calibration

Standardise the pH meter by using pH buffers. Follow the instructions given in the manual of pH meter.

9.1.5 Procedure

a. Take 25 or 50mL sample in a conical flask and add 2-3 drops of phenolphthalein indicator.

b. If pink colour develops titrate with 0.02N H_2SO_4 till disappears or pH is 8.3. Note the volume of H_2SO_4 required.

c. Add 2-3 drops of methyl orange to the same flask, and continue titration till yellow colour changes to orange. Note the volumes of H_2SO_4 required.

d. In case pink colour does not appear after addition of phenolphthalein continue as above.

e. Alternatively, perform potentiometric titration to preselected pH using appropriate volume of sample and titration assembly. Titrate to the end point pH without recording intermediate pH.

As the end point is approached make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant. The following pH values are suggested as equivalence points for corresponding alkalinity as mg $CaCO_3$/L (Table 11.5: I).

Table 3. End point pH values

End point pH		
Phenolphthalein Alkalinity		
Alkalinity, mg $CaCO_3$/L: 30 150 500 Silicates, phosphates known or suspended Industrial waste or complex system Routine or automated analyses	4.9 4.6 4.3 4.5 4.5 4.5	8.3 8.3 8.3 8.3 8.3 8.3

9.1.6 Calculations

Calculate total (T), phenolphthalein (P) alkalinity as follows:

P-alkalinity, as mg $CaCO_3$/L = A x 1000/mL sample

T-alkalinity, as mg $CaCO_3$/L = B x 1000/mL sample

In case H_2SO_4 is not 0.02 N apply the following formula:

Alkalinity, as mg $CaCO_3$/L = A/B x N x 50000 / mL of sample

Where,

A = mL of H_2SO_4 required to bring the pH to 8.3

B = mL of H_2SO_4 required to bring the pH to 4.5

N = normality of H_2SO_4

Once, the phenolphthalein and total alkalinities are determined, three types of alkalinities, i.e. hydroxide, carbonate and bicarbonate are easily calculated from the table given as under:

Table 4. Type of alkalinity

Values of P and T	Type of Alkalinity		
	OH^-	CO_3^{--}	HCO_3^-
P = O	0	0	T
P<1/2T	0	2P	T-2P
P = 1/2T	0	2P	0
P>1/2T	2P-T	2(T-P)	0
P = T	T	0	0

Once carbonate and bicarbonate alkalinities are known, then their conversions to milligrams CO_3^{--} or HCO_3^-/L are possible.

mg CO_3^{--}/L = Carbonate alkalinity mg $CaCO_3$/L x 0.6

mg HCO_3 = Bicarbonate alkalinity mg $CaCO_3$/L x 1.22

from above, molar concentration may be obtained as follows:

$[CO_3^{--}]$ = mg/L CO_3 / 60000

$[HCO_3^{-}]$ = mg/L HCO_3^{-} / 61000.

9.2 Analysis for Hardness in water

Water hardness is a traditional measure of the capacity of water to precipitate soap. Hardness of water is not a specific constituent but is a variable and complex mixture of cations and anions. It is caused by dissolved polyvalent metallic ions. In fresh water, the principal hardness causing ions are calcium and magnesium which precipitate soap. Other polyvalent cations also may precipitate soap, but often are in complex form, frequently with organic constituents, and their role in water hardness may be minimal and difficult to define. Total hardness is defined as the sum of the calcium and magnesium concentration, both expressed as $CaCO_3$, in mg/L. The degree of hardness of drinking water has been classified in terms of the equivalent $CaCO_3$ concentration as follows:

Soft 0-60 mg/L

Medium 60-120mg/L

Hard 120-180mg/L

Very hard >180mg/L

Although hardness is caused by cation, it may also be discussed in terms of carbonate (temporary) and non-carbonate (permanent) hardness. Carbonate hardness refers to the amount of carbonates and bicarbonates in solution that can be removed or precipitated by boiling. This type of hardness is responsible for the deposition of scale in hot water pipes and kettles. When total hardness is numerically greater then that of total alkalinity expressed as $CaCO_3$, the amount of hardness equivalent to alkalinity is called carbonate hardness[1]. When the hardness is numerically equal to less than total alkalinity, all hardness is carbonate hardness. The amount of hardness in excess of total alkalinity expressed as $CaCO_3$ is non-carbonate hardness. Non-carbonate hardness is caused by the association of the hardness-causing cation with sulphate, chloride or nitrate and is

referred to as “permanent hardness”. This type of hardness cannot be removed by boiling.

Public acceptability of the degree may vary considerably from community depending on local conditions, and the association. The taste threshold for magnesium is less than that for cation.

