PRELAB INFORMATION FOR "CHEMISTRY OF WHITE WINE"

Two periods have been allotted for this experiment, and there is a lot to accomplish, so it is important that you come to lab prepared, having read the entire experiment and completed the pre-lab questions below. On Day 1, you will determine the available and total SO_2 concentrations. On Day 2, you will measure the alcohol and acid content of the wine.

There are many ways to report concentration. In this lab you will encounter: molarity, M; percent by volume, (%v/v); percent by weight, (%w/w); and parts per million, ppm. Listed below are the definitions of the concentrations that may be unfamiliar to you. In percent by weight and percent by volume calculations, the units in the numerator and denominator must be the same. Consult your text for more information.

(%w/w) = (mass solute/mass of solution) x 100

(%v/v) = (volume solute/volume of solution) x 100

For solutions: ppm = mg solute/L of solution

Prelab Questions

On a separate sheet of paper, complete the following prelab questions **before** coming to lab. Show all of your work, report all answers to the correct number of significant figures, and include proper units. Check your calculations in questions 2, 3 and 4 with the answers provided below.

1. What chemical components of wine will you be measuring in this lab?

2. A 15.00 mL sample of white wine was analyzed for total SO_2 concentration using the procedure outlined in this experiment. In the titration 32.13 mL of 5.00×10^{-4} M iodine solution was required to reach the endpoint. Calculate the molar concentration of the total SO_2 in the wine.

3. Calculate the molarity, percent by volume, percent by weight, and parts per million of a solution that has 1.18×10^{2} mL of ethanol in a 2.0 L solution. The density of ethanol is 0.798 g/mL. Use the table on page 9 of the lab in order to determine the specific gravity of the solution. Consider specific gravity and density to be equivalent.

4. A sample of wine was diluted 1:10 and analyzed for alcohol content using a colorimeter. A calibration curve was created from a set of standard solutions, producing a plot of absorbance vs. percent alcohol. The calibration curve had a slope of 8.067×10^{-2} with an intercept of 6.027×10^{-3}. Keeping in mind that you diluted the wine sample by a factor of 10, what is the percent by volume of alcohol in your sample if the absorbance of your sample was 0.593?

Answers: (2) 0.001071 M SO_2
(3) 1.02 M; 5.9 % v/v; 4.748 % w/w, 4.708×10^{4} ppm
(4) 72.76 % v/v

Chemistry 123

THE CHEMISTRY OF WHITE WINE

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Western Washington University

LEARNING OBJECTIVES

The objectives of this experiment are to...

- measure both the free and total SO_2 concentrations of a variety of white wine.
- determine the ethanol content of a variety of white wine.
- determine the acidity and tartaric acid concentration of a variety of white wine.
- compare experimental results with typical data for bulk white wine of the variety tested.

BACKGROUND

The fermentation of fruit juice to yield alcoholic beverages is undoubtedly one of the oldest ways in which man has used chemistry to serve himself. Today, the manufacture of wines is a huge industry in which chemistry plays a central role.

The process of wine making begins with growing and harvesting the fruit (usually grapes). Next the juice, called must, is extracted from the grapes. The must is the reagent for the fermentation process. Fermentation is an oxidation carried out in an anaerobic (no oxygen) environment by microorganisms that grow and thrive by breaking down the sugars. Yeasts are the most common microorganisms used to carry out the fermentation process, but there are many other species, primarily bacteria, which can also cause fermentation.

The end products of yeast fermentation are carbon dioxide and ethyl alcohol (ethanol). Other types of fermentation yield lactic acid; alcohols such as methanol and 2,3-butanediol; carboxylic acids such as acetic, propanoic, butanoic, and heptanoic; and less common substances, including acetoin and diacetyl. In any case, yeast or bacteria carry out fermentation to produce energy for living, reproduction, and growth.

A simple representation of the chemical equation for fermentation is:

$$\text{Yeast} + C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + \text{energy}$$

where $C_6H_{12}O_6$ is the molecular formula for a sugar, fructose, and its many forms (isomers), including glucose and galactose.

The wine making process has been much refined over the centuries. There are many variables that come into play when producing wine, which include: the proper length of time to ferment the wine, the temperature at which the fermentation should be carried out, the length of time the wine should age, the kind of container in which the wine should age, the position in which it should age, the final alcohol content and the final sugar content.

