

#18 Analysis of Water (Chlorine, Phosphorus, Fluoride, and Color)

Purpose:

The purpose of this experiment is to test water samples for the presence of chlorine, phosphorus, fluoride and color.

Introduction:

The concentration unit of mg/L of a species is mg per 1,000,000 mg water. So mg/L is numerically equal to parts per million, ppm. It is ppm that the Philadelphia Water Department uses. The water kits include reagents in foil packets, along with a color comparator that measures colors produced when the testing reagents react with species in water. The reagent makes a colored compound with the chemical being tested for. A brief description of how this works is given below.

Total Chlorine

There are two kinds of chlorine, *free* and *combined*.

Free chlorine is Cl₂ itself, or hypochlorous acid, HClO (or hypochlorite ion, ClO⁻) which forms when Cl₂ is added to water:



Combined chlorine is present in the N compounds, NH₂Cl, NHCl₂ and NCl₃.

Total chlorine includes both free and combined chlorine.

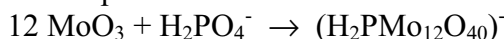
The reagent packet for total chlorine contains a colorless organic compound abbreviated DPD and potassium iodide, KI. The N-Cl compounds first react with KI to produce iodine, I₂. The DPD reagent then measures both free and combined Cl as follows:



The more intense the red color, the more total chlorine is present.

Phosphate Test

In this analysis, any orthophosphate in the water reacts with molybdate in acid solution to form a yellow phosphomolybdate complex.



The yellow complex, (H₂PMo₁₂O₄₀)⁻, then reacts with ascorbic acid producing a Mo compound with a characteristic blue color. The more intense the blue, the more phosphate there is.

Color

Water color is due to the presence of a yellowish compound called tannic acid or tannin which has the formula C₇₆H₅₂O₄₆. No reagent is added to the water for this test. The color on the disc is that of a platinum-cobalt complex which has a similar color to tannic acid. The color of the water sample is simply compared to the disc. One color unit is defined as the color that would be produced from 1 mg Pt/L water.

Note: “Apparent” color refers to a sample that is not filtered. Color measured after filtering is called “true” color. Since our water samples have no significant suspended matter, we will measure apparent color.

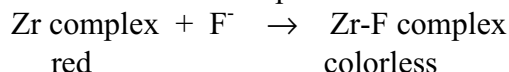
Fluoride

Fluoride is added to drinking water to prevent dental cavities. Excessive amounts of fluoride cause a discoloration of tooth enamel called “mottling.”

In the fluoride test a red compound is first produced by reacting zirconium oxychloride, $ZrOCl_2$, with a derivative of a dye called alizarin.



This time the fluoride ion forms a colorless complex with this compound.



Thus color disappears in this test, and a decrease in color intensity provides an accurate determination of fluoride concentration.

Apparatus

We have two different kinds of testing systems, the smaller Hach system, and the Orbeco-Hellige Aqua Tester which is larger and includes a bulb for easier viewing.

Procedure:

For all species, record result on data sheet and compare with the typical amount in Philadelphia drinking water, numbers provided to SIM by the Phila Water Department.

A. Phosphate Test (Hach System)

1. Rinse a color viewing tube several times with the water to be tested; fill to the 20-mL mark.
2. Add the contents of one PhosVer[®] 3 Phosphate Reagent Powder Pillow to the tube. Swirl to mix. Allow at least 2 but not more than 10 minutes for color development. If phosphate is present, a blue-violet color will develop.
3. Place the blue phosphates color disc in the comparator box. Then place the prepared water sample in the right opening of the comparator.
4. Fill another viewing tube to the 5-mL mark with some of the original untreated clear water sample, and place it in the left opening of the comparator.
5. Hold the comparator up to a light source such as the sky, a window, or a lamp and view through the two openings in front. Rotate the disc until a color match is obtained. Read the mg/L through the scale window.
6. To obtain the value as mg/L phosphate, divide the reading by 50. Record.

Total Chlorine Test (Hach System)

1. Rinse a color tube several times with the water to be tested; fill to the 5-mL mark.
2. Open one DPD Total Chlorine Reagent Powder Pillow. Add the contents of the pillow to the tube. Swirl to mix. Allow 3 to 6 minutes, but no longer than 6 minutes, for color development. If chlorine is present, a reddish-pink color will develop.

