TEXTILE CHEMISTRY
in the
LABORATORY

BOOKS BY BRUCE E. HARTSUCH

INTRODUCTION TO TEXTILE CHEMISTRY

TEXTILE CHEMISTRY IN THE LABORATORY

ELEMENTARY QUALITATIVE ANALYSIS

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LABORATORY

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PREFACE

The experiments outlined in this book have been designed to illustrate the chemical reactions involved in the preparation, manufacture, processing, and maintenance of textile materials. Detailed directions for fifty-five experiments are given, covering the chemistry of wool, silk, cotton, rayon, hard water, and soap. These are not tests in the ordinary sense of the word but are examples of chemical reactions that have good theoretical foundations and that are discussed in the companion textbook, Introduction to Textile Chemistry. For example, experiments are described that deal with the hydrolysis and oxidation of cellulosic fibers, the preparation of cellulose acetate and nitrate, the chemistry of bleaching and mercerization, the weighting and degumming of silk, the scouring and chlorination of wool, the hardness of water, and the analysis of soap. One entire section is devoted to the identification of fibers.

The purpose of this laboratory manual is not to make expert textile chemists of students, but to give the opportunity of carrying out some visual and manual experiments that will correlate the fundamental facts and concepts of textile fibers with their behavior in practice and use. To emphasize this correlation, most of the experiments have references to the textbook, indicating pages where the subject is discussed.

Part of one section is devoted to the preparation of all solutions and reagents required for this laboratory work. A discussion of solutions, methods for expressing concentrations, and diluting solutions is contained in the introduction.

The student is guided in making the proper observations by the question blanks in many of the directions. These short answers are to be filled in at the time the experiment is being performed. Here again, correlation with the textbook by means of questions tests the students' knowledge of the subject. Blanks are provided for all formal weights, volumes, percentages, etc. The result is that no notebook is necessary and teacher evaluation of student knowledge is readily ascertained. Sets of questions will be found at the end of all major topics.

Some pertinent suggestions to teachers follow this preface.

It is obvious that many other experiments might have been included in this book, but it is flexible enough so that teachers may omit what they please or introduce additional experiments. However, we feel that we have outlined laboratory work which has the maximum of useful and thought-provoking experiments and the minimum of cookbook tests.

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CONTENTS

SUGGESTIONS TO TEACHERS

It is hoped that the following few pages will be of help to teachers of textile chemistry, especially to younger and less experienced teachers. The suggestions are written in an effort to assist in organizing the course, arranging the laboratory, planning the laboratory work, and handling the students. Teachers may hesitate to introduce a formal textile chemistry course in a school because it is not widely done and they may have had no special training along these lines. If the reader is among these teachers, then it is to you personally that these remarks are addressed.

In the first place, you must become thoroughly familiar with the book, the parts into which it is divided, those experiments which are quantitative in nature and those which are qualitative, the system for numbering samples, the sets of questions following general topics, the sections dealing with the preparation of reagents, etc. You must become acquainted with the aims and purposes of the book and what it hopes to accomplish, and you should make the work fit in with other courses being given, realizing that this work is approached from the chemical point of view. It is a simple, brief but illuminating laboratory study of the raw materials from which textiles are made, together with the two most important substances used in connection with textiles--soap and water.

The proper teacher-student relation is one of the most important factors in successful teaching, and in view of this fact a few suggestions will be made. It is probable that the majority of students doing this work will be beginners in this kind of study. They will not have developed much imagination or the ability to organize scientific facts. They must not only be guided very carefully by means of definite and clearly stated laboratory directions, but they must also be led with sympathetic understanding. The book is intended to take care of the first, but you are responsible for the second. This means that you must call to their attention and emphasize many things which, even though printed in the book, do not impress them sufficiently. Many of these statements may seem to be so simple and so apparent that they need not be mentioned, and yet it is our experience that they are very definitely worth emphasizing at the proper time. The following items have been found necessary to get teaching results.

It is obvious that intelligent reading cannot be done without a knowledge of the vocabulary being used. The student should be impressed with this fact, especially since textile chemistry involves the use of many new terms with which the student is unfamiliar. For this reason it is strongly urged that the Glossary in Introduction to Textile Chemistry be used.