In addition to general properties, certain wines have special characteristics. Champagne and other "sparkling" or bubbly wines undergo a second fermentation after being bottled. The CO_2 given off in this second fermentation is captured and, hence, is preserved as "sparkle". Some wines, notably the ports, Sherries, and Madeiras, have higher alcohol contents than the average table wine because brandy or some other distilled spirit with a higher alcohol content has been added. Some dessert wines are made from grapes which have been permitted to rot while still on the vine. The grapes are attacked by fungus, *Botrytis cinerea*, which drastically reduces the liquid content of the grape but leaves the amount of sugar unchanged, hence these wines tend to be very sweet and concentrated.

Commercial wine making today is a scientific process. All the steps of fermentation are rigidly controlled, and the final product is subject to numerous regulations as to alcohol content, sugar content, acidity, percent of each kind of grape which can be used in its production, amount of preservatives, etc. Thus producing wine is truly chemistry in action on many fronts.

EXPERIMENTAL OVERVIEW

In this experiment, you will analyze three components of wine, the sulfur dioxide concentration, the alcohol content and the tartaric acid content. On the first day of lab, you will complete the sulfur dioxide analysis, and on day two, you will do the alcohol and acid analyses.

Sulfur Dioxide Analysis

Sulfur dioxide, SO_2, is used commercially as a preservative in wines to protect the wine from bacteriological growth and subsequent infection. Sulfur dioxide is generated by the addition of potassium metabisulfite, $K_2S_2O_5$ to the slightly acidic must:

$$K_2S_2O_5 + H_2O \rightarrow 2KHSO_3$$

$$KHSO_3 + H_3O^+ \rightarrow SO_2 + 2H_2O + K^+$$

The preservative concentration is strictly regulated because the added sulfites and the SO_2 produced from the reaction can be harmful to certain people. Legal limits vary from country to country, from 200-450 mg/L. Much of the added SO_2 reacts with other components of wine to form bisulfite complexes leaving only about 10% (20-40 mg/L) free in solution to protect the product from spoilage.

In the laboratory, you will need to perform titrations in order to determine sulfur dioxide concentration of the wine. The *concentration of **free** SO_2* can be determined by the following reaction:

$$SO_2(aq) + I_2(aq) + 2H_2O(1) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$$

An aqueous solution of iodine is reddish-brown, whereas the products of the reaction are colorless. As iodine is added, the color of the wine will remain unchanged until all the sulfur dioxide is consumed. As soon as iodine is present in excess, the following reaction occurs:

$$I_2 + I^- \rightarrow I_3^-$$

The triiodide ion is slightly yellow. However, if starch is added, a dark blue-black starch-triiodide complex forms and serves as an endpoint indicator:

$$I_3^- + \text{starch} \rightarrow \text{blue complex}$$

To measure the ***total*** *concentration of SO_2*, sodium hydroxide is added to the wine to break down bisulfite complexes. Then it is acidified and titrated using the same technique and the same titration reaction as in the determination of the free SO_2. You can then compare the free and total concentrations of SO_2 in your wine sample.

Determination of Alcohol Content

Ethanol and certain other alcohols react with ammonium hexanitrate cerium(IV), $(NH_4)_2Ce(NO_3)_6$, to yield a corresponding carboxylic acid and a cerium(III) complex (compound). This reaction is depicted below.

$$\text{alcohol} + (NH_4)_2Ce(NO_3)_6 \rightarrow \text{red complex}$$

Since the reaction stoichiometry is 1:1 between alcohol and the red complex, the red complex concentration will be equal to the initial alcohol concentration of the solution. It is important to note that the cerium(III) complex is not stable for long periods of time, therefore timely measurements are important.

The colored species obeys Beer's Law, meaning that the absorbance of light by the colored substance is directly proportional to the concentration of the substance in solution:

$A = \varepsilon bC$ where A = absorbance (no units)
ε = molar absorptivity constant ($M^{-1}cm^{-1}$)
b = path length of cell (cm)
C = concentration (mol/L)

This direct proportionality will be used to determine the percent of alcohol in the wine. A Beer's Law plot of absorbance vs. concentration of the red complex allows direct determination of the quantity of alcohol oxidized by ammonium hexanitrate cerium(IV). By measuring the absorbance of the complex formed by the wine, the percent alcohol and concentration (*M*) can be determined from a computer-generated calibration graph.