3. Place the total chlorine color disc (pink) in the comparator box. Then place the prepared water sample in the right opening of the comparator.
4. Fill another viewing tube to the 5-mL mark with some of the original untreated (clear) water sample, and place it in the left opening of the comparator.
5. Hold the comparator up to a light source such as the sky, a window, or a lamp and view through the two openings in front. Rotate the disc until a color match is obtained. Read the mg/L through the scale window.
6. The screen window reading is mg/L total chlorine

Color Test (Orbeco System)

1. Fill one of the two Nessler tubes to the marked line with the water to be tested. Insert the glass stopper in the tube.
2. Open the back cover of the AquaTester. Put the tube in the slot to the right.
3. Fill the second tube to the mark with distilled water. Insert the glass stopper in the tube. Place the second tube in the other slot next to the first inserted sample.
4. Close the apparatus and switch on the light bulb.
5. Insert the color testing disc under the light shield with the numbers facing upward.
6. Compare the color of the solutions in the two tubes by revolving the color disc so that the two colors match. Record the value that is obtained.

Fluoride Test (Orbeco System)

1. Measure 50mL of the sample and pour into a 150mL Erlenmeyer flask.
 2. Pipet 2.5 mL of the fluoride reagent and combine with the sample in the flask.
 3. Close the flask with the stopper and swirl.
 4. Let this solution stand for exactly 1 hour at a temperature between 23-27°C. In order to maintain the correct temperature, the flask can be placed in a large beaker containing a mixture of hot and cold tap water using a thermometer to monitor the temperature.
 5. Fill one of the Nessler tubes to the mark with the treated sample and insert glass stopper. Place the sample in the right-hand slot.
 6. Fill the second Nessler tube with an untreated sample. Insert the stopper, and insert this tube in the left-hand slot.
 7. Close the cover and switch on the light bulb.
 8. Place the fluoride color disc with the numbers facing up underneath the light shield.
 9. Compare the color of the solutions in the two tubes by revolving the color disc so that the two colors match. Record the value that is obtained.
- Note:* Make the color comparison within 5 minutes after the 1-hr waiting period.

Data and Results (Water-Testing)

Name(s) _____

species	Color of Solution	mg/L on scale window	mg/L * Phosphate	ppm measured	ppm typical
P					
Cl ⁻			---		
F ⁻			---		
Color			---		

Questions:

1. The color disk for fluoride reads from 0 to 1.6 ppm fluoride. Suppose your sample has a concentration of fluoride that is greater than 1.6 ppm. How could you modify the procedure to analyze this sample?
 2. What change in the procedure for color determination would allow you to measure true color?
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Instructor's Guide

Water Testing: P, Cl, F, color

species	Color of Solution	mg/L on scale window	mg/L Phosphate	ppm/units measured	ppm/units typical
P	<i>light blue</i>	<i>13.5</i>	<i>0.27*</i>	<i>0.27</i>	<i>0.3</i>
Cl ⁻	<i>pink</i>	<i>1.1</i>	<i>---</i>	<i>1.1</i>	<i>1.1 – 1.2</i>
F ⁻	<i>yellow-green</i>	<i>1.0</i>	<i>---</i>	<i>1.00</i>	<i>1.00</i>
Color	<i>clear</i>	<i>0</i>	<i>---</i>	<i>0</i>	<i>0.0 - 5.0</i>

* Divide scale window reading by 50.

Questions:

1. The color disk for fluoride reads from 0 to 1.6 ppm fluoride. Suppose your sample has a concentration of fluoride that is greater than 1.6 ppm. How could you modify the procedure to analyze this sample?
2. What change in the procedure for color determination would allow you to measure true color?

1. Dilute the sample with distilled water, then multiply the result by the dilution factor. For example, if 5 mL sample is diluted to 50 mL, multiply the result by 10.

2. Filter the sample first.

Instructor's Guide

Water Testing: P, Cl, F, color

Time: 1 hr 15 min (significantly shorter if Fluoride test is omitted)

Equipment and Materials per groups

Items	Number	Comment
comparator boxes	1	
viewing tubes	2	
Hach phosphate reagent powder pillows	1 pack per class	
Hach total chlorine reagent powder pillows	1 pack per class	
Fluoride reagent*	2.5 mL	
Hach phosphate color disk	1	
Hach total chlorine color disk	1	
Wash bottles	1	Distilled water
Aqua Testers	1	With bulbs & light shields
Nessler Tubes	2	With plungers
O-H color testing disk	1	
O-H fluoride color disk	1	
125 mL Erlenmeyer flasks	1	
100 mL graduated cylinder	1	
stopper	1	
5 mL Mohr pipette	1	
timers	1	
600 mL beakers	1	
thermometers	1	
Sample water		From school tap
Safety glasses	1 per student	
Rubber gloves	1 box per class	

*Preparation of Fluoride Reagent (Orbeco System)

1. Measure 5 mL Zirconium Oxychloride (Cat. No. R-487) into a 125-mL Erlenmeyer Flask using a Mohr Pipette (Cat. No. 2025).
2. Rinse the pipette, shake out excess water, and add 5 mL Sodium Alizarin Monosulfonate (Cat. No. R-445). Mix.
3. Measure 90 mL Acid Diluting Solution (Cat. No. R-379) in a 100-mL graduated cylinder and add to the flask. Stopper and mix immediately.
ALLOW TO STAND ONE HOUR BEFORE USE.

