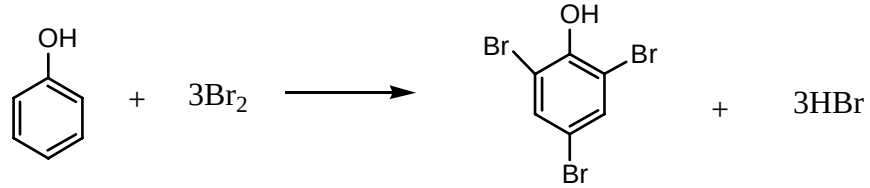
EXPERIMENT 6
ASSAY FOR PHENOL

Phenol is an important industrial chemical. In 1865 this compound, then known as carbolic acid, was first employed as a surgical antiseptic by Dr. Lister. (His name survives in the trade name "Listerine" and many of his patients survived too.) Phenol has current medical application as a mild disinfectant (for example in Chloroseptic, a sore throat spray) but its main use is in plastics manufacture.

You will no doubt recall from your study of Organic Chemistry that the hydroxy substituent strongly activates the phenyl ring and is an ortho-, para- director. Thus, phenol reacts quantitatively with three mol Br_2/mol phenol to form 2,4,6-tribromophenol.

Equation (1)



This reaction may be used as a basis for phenol analysis. However, the use of bromine in this determination presents some practical difficulties. Bromine is quite volatile even at room temperatures so that standardization and storage of bromine solutions is impractical. Instead, accurately known quantities of Br_2 may be introduced by reaction of BrO_3^- (bromate) with Br^- in acid media.

Equation (2)

$$BrO_3^- + 5\,Br^- + 6\,H^+ = 3\,Br_2 + 3\,H_2O$$

Pure $NaBrO_3$ and $KBrO_3$ are readily available and their solutions may be accurately standardized and are quite stable.

The present phenol analysis employs a measured quantity of BrO_3^- solution to generate an excess of Br_2 which reacts with phenol. The excess of Br_2 is determined by a technique called "**iodimetry**". After completion of the Br_2, phenol reaction, excess I^- is added to the mixture. This reacts with any Br_2 still present to form I_2.

Equation (3)

$$Br_2 + 2\,I^- = 2\,Br^- + I_2$$

The quantity of I_2 formed in this way is determined by titration with thiosulfate, $S_2O_3^{2-}$. The endpoint is signaled by the disappearance of the blue-black starch-iodine complex.

Equation (4)

$$2\,S_2O_3^{2-} + I_2 = S_4O_6^{2-} + 2\,I^-$$

In other words, we will introduce a known quantity of Br_2 to the phenol sample. Some will react with the phenol and some will remain in excess. We determine the amount of excess Br_2 by titration. (This is termed a "back titration".) By knowing both the total Br_2 added and the excess Br_2 remaining we may deduce the amount of Br_2 that reacted with phenol in the sample. From this we calculate the quantity of phenol initially present.

A sodium bromate solution of precisely known concentration will serve as a primary standard in this experiment. A suitable thiosulfate solution is available in the lab. The actual concentration of $Na_2S_2O_3$ reagent will be determined by "blank" titrations, ones made in the absence of the phenol sample. A description of the lab procedures and calculations follows.

NOTE: Thiosulfate solutions are subject to "infections" by certain bacteria - thiobaccillus baccillus - sulfur eating bacteria. The bacterial growth has the unfortunate property of changing the thiosulfate concentration with time. The thiosulfate solution has been "preserved" by addition of a few drops per liter of chloroform which puts the bugs to sleep.

You will add identical quantities of $NaBrO_3$ {(V_{BrO3}-[BrO_3^-]) mmol} to each of eight flasks. Four of these are blanks in which no phenol sample is present that will be used to standardize the thiosulfate solution. For these four solutions, addition of excess NaBr and H_2SO_4 produces $3V_{BrO3}$-[BrO_3^-] mmol of Br_2 (reaction 2). Then, subsequent addition of excess KI produces $3V_{BrO3}$-[BrO_3^-] mmol of I_2 (reaction 3). Because each mmol of I_2 reacts with exactly 2 mmol of $S_2O_3^{2-}$ (reaction 4) a quantity of $6V_{BrO3}$-[BrO_3^-] mmol of thiosulfate reagent is required to titrate each of the blank flasks. We call the volume of thiosulfate solution used in these titrations V_1^* so that the concentration of thiosulfate reagent is $6V_{BrO3}$-[BrO_3^-] /V_1^*. In summary, we find the concentration of the thiosulfate solution from the known values of the volume and concentration of BrO_3^- and the measured titration

volume, V_1^*.