9.2.1 Principle

Hardness is determined by the EDTA method in alkaline condition [3]; EDTA and its sodium salts from a soluble chelated complex with certain metal ions. Calcium and Magnesium ions develop wine red colour with Eriochrome black T in aqueous solution at pH 10.0 ± 0.1. When EDTA is added as a titrant, Calcium and Magnesium divalent ions get complexed resulting in sharp change from wine red to blue which indicates end-point of the titration. Magnesium ion must be present to yield satisfactory point of the titration. Hence, a small amount of complexometically neutral magnesium salt of EDTA is added to the buffer. The sharpness of the end point increases with increasing pH. However, the specified pH of 10.0 ± 0.1 is a satisfactory compromise. At a higher pH i.e. at about 12.0 Mg^{++} ions precipitate and only Ca^{++} ions remain in solution. At this pH murexide (ammonium purpurate) indicator forms a pink colour with Ca^{++}. When EDTA is added Ca^{++} gets complexed resulting in a change from pink to purple which indicates end point of the reaction. To minimise the tendency towards $CaCO_3^-$ precipitation limit the duration of titration period to 5 minutes.

9.2.2 Apparatus

a. Conical flasks 100mL

b. Burette

c. Pipette

d. Spatula

9.2.3 Reagents and standards

a. Buffer solution: Dissolve 16.9 g NH_4Cl in 143mL NH_4OH. Add 1.25 g magnesium salt of EDTA to obtain sharp change in colour of indicator and dilute to 250mL. If magnesium salt of EDTA (AR grade) and 780 mg $MgSO_4.7H_2O$ or 644 mg

$MgCl_2.6H_2O$ in 50mL distilled water. Add this to above solution of NH_4Cl in NH_4OH and dilute to 25

b. Inhibitor: Dissolve 4.5g hydroxylamine hydrochloride in 100mL 95% ethyl alcohol or isopropyl alcohol.

or

Add 250mg NaCN in powder form to a sample adjusted to a pH 6.0 or above. Add sufficient buffer to adjust to pH 10.0±0.1 (NaCN is extremely poisonous. Take extra precautions in it use).

or

Dissolve 5.0g sodium nonahydrate ($Na_2S{\cdot}9H_2O$) or 3.7g $Na_2S{\cdot}5H_2O$ in 100mL distilled water. Exclude air with a tightly fitting rubber stopper. This inhibitor deteriorates through air oxidation.

or

MgCDTA: Add 250mg per 100mL sample magnesium salt of 1,2-cyclohexane-diamine tetra acetic acid and dissolve completely before adding buffer solution. Use this complexing agent to avoid using toxic or odorous inhibitors when interfering substances are present in concentration that affect end point but will not contribute significantly to hardness value.

c. Eriochrome black T indicator: Mix 0.5g dye with 100g NaCl to prepare dry powder.

d. Murexide indicator: Prepare a ground mixture of 200mg of murexide with 100g of solid NaCl.

e. Sodium hydroxide 2N: Dissolve 80g NaOH and dilute to 1000mL.

f. Standard EDTA solution 0.01 M: Dissolve 3.723 g EDTA sodium salt and dilute to 100mL. Standardise against standard Calcium solution 1mL = 1 mg $CaCO_3$.

g. Standard calcium solution: Weigh accurately 1g $CaCO_3$ (AR grade) and transfer to 250mL conical flask. Place funnel in the neck of a flask and add 1+1 HCl till $CaCO_3$ dissolves completely. Add 200mL distilled water and boil for 20-30 minutes to expel CO_2. Cool and add few drops of methyl red indictor. Add 8N NH_4OH drop-wise till intermediate orange colour develops. Dilute to 1000mL to obtain 1mL = 1mg $CaCO_3$.

9.2.4 Sample collection, preservation and storage

The procedure is given in detail in collection preservation and storage of the sample.

9.2.5 Calibration

The EDTA solution needs be standardize against standard calcium solution such that the strength of EDTA will be 1mL = 1mg as $CaCO_3$.

9.2.6 Procedure

Total hardness

a. Take 25 or 50mL well mixed sample in porcelain dish or conical flask.

b. Add 1-2mL buffer solution followed by 1mL inhibitor.

c. Add a pinch of Eriochrome black T and titrate with standard EDTA (0.01M) till wine red colour changes to blue, note down the volume of EDTA required (A).

d. Run a reagent blank. Note the volume of EDTA (B).

e. Calculate volume of EDTA required by sample, C = (A-B).

f. For natural waters of low hardness, take a larger sample volume, i.e. 100-1000mL for titration and add proportionately larger amounts of buffer, inhibitor and indicator. Add standard EDTA titrant slowly from a micro burette and run a blank using redistilled, deionised water of the same volume as sample. Apply blank correction for computing the results.

Calcium hardness

a. Take 25 or 50mL sample in a porcelain dish.

b. Add 1mL NaOH to raise pH to 12.0 and a pinch of Murexide indicator.

c. Titrate immediately with EDTA till pink colour changes to purple.