Acid Content Analysis

The acidity of the wine will also be determined by titration. While the titration reaction is a little different from the reaction used in the sulfur dioxide analysis titration, the titration technique is the same, and the quantitative information obtained is similar. The acidity in wine is primarily due to tartaric acid, a dicarboxylic acid with the chemical formula:

HOOCCHOHCHOHCOO**H**

Tartaric acid, $H_2C_4H_4O_6$, is a weak diprotic acid with two acidic protons; these two acidic protons have been highlighted in the chemical formula above. Because tartaric acid has two acidic protons, *neutralization of each mole of this acid will require two moles of NaOH base*, with the neutralization reaction:

$$H_2C_4H_4O_6 + 2NaOH \rightarrow Na_2C_4H_4O_6 + 2H_2O$$

SAFETY PRECAUTIONS

Wear departmentally approved eye protection at all times in the laboratory. Follow all additional laboratory rules and regulations provided by your instructor. Know the location and proper use of all laboratory safety equipment (safety showers, eye washers, fire extinguishers, etc.). Dispose of all chemicals in the proper waste containers located in the Waste Hood.

A material safety data sheet (MSDS) for each chemical used in this experiment is located in a binder in the lab. You should be familiar with the hazards associated with each chemical, as well as the instructions on safe handling and appropriate disposal. Your instructor will be available to assist you in interpreting this information.

EXPERIMENTAL PROCEDURE

Select which variety of white wine you will analyze, and record the name and alcohol content in your lab notebook. Obtain a 200 mL sample of the wine in a clean, dry beaker. Next you will transfer your wine sample to a 500-mL poly bottle from your drawer for storage. Before pouring the wine into the bottle, clean the bottle and rinse it with wine. Pour a few milliliters of wine into the bottle, cap it, shake well, and dump the wine down the drain. Repeat two more times. Finally, pour the remaining wine into the bottle and label it with your name and the variety of wine. This will be your stock bottle of wine to use for the entire experiment. Be sure not to be wasteful.

This experiment requires the use of 10-mL measuring and volumetric pipets and a 50-mL buret. All volumetric glassware should be cleaned and rinsed before each use so that water drains to leave a uniform film (no drops). Before using, pipets must be rinsed with several small portions of the solution to be measured. Likewise, the buret should be rinsed with several small portions of the solution to be dispensed prior to filling.

Determining the Available and Total SO_2 Concentrations – to be done individually

Determining the Concentration of ***available (free) SO_2***

1. Obtain 250 mL of the standard iodine, I_2, solution. Record the exact concentration from the bottle label. Prepare your buret as described above, loading the buret with the I_2. Since I_2 is light sensitive, store the solution in the shade of your hood when not in use.
2. Using your 10-mL volumetric pipet, add 20.00 mL (2 x 10.00 mL) of wine into a 250-mL Erlenmeyer flask.
3. Add 4 mL of 6 M H_2SO_4 (using four additions with a plastic dropper filled to the 1-mL line) and 5 mL of starch solution (using five 1-mL additions from a plastic dropper).
4. Add 1.0 g of solid KI to the flask, using the top-loading balance, and swirl to dissolve.
5. Record the initial buret volume, and perform a quick titration with standard iodine solution to determine the approximate volume of I_2 needed to react with the SO_2 in the wine sample. As you add the I_2 titrant you will notice a temporary appearance of the dark blue-purple starch-triiodide complex - this is due to a localized excess and will disperse upon swirling. The end-point is somewhat difficult to determine – ultimately you should look for a *uniform* color change of your wine solution, which, when combined with the yellowish color of the wine itself will appear a faint peach color. After the titration, oxidation by air will occur and the color will fade and disappear within a few minutes, but DO NOT ADD MORE I_2.
6. Prepare and carefully titrate two more samples. Refill the buret between titrations and record the initial buret reading before titrating. The titration volumes of I_2 should be within 1.0 mL range. If they are not, consult your lab instructor about performing a third careful titration.
7. Using the data from the two most precisely titrated samples, calculate the mean volume of I_2 solution used. With the mean volume, calculate the *free SO_2 concentration* in units of **both** molarity and ppm (parts per million or mg solute/L solution).