The second set of four flasks will contain the same quantity of BrO_3^- as the first four along with the Chloroseptic sample. Addition of excess sodium bromide and sulfuric acid forms the same quantity of Br_2 in these flasks as in the first four. In this case some of the Br_2 reacts with phenol (reaction 1) and some remains in excess. The amount of excess Br_2 is determined by addition of iodide (KI) which reacts with Br_2 to form I_2 and this is subsequently titrated with portions of the same thiosulfate solution that was used earlier. The equivalence point of the titration is reached upon addition of V_2^* mL of $S_2O_3^{2-}$. The concentration of the thiosulfate solution was found is used to determine the mmoles of $S_2O_3^{2-}$ in v_2^*. Because 2 mmol of thiosulfate reacts with 1 mmol of I_2, the thiosulfate used here reacted with ½ $V_2^*(6V_{BrO3}\text{-}[BrO_3^-]/V_1^*)$ or $3V_2^*V_{BrO3}\text{-}[BrO_3^-]/V_1^*$ mmol of I_2. This amount of I_2 was produced by the presence of an equal number of millimoles of Br_2, that is, $3V_2^*V_{BrO3}\text{-}[BrO_3^-]/V_1^*$ mmol Br_2. This is the excess of Br_2 present in the flask after reaction with phenol. Recalling that a total of $3V_{BrO3}\text{-}[BrO_3^-]$ mmol Br_2 was produced in the sample flasks (just as in the blank flasks), the quantity of Br_2 that reacted with phenol is $\{3V_{BrO3}\text{-}[BrO_3^-] - 3V_2^*V_{BrO3}\text{-}[BrO_3^-]/V_1^*\}$. Because 3 mmol Br_2 react with 1 mmol of phenol, the quantity of phenol initially present in each flask is $\{V_{BrO3}\text{-}[BrO_3^-] - V_2^*V_{BrO3}\text{-}[BrO_3^-]/V_1^*\}$. Finally, the weight of phenol initially present in each titration flask is $94.11\{V_{BrO3}\text{-}[BrO_3^-] - V_2^*V_{BrO3}\text{-}[BrO_3^-]/V_1^*\}$ mg. The concentration of phenol in mg/mL units in the unknown sample solution is the weight of phenol divided by the known sample volume.

NOTE: The last paragraphs are a bit dense. Let's do it again, this time with numbers. Suppose that 15 mL of 0.010 F $NaBrO_3$ is added to each flask. When excess NaBr and H_2SO_4 are added, the $NaBrO_3$ reacts to form (15 x 0.150) mmol BrO_3^- x (3 mmol Br_2/1 mmol BrO_3^-) = 0.45 mmol Br_2. Some flasks (the blanks) contain no phenol and some (the samples) contain phenol.

the blanks: Excess KI is added to the blank flasks and this reacts with 0.45 mmol Br_2 to form 0.45 mmol I_2. The Br_2 is now gone. The 0.45 mmol of I_2 is titrated with {0.45 mmol I_2 x (2mmol $S_2O_3^{2-}$/1 mmol I_2) =} 0.90 mmol $S_2O_3^{2-}$. Suppose that 18.11 mL of $Na_2S_2O_3$ solution is used in this titration. Thus, the concentration of the thiosulfate solution is {0.90 mmol/18.11 mL =} 0.050 F. We now know the concentration of this thiosulfate solution and will use the same solution to titrate the sample mixtures later.

the samples: At the start the sample flasks contain the same amount of Br_2 that was formed in the blank flasks, 0.45 mmol. Some of this reacts with phenol in the sample but an excess of Br_2 remains after the phenol is used up. KI is added and reacts with the remaining Br_2. This forms I_2 which is then titrated with the thiosulfate solution. Suppose that 6.0 mL

of the 0.050 F $Na_2S_2O_3$ solution is required. This amount of the titrant contains {6.0 x 0.050 =} 0.30 mmol $S_2O_3^{2-}$. This amount of $S_2O_3^{2-}$ reacted with {0.30 mmol $S_2O_3^{2-}$ x (1 mmol I_2/2 mmol $S_2O_3^{2-}$) =} 0.15 mmol I_2. This amount of I_2 was present because 0.15 mmol Br_2 was in the flask when KI was added. In other words, the amount of Br_2 excess must have been 0.15 mmol.

At the start the flask contained 0.45 mmol of Br_2. After the reaction with phenol 0.15 mmol of Br_2 remained in excess. Consequently, {0.45 - 0.15 =} 0.30 mmol Br_2 must have reacted with the phenol and the amount of phenol present at the start was {0.30 mmol Br_2 x(1 mmol phenol/3 mmol Br_2) =} 0.10 mmol phenol. Because 1 mmol of phenol weighs 94.11 mg. the sample flask contained 9.4 mg of phenol at the start.