Note the volume of EDTA required (A^1).

d. Run a reagent blank. Note the mL of EDTA required (B^1) and keep it aside to compare end points of sample titrations.

e. Calculate the volume of EDTA required by sample, $C^1 = A^1-B^1$.

f. Standardise the EDTA (0.1M) solution following the procedure of calcium hardness from 1 to 4, using standard calcium solution.

Titrations are best conducted at or near normal room temperatures. The colour change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition presents a problem in hot water.

The pH specified in the recommended procedure may result in $CaCO_3$

Titrations are best conducted at or near normal room temperatures. The colour change becomes impractically slow as the sample approaches freezing temperature. Indicator decomposition presents a problem in hot water.

The pH specified in the recommended procedure may result in $CaCO_3$ precipitation. Although the titrant can redissolve such precipitates slowly, a drafting end point often will yield low results. A time of 5 min of the overall procedure minimises the tendency for to $CaCO_3$ precipitate.

Dilute sample with distilled water to reduce $CaCO_3$ concentration. If precipitation occurs at the dilution of 1+1, use following modifications because too small a volume contributes a systematic error due to the burette-reading error.

If the approximate hardness is known or is determined by a preliminary titration, add 90% or more titrant to sample before adjusting pH with buffer.

9.2.7 Calculation

a. Total hardness as $CaCO_3$ mg/L = C x D x 1000 / mL sample

where, C = volume of EDTA required by sample

D = mg $CaCO_3$ equivalent to 1mL EDTA titrant

b. Calcium hardness $CaCO_3$ as mg/L = C1 x D x 1000 / mL sample

where C^1 = volume of EDTA used by sample

D = mg $CaCO_3$ equivalent to 1mL EDTA titrant

c. Magnesium hardness = Total hardness as $CaCO_3$,

mg/L – Calcium hardness as $CaCO_3$, mg/L

d. Alkaline (Carbonate) hardness and non-alkaline (non-carbonate) hardness

These types of hardness can be calculated from total hardness and total alkalinity as follows:

i. If total hardness as $CaCO_3$ > total alkalinity as $CaCO_3$

Then, a. Alkaline hardness = Total alkalinity

b. Non-alkaline hardness = Total hardness – Total alkalinity

ii If total hardness as $CaCO_3$ < total alkalinity as $CaCO_3$

Then, a. Alkaline hardness = Total hardness

b. Nonalkaline hardness = Nil

9.2.8 Precision and Bias

Run a blank to check the analyte contamination. Analyse the sample in duplicate to see the precision of method. A synthetic sample containing 610 mg/L total hardness, contributed by 108 mg/L calculate and 82 mg/L showed 2.9% standard deviation and 0.8% relative error, when analysed by 56 different laboratories.

9.2.9 Interferences

Some metal ions interfere by causing fading or indistinct end points or by stoichiometric of EDTA but can be reduced by addition of inhibitors. Suspended or colloidal organic matter may also interfere with the end point. This interference can be eliminated by evaporating 50mL sample to dryness on a steam bath and then heating in a muffle furnace at 550єC. Residue may be dissolved in 20mL of 1N hydrochloric acid and on neutralization to pH 7 with 1N sodium hydroxide, volume be made to 50mL with distilled water. Run a reagent blank following the same procedure.

9.3 The water treatment

The investigation of flowing coagulation is carried at the experimental installation (fig. 5).

The chemical analysis for the determination of content of suspended particles; hardness, alkalinity and pH of the environment are determined in chemical samples of initial water, water after lighter and after mechanic filter.