Determining the Concentration of ***total (free and combined) SO_2***

1. Use your 10-mL volumetric pipet to add 10.00 mL of wine to a 250-mL Erlenmeyer flask. Add 5.0 mL of 1 M NaOH. Swirl the flask and wait 15 minutes.
2. As above, add 4 mL of 6 M H_2SO_4, 5 mL starch indicator, and 1.0 g of KI.
3. Refill the buret with I_2 solution, record the initial volume, and quickly titrate to the same end point as in the titration of free SO_2 above.
4. Prepare and carefully titrate two more samples. As above, the titration volumes of I_2 should be within a 1.0 mL range. Perform a third titration if needed.
5. Using the data from the two most precisely titrated samples, calculate the mean titration volume of I_2 solution. Then calculate the *total SO_2 concentration* in units of **both** molarity and ppm.

Measuring the Alcohol (ethanol) Content of Wine – to be done in pairs

You and your partner will prepare a set of standard solutions with **known** alcohol concentrations, in this case concentration in percent volume (% v/v). You can each then "compare" your wine samples in order to determine the alcohol content.

For this portion of the experiment, you will use LabPro interface and software to measure your solution absorbances. Obtain a colorimeter and a cuvette. Connect the colorimeter to channel CH1

on the side of the LabPro interface unit. Turn on your computer, and open Logger Pro 3.6.1 by double-clicking on the Logger Pro icon on the computer desktop. Open the experiment file by clicking **File**, *Open*, opening the *Chemistry with Vernier* folder and selecting ***11B Beer's Law (Percent).cmbl***. Use the arrow keys on the colorimeter to select 565 nm, and let the system stabilize at this wavelength while your prepare your solutions.

Sample	Stock Ethanol Soln (mL)	DI H_2O (mL)	Final Ethanol Conc. (% v/v)
A	0.00	10.00	0.00
B	1.00	9.00	1.00
C	2.00	8.00	2.00
D	3.00	7.00	3.00
E	4.00	6.00	4.00
F	5.00	5.00	5.00
G	6.00	4.00	6.00
U 1	*2.00 mL wine (partner 1)*	8.00	Unknown
U 2	*2.00 mL wine (partner 2)*	8.00	Unknown

Preparing Dilutions of the Stock Ethanol Solution (10% aqueous v/v)

1. Prepare nine clean, dry, labeled snap-cap vials to receive the solutions listed in the table above.
2. Clean and rinse a 10-mL measuring pipet to deliver the volumes of ethanol stock solution shown in the table above. The pipet must be rinsed with several small portions of ethanol stock solution before making a transfer. Deliver each volume of ethanol into the appropriate vial. Note: Samples U1 and U2 do not contain stock ethanol solution.
3. Use a second cleaned and rinsed 10-mL measuring pipet to deliver each volume of DI H_2O shown in the table above into the appropriate vial, including samples U1 and U2.
4. To prepare samples U1 and U2, each partner should clean a 10-mL measuring pipet, rinse it with several small portions of your wine sample, and pipet 2.00 mL of wine into the vial, which should contain 8.00 mL of DI H_2O.
5. Secure the caps on all nine vials, and shake well to mix.

Preparing Standard Solutions of Ethanol

1. With a plastic calibrated 1-mL syringe, carefully transfer 1.00 mL of each dilution that you prepared into another set of nine clean, dry, labeled snap-cap vials. *Be sure to rinse the syringe with several small portions of the solution you will be transferring.* Start with the most dilute solution, sample A. After measuring sample A, rinse the pipet with sample B before transferring 1.00 mL of B, etc.
2. Add 5.0 mL of ammonium hexanitrate cerium(IV), $NH_4Ce(NO_3)_6$, color reagent to each vial in this second set. Secure the snap-caps, and shake to mix well. Keep the caps on to protect the contents. Let the color develop for 5 minutes. Complete steps 1-2 below while you wait.

Measuring Solution Absorbances

1. The cuvette will serve as the sample holder for the colorimeter measurements. Look closely at the cuvette and note that there are only two clear faces. The cuvette must be aligned in the colorimeter so that the beam of light passes through the clear faces. This is done by lining up one of the clear sides of the cuvette with the arrow at the top of the cuvette slot in the colorimeter. Always use the lid with the cuvette to prevent spillage inside the colorimeter.

2. Before measuring your solution absorbances, you must calibrate the colorimeter with a sample of DI H_2O, which has an absorbance value of zero. Fill the cuvette about three-fourths full with DI H_2O, making sure there are no bubbles, wipe the clear outside faces with a KimWipe, insert the cuvette into the colorimeter, and close the colorimeter door. Press the ***Cal*** button in the center of the colorimeter until the red light begins to flash, and then release the button. The light will stop flashing when the calibration is finished.