The present method is an analysis by difference, also called a "back titration". A certain known amount of a reagent is added to a sample. Some reacts with the sample and some remains in excess. The unknown quantity of sample is deduced from the difference between the quantity of reagent added and that remaining after reaction. In fact the present analysis is not specifically one for phenol but rather utilizes a property of phenol, namely that it reacts with Br_2. Other substances present in the sample that share this property will also react with Br_2 and lead to errors in the analysis. This constitutes a limitation to this method and in fact to all "difference" methods.

Certain other features of the procedure used here are listed below.

1. In principle one might titrate the phenol sample containing acid and Br^- directly with standardized BrO_3^- solution and somehow detect the first Br_2 excess. (There are appropriate indicators for this purpose.) Why not?

   The reaction between phenol and Br_2 is slow, so that a direct titration where reagent is added in small quantities would require a very long time. The present technique of adding an excess of reagent, allowing time for complete reaction, and then determining the excess by back titration is widely used with slow reactions.

2. The excess of Br_2 is not titrated directly with $S_2O_3^{2-}$. Instead excess KI is added to produce I_2. Why?

   Two moles of thiosulfate react cleanly and quantitatively with one mole of I_2 to form I^- and tetrathionate ($S_4O_6^{2-}$) as the only products. However, Br_2 (and most other oxidants) react

with thiosulfate to form a complex mixture of products with different stoichiometric proportions depending on circumstances of temperature, concentrations and the nature of other solution components. That is, there is no simple relationship between the number of moles of $S_2O_3^{2-}$ and the number of moles of Br_2 that might react with it.

3. The starch indicator is a solution containing about 1% soluble starch (amylose) in water along with a bit of disinfectant to prevent bacterial and mold growth. The starch molecule is a string of a few hundred glucose rings joined through oxygen atoms at the 1 - and 4 - ring positions. The starch forms intensely colored complexes with I_2, particularly in the presence of I^-. Before the endpoint in these titrations, when starch, I^-, and I_2 are all present, the complex between these species gives the solution an intense blue-black or purple-black color. When adequate $S_2O_3^{2-}$ has been added, the I_2 concentration drops essentially to zero so that no complex is possible and the color disappears. In this experiment none of the solution species present at the endpoint has a visible color. Consequently, the endpoint color change is from blue or purple-black to clear and colorless. The transition is very sharp.

IN THE LABORATORY

Obtain the reagents below from the laboratory stock:

$Na_2S_2O_3$ solution, approximately 0.05 F, about 200 mL
$NaBrO_3$ solution, about 0.01 F, 200 ml, **RECORD THE CONCENTRATION**
NaBr 15-20 g., a heaping tablespoon
KI, 1.5-2.0 g., a heaping tablespoon. Dissolve in about 50 mL of water in a small Erlenmeyer flask; cover with parafilm.
H_2SO_4, 1 F, 50 mL
Starch indicator solution, 30 mL
Chloroseptic throat spray
Cyclohexane

STORE THESE IN CLEARLY LABELED VESSELS.

In the procedure that follows you will make a sequence of additions to each reaction flask.

After making each addition record the appearance of the mixtures. For example: (1) The $NaBrO_3$ solution is clear and colorless. (2) Colorless solid NaBr is added and dissolved to form a clear colorless solution. (3) Clear colorless H_2SO_4 is added and the mixture formed a yellow color. etc.

1. Line up eight clean 250 mL Erlenmeyer flasks. Pipet 0.500 mL portions of the Chloroseptic Throat Spray into the first four. Into each of the eight flasks pipet 15.00 mL of bromate solution and add a roughly 2 g portion (about 1/3 teaspoon) of NaBr. Cover each flask with a layer of parafilm. Use a syringe to add about 5 mL of 1 F H_2SO_4 into the first flask **THROUGH** the parafilm covering. **IMMEDIATELY** cover the flask with an additional layer of parafilm to prevent loss of volatile Br_2. Repeat the addition of acid with each of the remaining flasks.
   Set the first four Chloroseptic containing flasks aside because the Br_2, phenol reaction requires about 15-30 minutes for completion.

2. Rinse and fill a 25 mL buret with thiosulfate solution. (Read the buret to 0.01 mL.) (Do not try to set 0.00 mL.)

3. Rinse the syringe with several portions of distilled water. Into each of the last four flasks (that do not contain phenol) add about 5 mL of the KI solution **THROUGH** the parafilm. Cover with another layer of parafilm and swirl for a minute or two to mix. Remove the parafilm from one of the KI containing flasks and titrate with thiosulfate. When the I_2 color begins to fade add 2 - 3 mL of starch indicator solution and titrate to the disappearance of the blue-black color. Repeat with the other KI containing flasks.