Many students never learn how to use a book as a whole, but merely work from hour to hour with it or from page to page. They should be urged to read the Contents of the manual, in order to see how it is organized, and to make free use of the text. Emphasis should be placed on the importance of cross-references. If a reference is given at the beginning of a topic or an experiment, the student should certainly be aware of the fact that helpful information will be gained by reading it.

The student must realize the importance of filling in the question blanks in most of the experiments. The questions should be answered in the laboratory at the time the work is done. It must be understood that answering these questions is not an added burden but really saves the student a great deal of time. Explain how it makes a notebook unnecessary. In addition to saving time, it calls attention to the important things about the experiments. The instructor should check the book frequently, concentrating on calculations that are required and on the question blanks. If questions are found unanswered the student should be asked about it, and if it is due to a lack of understanding a full explanation should be given. The student should not be severely criticized for a lack of understanding, but should be given help in the matter. You will have a chance to do a great deal of teaching while checking the book, and we feel that teacher evaluation of student knowledge can readily be ascertained by this method.

A chemical laboratory is a place where students work with solutions and reagents, and yet many students are not trained to be reagent-conscious. That is, there is not enough emphasis on the concentrations of reagents. All of these reagents and solutions should be labeled so as to have some meaning, and the student should be trained to use the proper reagent in the proper place. You should require all students to read pages 1 to 5 in the manual and to learn how to talk about solutions in an intelligent manner. Each student should be made to fill in the chart on page 4 and should be impressed with the fact that these acids and bases are the ones most used.

The use and care of the laboratory is briefly discussed on page 5. You should talk over this matter with your students, making what changes are necessary to satisfy the conditions in your own laboratory. One of the first responsibilities of the teacher is to have the laboratory ready for the student to work in. It must be arranged according to some definite plan, which will depend on local conditions. These will vary so much that very little can be said about preparation here. We are simply pointing out that the materials, apparatus, reagents, etc., with which the student is to work must be easily available, so that time is not wasted in unnecessary preparation or searching.

The directions for preparing all solutions will be found on pages 72-75. The solutions should not be prepared until you have decided what experiments are to be performed. Students will get good experience if they make up some of their own solutions. However, this should not be carried to an extreme. The directions given in this book require a fair amount of this, particularly when stock solutions must be diluted to some definite concentration. If you make up ordinary reagent strength acids and bases in a way different from that shown on page 72, you should tell the students and have them write in the new figures in the chart on page 4.

Each student should be provided with a set of apparatus (see page 74). If this is not possible or practical, divide the class into small groups and let each group work with one set of apparatus. It is not at all necessary that the apparatus be exactly as given in the laboratory directions. There are many reasons for making changes, and you may do so as much as you wish (it is probably best to tell the students why such changes are being made). Some type of balance is required. This need not be a sensitive quantitative balance; one which will weigh to 0.01 is satisfactory. Another means for weighing, such as open-pan scales, should be provided for rough weighings.

The laboratory work as outlined in this book is very flexible; it is not necessary to perform all the experiments; others may be added, some omitted, or the order changed if you wish. You should become thoroughly acquainted with the book and then decide what is to be done and what omitted. In making such a decision you will be influenced by several things: the apparatus, equipment, and space available; the time factor; cost; previous training of the students; and finally the possibility of fitting in the work with other courses being offered.

You must decide what to do about the sets of questions that follow the major topics. We feel that it is inadvisable to require students to write answers to such questions out of class and then hand them in for a grade. Such a procedure makes too much work for the teacher, and there is no assurance that the papers are the work of each individual student. A better plan is to advise the students that the answering of such questions is a fine way to study, that they will be held responsible for the knowledge, and that examinations will include such questions.

It may help if we make some comments about some specific experiments. Some of the directions may seem to be too detailed or too simple, but it must be remembered that many of the students doing this work may not be very well trained and must be given a lot of help.

In Experiment 3 (page 9) tensile strength measurements are made. Even if a tensile strength machine is not available, we think the experiment should be performed. There is much to be learned from it without determining exact losses in strength.

In Experiment 8 (page 19) note the remarks regarding the checking of the cellulose acetate preparations left by the students.

In Experiment 12 (page 26), where the difference between hydrocellulose and oxycellulose is demonstrated, the material for the entire class should be prepared ahead of time according to the directions on page 73.

Experiment 13 (page 27) shows how to determine the strength of bleach liquor. This should be done by one of the two methods given. It will serve to impress the student with the importance of this matter in all bleaching operations. Most of the damage done to cottons and linens is due to faulty bleaching.