3. Next measure the absorbance of each of the standard solutions, samples A-G, in order of increasing concentration. Before filling the cuvette with a new solution, be sure to rinse it several times with small portions of the new solution and wipe the clear faces with a KimWipe prior to inserting it into the colorimeter. Be sure to insert the cuvette in the same orientation each time. **Use the cuvette lid and do not spill inside the colorimeter!**

   With the first sample loaded, begin data collection by clicking the green *Collect* icon from the toolbar at the top of the screen. When the absorbance reading stabilizes, click the *Keep* icon to capture the data point. In the Events window, enter the percent ethanol concentration and click "OK". As each sample is loaded into the colorimeter, click *Keep* once the absorbance reading has stabilized and enter the appropriate percent ethanol concentration.

4. After you have measured each standard solution click the *Stop* icon on the toolbar.

5. Rescale the Beer's Law plot by clicking the *Autoscale* icon on the toolbar.

6. Next perform a linear regression (first-order curve fit) to generate an equation relating absorbance to ethanol concentration. Do this by clicking the *R = Linear Fit* icon on the toolbar. The line with the best fit to your data will appear on the graph along with an information box with the equation for the line and the correlation coefficient, which indicates how well your data fits the line. (The correlation coefficient should be 0.99 or greater. If it is less than 0.99 then the solutions corresponding to the outlying points should be remade and re-measured before proceeding.)

7. Click the green *Collect* icon again and choose 'Append to Latest' when prompted.

8. Load your wine samples into the colorimeter one at a time and measure their absorbance by capturing the live reading in the lower left hand corner of the screen and recording it directly into your lab notebook - *do not click 'Keep'*.

9. Print your data table and graph, with the linear regression information displayed, by selecting **File**, *Print Data Table* and **File**, *Print Graph*.

10. After printing, close Logger Pro *without* saving changes to the experiment file.

11. **When cleaning up, be sure to remove the cuvette from the colorimeter and clean it out before returning the colorimeter and cuvette!!**

Data Analysis

Complete acid content experimental work before doing the following calculations.

Calculations

Note that since the ethanol solutions you prepared were known to three significant figures, the values you calculate should be reported to three significant figures. You must show complete calculations for all values below on the back of your Summary Sheet.

1. With the linear regression equation from your Beer's Law plot and the absorbance value of your wine sample calculate the percent alcohol (ethanol) of your wine sample by volume (%v/v). Recall that you diluted your wine by a factor of 2:10 when preparing the unknown samples.
2. Use the table on the next page to determine the density, in g/mL, of your wine sample based on the alcohol concentration by volume calculated in step 1. When using the table, assume that density and specific gravity are the same, with units of g/mL. Be sure to use all digits given in the table.
3. Calculate the percent alcohol (ethanol) of your wine sample by weight (% w/w). You will need to use the percent alcohol by volume, the density of your wine sample, and the density of pure ethanol (alcohol), which is 0.798 g/mL.
4. Finally, calculate the molar concentration of ethanol in your wine sample.

Determining the Acid Content of Wine – to be done individually

1. Obtain about 100 mL of standard NaOH solution, approximately 0.05 M. Record the exact concentration from the bottle label. Prepare your buret to titrate with the NaOH solution.
2. Using your 10-mL volumetric pipet, pipet 10.00 mL samples of wine into each of three 250-mL Erlenmeyer flasks. The flasks do not need to be dry prior to pipeting. To each flask, add approximately 40 mL of DI water, using a graduated cylinder, and add 6 drops of 0.1% phenolphthalein indicator solution.
3. After recording the initial buret reading, position the buret so that its tip is 2-3 cm inside the flask opening, and place a piece of white paper under the flask. Titrate with NaOH solution to a stable, faint pink end-point (see below). Upon reaching the end-point, read the end-point volume of NaOH to the nearest ± 0.01 mL, and record the volume.

   As you titrate, the color of the solution in the flask will change from clear, to yellowish, to peach, and finally to pink. The white paper under the flask helps in seeing the color. The ideal end-point is the appearance of the *first* faint pink color which remains after a few seconds of swirling. As you get close, add NaOH drop-by-drop. The color may fade after a while due to absorption of atmospheric CO_2.
4. Repeat step 3 with the second and third samples, being sure to refill the buret and record the initial and final volumes each time. The final three titration end-point volumes of NaOH should closely agree. A fourth titration should be done to replace any suspicious outliers.
5. Calculate the molarity of tartaric acid to four significant figures for each sample of wine. In addition, report the mean, standard deviation, and relative standard deviation in parts per thousand for the tartaric acid molarity. You will be graded on the rsd of your results, which indicates the precision of your titrations.