4. Use the syringe to add about 5 mL of KI solution into each of the four phenol containing flasks. Swirl for a minute or two. Remove the parafilm from the first flask and add about 2 mL of cyclohexane. Swirl to dissolve the precipitate of tribromophenol. Titrate with thiosulfate as above. Repeat with the remaining flasks. Check results with the instructor.

5. Dispose of the contents of the sample flasks (the ones containing cyclohexane, etc.) in the waste containers in the fume hoods.

6. Remember to record the exact concentration of bromate solution as well as your sample

number. CLEAN UP using a brush and soap on the flasks.

THE LAB REPORT

1. Concentration of the Thiosulfate Solution

Calculate:

a. the number of millimoles of BrO_3^- added to each flask;

b. the number of millimoles of Br_2 produced in each flask;

c. the number of millimoles of I_2 produced in the blank flasks;

d. the number of millimoles of $S_2O_3^{2-}$ that titrated I_2 in the blank flasks;

e. the average V_1^*, along with its standard deviation (s_e), standard error (s_m), and its 95 % CL.

f. the average V_2^*, along with its standard deviation (s_e), standard error (s_m), and its 95 % CL.

g. the % phenol (w/v) in the chlorseptic throat spray. Use the standard procedures outlined in the Introduction to Measurement (available on the course website) to propagate all errors and reports a reasonable error in the % phenol. You should used the 95 % CI of V_1^* and V_2^* in these calculations.

HINT: This is a bit tricky since the overall equation has terms that are multiplied and terms that are subtracted.

% phenol =

$100\{(94.11mg/mmol)(1g/1000mg)\{V_{BrO3-}[BrO_3^-] - V_2^* V_{BrO3-}[BrO_3^-]/V_1^*\}/V_{phenol}$ or

$X\% = 9.411\{AB - CAB/D\}/E$

Where these variables represent the following quantities (errors in these quantities are also given .

$V_{BrO3-} = A$	$s_A =$ 0.02 mL
$[BrO_3^-] = B$	$s_B =$ 0.0003 M
$V_2^* = C$	$s_C =$ 95 % CI for V_2^*
$V_1^* = D$	$s_D =$ 95 % CI for V_1^*
$V_{phenol} = E$	$s_E =$ 0.02 mL

You have to break the calculation of $s_{\%phenol}$ into separate steps. First apply the rule of

multiplication to the formula, (mmoles $BrO_3^-)_i$ = AB, to calculate $s_{(mmolesBrO3-)i}$ and to the formula, (mmoles $BrO_3)_{excess}$ = CAB/D, to calculate $s_{(mmoles\ BrO3)excess}$. Then, apply the subtraction rule to the formula, (mmoles $BrO_3^-)_{reacted}$ = {(mmoles $BrO_3^-)_i$ - (mmoles $BrO_3)_{ex}$, to calculate $s_{(moles\ BrO3-)reacted}$. Finally, apply the multiplication rule to the formula, % phenol = 9.411 (moles $BrO_3^-)_{reacted}/V_{phenol}$, to calculate $s_{\%phenol}$.

2. The present analysis relies on a determination of excess Br_2 present after reaction with phenol. Suppose that there is so much phenol present that there is no excess of Br_2.

a. How would this be visually apparent during the experiment? (You have seen certain colors and color changes at each stage of the procedure. The mixture of $NaBrO_3$, NaBr and phenol was clear and colorless, etc. What would you see <u>at each stage</u> if excess phenol were present?)

b. What is the maximum concentration of phenol (in mg/mL units) that could be analyzed by the present procedure?

c. Using the same bromate and thiosulfate solutions, how might the procedure be changed to allow analysis of a sample with a higher phenol concentration?

5. The Vohlhard method for chloride is a back titration procedure. A sample containing chloride is treated with an excess of $AgNO_3$ solution. Cl^- is precipitated as AgCl and excess Ag^+ remains in solution. $Fe(NO_3)_3$ is added as an indicator. The excess Ag^+ is determined by titration with potassium thiocyanate (KSCN). Addition of the thiocyanate titrant first forms an insoluble salt, AgSCN. The first excess of thiocyanate is detected by the appearance of the red $Fe(SCN)^{2+}$ complex.

A solution of KSCN is standardized against $AgNO_3$. It is found that 42.50 mL of the KSCN solution is required to titrate a 20.00 mL portion of 0.1210 <u>F</u> $AgNO_3$ to the $Fe(SCN)^{2+}$ endpoint.

A 0.750 gram sample of an organic compound containing chlorine is treated with 25.00 mL of the 0.1210 <u>F</u> $AgNO_3$. After a series of operations all of the chlorine originally present in the sample is converted to AgCl. The excess of silver is titrated with 10.80 mL of the KSCN solution above.

a. Calculate the concentration of the KSCN solution.

b. What percentage by weight of chlorine in mg was present in the organic sample?