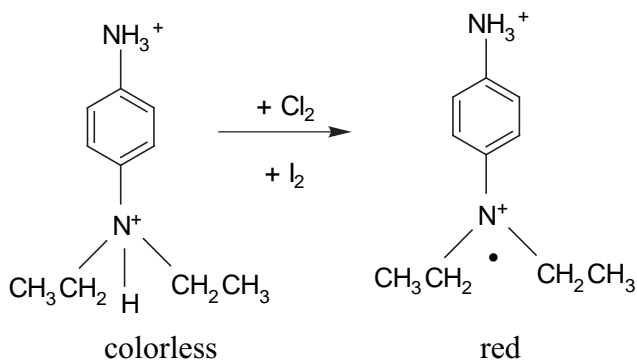
(Fluoride reagent may be used for 6 to 8 weeks if kept refrigerated, and remains stable about 10 days at room temperature. The three solutions used to prepare the fluoride reagent are stable for at least 8 months.)

Ideas/ Information

More on the chemistry of the tests is given below.

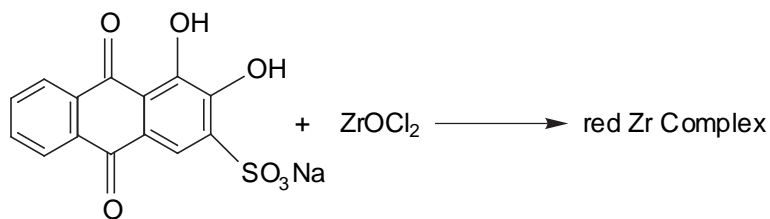
1. Total Chlorine

DPD used in the chlorine test is N,N-diethyl-*p*-phenylenediamine. (The amine groups are protonated, NH_3^+ not NH_2 , under the conditions of this test.) The red species forms upon oxidation with Cl_2 (HClO or ClO^-) or with I_2 liberated from reaction of KI with the chloramines (NH_2Cl , NHCl_2 , NCl_3). The equation is not balanced.



2. Fluoride

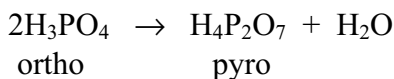
The fluoride reagent is made by combining ZrOCl_2 with sodium alizarin monosulfonate, alizarin red S, to produce a red zirconium dye complex:



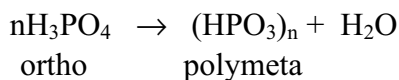
The red Zr complex reacts with fluoride ion to form a colorless complex.

3. Phosphate

Phosphorus is classified as orthophosphate, condensed phosphate (metaphosphate, polymetaphosphate or pyrophosphate). Condensed phosphates come from combinations of phosphoric acids with loss of water molecules. Two phosphoric acids produce pyrophosphoric acid:



Loss of water from 1 orthophosphoric acid gives metaphosphoric acid. Loss of a large number (n) molecules of orthophosphoric produces polymetaphosphoric acid:

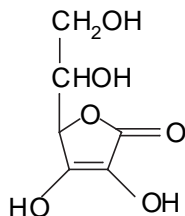


Formulas of the phosphoric acids are summarized in the table below.

Phosphoric acid name	Formula
Orthophosphoric	H_3PO_4
Pyrophosphoric	$\text{H}_4\text{P}_2\text{O}_7$
Metaphosphoric	HPO_3
Polymetaphosphoric	$(\text{HPO}_3)_n$

In this test “reactive phosphorus” is measured which includes orthophosphate and small amounts of condensed phosphate formed during the test itself. To measure other forms of phosphate, a pretreatment step would be needed.

The formula for the ascorbic acid, vitamin C, used to reduce the P-Mo complex to the blue Mo compound is:



Ascorbic is easily oxidized and is used in low range phosphorus tests. The structure of the blue P-Mo complex is not well understood.

4. Color

In this test there is no reagent added to the water. The color disc is used to match the tannic acid that causes water to be colored. One Pt-Co color unit, as chloro-platinate ion, is equivalent to a solution containing 1 mg Pt/L.