Experiment 14 (page 30) uses 23% NaOH. This solution can be used by one student after another. Each student may use it and then return it to the stock bottle, or some of the solution may be poured out into a large evaporating dish or a flat enameled pan and used by the entire class. It must be remembered that such a solution is very corrosive and will destroy paint, varnish, wool clothing, and skin.

If Experiment 37 (page 47) is done the teacher should prepare the standard hard water and standard soap solutions ahead of time.

Experiment 43 (page 52) is a good practical experiment that usually proves interesting to students. The alcoholic soap solutions should be prepared ahead of time according to directions.

Experiments 44 to 48 on soap analysis should not be attempted unless the students have had some training in quantitative analysis.

The possibilities of laboratory work on the identification of fibers (page 64) are very great. Small swatches of many fabrics may be provided. Novelty goods, faddy fabrics, and newly advertised goods are perhaps the most interesting. The report blank on page 65 may be modified to suit your own ideas.

Introduction

SOLUTIONS

The study and practice of chemistry require an almost constant use of solutions -- solutions of all kinds of chemicals, strong, weak, and saturated; solutions of fairly definite known concentrations; and solutions the concentrations of which are very exactly known. Books, journal articles, laboratory directions, patent papers, etc., are filled with references to solutions for certain purposes. Many college students, even after a year's study of chemistry, seem to know very little about solutions. True, they have used many of them, but in ways that require very little thought. They have taken bottles from shelves and used the solutions without being concerned about how strong or dilute they were; they have used concentrated acids without knowing whether or not they contained any water.

In the more or less specialized field of textile chemistry, it is necessary that the student have an appreciation for the use of the proper solution in the proper place. For example, the effect of a 12% NaOH solution on cotton is entirely different from the effect of an 18% NaOH solution; a 30% NaOH solution causes wool to lose 5% of its strength, whereas a 22% NaOH solution, under the same conditions, will cause a loss of 60%; cotton treated with HCl (0.08 gm/l) and dried at room temperature will lose strength, but the same effect can be obtained by HCl (0.025 gm/l) if the cotton is dried at 100° C.

All of this means that we must be conscious of the fact that solutions may be made with different concentrations and for different purposes. We shall therefore, at the beginning of this laboratory work in textile chemistry, discuss the subject of solutions in detail, emphasizing methods for describing concentrations and labeling, preparing, and diluting solutions, etc.

A solution is a homogeneous mixture made up of two parts, the solute and the solvent. The solvent is the liquid medium in which the solute is dissolved, and it is the part that is present in the larger amount. For example, one might dissolve a teaspoon of salt in a pint of water; this mixture has a large proportion of solvent (water) and a fairly small amount of solute (salt). Water is so frequently used as a solvent that it has been called the universal solvent. However, many organic liquids, such as alcohol, ether, carbon tetrachloride, and gasoline, are used as solvents. The solute is the material that goes into solution and distributes itself uniformly throughout the solvent. It is usually thought of as a solid, such as sugar, salt, or KNO_3, but it may as well be a liquid or a gas, such as glycerin dissolved in water or H_2S dissolved in water.

In order to work in a chemical laboratory and understand what is to be done, it is necessary to know how strong solutions are (the concentration) and to understand the meaning of the labels on the bottles. We shall therefore discuss the various methods of expressing the concentration of solutions and how to label them properly.

METHODS OF EXPRESSING CONCENTRATION OF SOLUTIONS

In the most general way, solutions may be divided into concentrated and dilute solutions. For example, in most laboratories you will find at least two kinds of HCl, concentrated HCl and dilute HCl (reagent HCl); also concentrated HNO_3 and H_2SO_4, together with reagent HNO_3 and reagent H_2SO_4. The two words, concentrated and dilute, don't tell us much about the strength of solutions. The words are indefinite because the dilute acids in various laboratories may be prepared in different ways, so as to contain varying amounts of real acid. The ordinary mineral acids are usually purchased in the form of concentrated acids and are then diluted in any way that serves a definite purpose. But note that the strength of concentrated acids varies greatly. For example, concentrated H_2SO_4 is about 95% acid, concentrated HNO_3 is about 67% acid, but concentrated HCl is only about 38% acid. The words concentrated and dilute merely tell us that the concentrated solution contains a considerable amount of dissolved substance and the dilute solution contains a fairly small amount of solute.