Laboratory Report

Remember that buret readings are estimated to 0.01 mL and pipets are accurate to two decimal places. Read the experiment carefully for instructions on calculations, significant figures and units. Show your *full* calculations of percent alcohol by volume and by weight and molar ethanol concentration on the back of the Summary Sheet. Leave space in your lab notebook to neatly attach your spreadsheet and Beer's Law plot from the ethanol analysis.

Specific Gravity (use as density) of Aqueous Solution Ethyl Alcohol at 15ºC

Specify Gravity	% Alcohol by Volume	Specify Gravity	% Alcohol by Volume	Specify Gravity	% Alcohol by Volume	Specify Gravity	% Alcohol by Volume
1.00000	0.00	0.99417	4.00	0.98897	8.00	0.98435	12.00
0.99984	0.10	0.99403	4.10	0.98885	8.10	0.98424	12.10
0.99968	0.20	0.99390	4.20	0.98873	8.20	0.98413	12.20
0.99953	0.30	0.99376	4.30	0.98861	8.30	0.98402	12.30
0.99937	0.40	0.99363	4.40	0.98849	8.40	0.98391	12.40
0.99923	0.50	0.99349	4.50	0.98837	8.50	0.98381	12.50
0.99907	0.60	0.99335	4.60	0.98825	8.60	0.98370	12.60
0.99892	0.70	0.99322	4.70	0.98813	8.70	0.98359	12.70
0.99877	0.80	0.99308	4.80	0.98801	8.80	0.98348	12.80
0.99861	0.90	0.99295	4.90	0.98789	8.90	0.98337	12.90
0.99849	1.00	0.99281	5.00	0.98777	9.00	0.98326	13.00
0.99834	1.10	0.99268	5.10	0.98765	9.10	0.98315	13.10
0.99819	1.20	0.99255	5.20	0.98754	9.20	0.98305	13.20
0.99805	1.30	0.99241	5.30	0.98742	9.30	0.98294	13.30
0.99790	1.40	0.99228	5.40	0.98730	9.40	0.98283	13.40
0.99775	1.50	0.99215	5.50	0.98719	9.50	0.98273	13.50
0.99760	1.60	0.99202	5.60	0.98707	9.60	0.98262	13.60
0.99745	1.70	0.99189	5.70	0.98695	9.70	0.98251	13.70
0.99731	1.80	0.99175	5.80	0.98683	9.80	0.98240	13.80
0.99716	1.90	0.99162	5.90	0.98672	9.90	0.98230	13.90
0.99701	2.00	0.99149	6.00	0.98660	10.00	0.98219	14.00
0.99687	2.10	0.99136	6.10	0.98649	10.10	0.98209	14.10
0.99672	2.20	0.99123	6.20	0.98637	10.20	0.98198	14.20
0.99658	2.30	0.99111	6.30	0.98626	10.30	0.98188	14.30
0.99643	2.40	0.99098	6.40	0.98614	10.40	0.98177	14.40
0.99629	2.50	0.99085	6.50	0.98603	10.50	0.98167	14.50
0.99615	2.60	0.99072	6.60	0.98592	10.60	0.98156	14.60
0.99600	2.70	0.99059	6.70	0.98580	10.70	0.98146	14.70
0.99586	2.80	0.99047	6.80	0.98569	10.80	0.98135	14.80
0.99571	2.90	0.99034	6.90	0.98557	10.90	0.98125	14.90
0.99557	3.00	0.99021	7.00	0.98546	11.00	0.98114	15.00
0.99543	3.10	0.99009	7.10	0.98535	11.10		
0.99529	3.20	0.98996	7.20	0.98524	11.20		
0.99515	3.30	0.98984	7.30	0.98513	11.30		
0.99501	3.40	0.98971	7.40	0.98502	11.40		
0.99487	3.50	0.98959	7.50	0.98491	11.50		
0.99473	3.60	0.98947	7.60	0.98479	11.60		
0.99459	3.70	0.98934	7.70	0.98468	11.70		
0.99445	3.80	0.98922	7.80	0.98457	11.80		
0.99431	3.90	0.98909	7.90	0.98446	11.90		