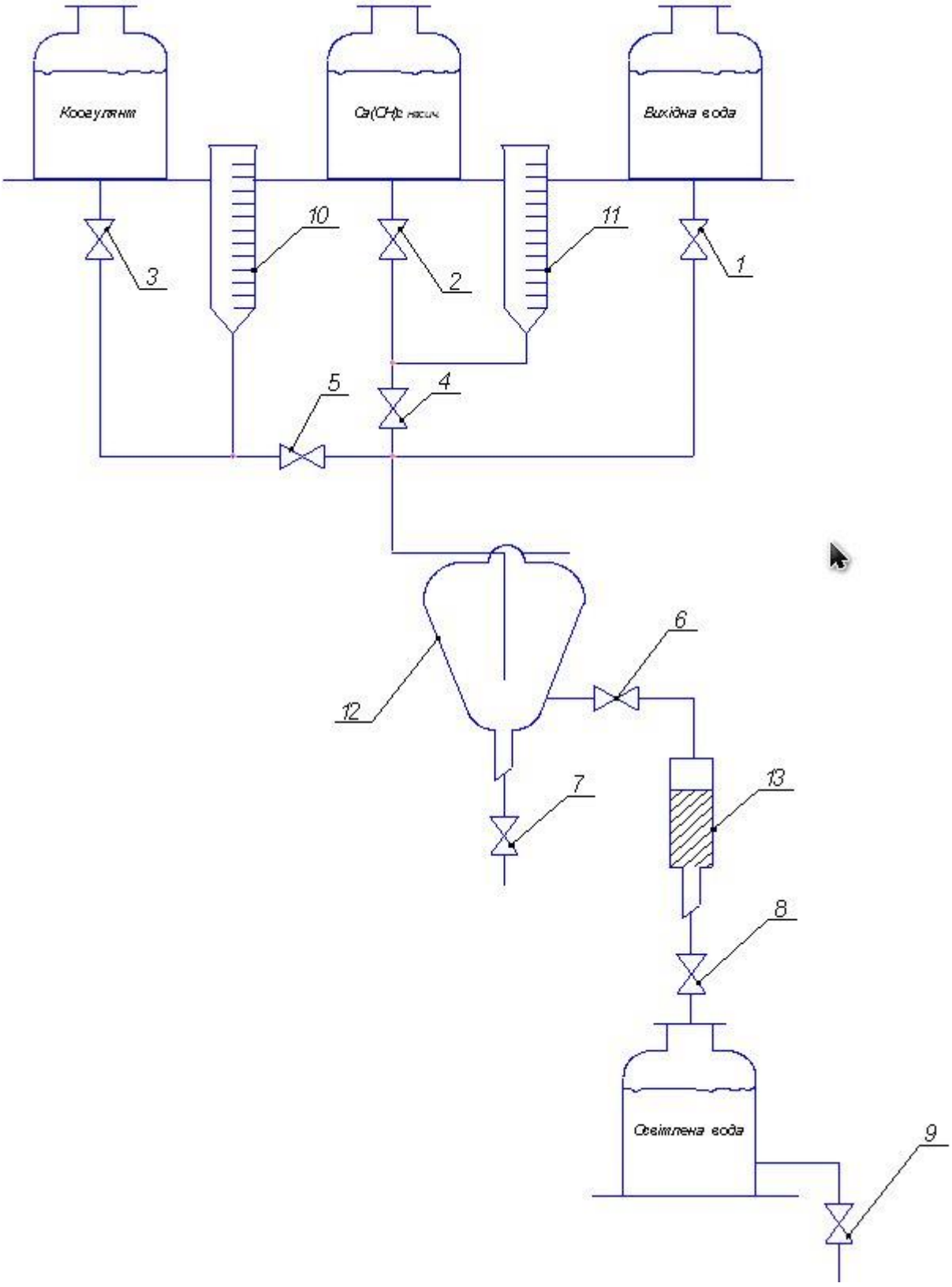

Figure 5. The scheme of experimental installation of coagulation with liming: 1 – 9 – taps 10, 11 – burettes; 12 - lighter; 13 – coal filter.

The task

For charging the coagulation it's necessary to check up the hermetically of the installation (fig. 5) and to prepare it to work by the following method:

1. The content of suspended particles, total hardness and pH of water are determined in the model (by the methods will have been presented below).
2. To determine the necessary quantity of coagulant and lime milk for coagulation-lightening. Coagulant and lime milk doses are given by teacher.
3. To close all taps at the installation.
4. By the tap 3 to fill the burette 10 by necessary volume of coagulant.
5. By the tap 2 to fill burette 11 by solution $Ca(OH)_2$ with concentration 0,04 mole/L.
6. To open the tap 1 for innings of initial water.
7. To open the tap 4 for innings saturated solution $Ca(OH)_2$ for mixing with initial water (tap 2 closed).
8. To open the tap 5 for innings the coagulant for mixing with initial water (tap 1 closed).
9. At the process of work, the sample of total hardness of water and content of suspended particles is charged by presented methods.
10. During the coagulation the taps 6 of heat water innings into the anthracite filter and the tap 8 of water innings into the tank of lightened water are opened.
11. From the tank of lightened water, the samples for the determination of suspended substances, total hardness and pH are selected after the coagulation with liming.

Experimental results

Water after mechanic filters	Water after lighter	Initial water	Indicators
			Muddy, mg/L
			Total water hardness, mmole-eq./L
			Alkalinity, mmole/L
			pH

Self-control question

1. Give the conditions (modes) of formation of the contact environment in suspended state.
2. How does the characteristic of treated water effect on the affectivity of process?
3. What conditions does the choose of coagulant type depend on from?
4. The comparison characteristic of coagulants based on iron and alumina compounds.
5. Give the types of lighters and principles of its action.
6. Characterize the backfilling of filters, using at water preparation technology.
7. The types of lightening filters and principles of its working.

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