Two other words that are used to describe the concentration of solutions are saturated and unsaturated. A saturated solution is one that contains the maximum amount of solute under normal conditions, at some definite temperature. If we have 100 gm water at 50° C and add NaCl to it until no more will dissolve and there is undissolved solid on the bottom of the container, we shall find that the solution will contain 36.7 gm NaCl, and this will be a saturated solution of NaCl in water. If some of this solution were poured off and more salt were added to it, the additional salt would not dissolve but would simply settle to the bottom and remain undissolved solid salt.

The concentration of solute in a saturated solution is known as the solubility. Thus the solubility of NaCl in water is 36.7 gm per hundred at 50° C. Note that the temperature must be stated, because it is a well-known fact that one can dissolve more salt or sugar in hot water than in cold water. Solubility is a physical property characteristic of each chemical compound, e.g., the solubility (per hundred) of KNO_3 is 85.5 and of KI is 168.0, but of $PbCl_2$ is only 1.7 and of $BaSO_4$ is 0.00023. Compounds with small solubilities, such as $BaSO_4$, are known as insoluble compounds. Solutions of these compounds, containing the amounts stated, are saturated solutions. Note that there is no connection between the terms concentrated and saturated. For example, a saturated solution of KI is also a concentrated one, but a saturated solution of $BaSO_4$ is extremely dilute. An unsaturated solution, of course, is one that is holding less than the maximum amount of solute. It is seen that these two terms do not tell us very much about the strength of solutions we might find in the laboratory.

There are six methods for expressing the concentration of solutions, that is, six different labels that might be put on a bottle to describe the strength of the solution in it. These are (a) weight per weight, (b) per cent, (c) weight per volume, (d) molarity, (e) normality, and (f) specific gravity.

(a) Weight per weight

We may say that a solution contains 50 gm solute in 1000 gm solution. Such a solution would be made by dissolving 50 gm of the solute in 950 gm water. The total would be 1000 gm. This method is not used frequently.

(b) Per cent

Remember that per cent means parts per hundred and that a percentage is calculated by dividing the part by the whole and multiplying by 100. In the preceding solution (50 gm ÷ 1000 gm) x 100 = 5%; 50 parts per thousand is the same as 5 parts per hundred, which is 5%. The solution in (a) would usually be labeled a 5% solution. Note that, in order to calculate per cent, we must divide weight by weight or volume by volume, etc. If we wish to prepare a 4.7% solution we must dissolve 4.7 gm of the solute in 95.3 gm water. This would make a total of 100 gm, of which 4.7 gm are solute. This is a very common method for labeling solutions.

(c) Weight per volume

If we dissolve 50 gm salt in some water and add enough water to make the total volume 1000 ml (1 liter), we shall have a solution that can be labeled 50 gm/l or 5 gm/100 ml. The usual way for writing a label for this solution is 50/l. This is a very common and useful method for expressing the concentration of solutions. It is useful because it makes it possible to get small quantities of substances without using a balance. Suppose we want 0.5 gm salt. If we have a 50/l solution, each milliliter of which will contain 0.05 gm salt, all we must do is to measure out 10 ml of this solution, and it will contain 0.5 gm salt.

Let us consider the difference between the solutions in (b) and (c). Solution (b) is a 5% solution, meaning that 5 gm salt are in 100 gm solution. Solution (c) is very similar; it contains 5 gm salt in 100 ml solution instead of 100 gm solution. The weight of 100 ml water is 100 gm, and the weight of 100 ml of 5% salt solution is very little more than that. In other words, with only a small error we can say that 100 ml of a dilute solution will weigh 100 gm. Therefore, a solution labeled 50 gm/l (5 gm per 100) is the same as a 5% solution. The more concentrated the solution, the greater the error. For most practical purposes, solutions up to about 15% can be labeled either way.

(d) Molarity

A molar solution is one containing one gram-molecular weight (1 mole) of solute in 1 liter of solution. Such a solution of H_2SO_4 would be labeled 1 M. If a liter of solution contains one-tenth of a gram-molecular weight, it is known as a 0.1 molar solution and would be labeled 0.1 M.

(e) Normality

A normal solution is one containing 1 gram-equivalent weight of a substance in 1 liter of solution. If 1/10 of an equivalent weight of a substance is dissolved in enough water to make 1 liter, it is a 0.1 normal solution. The two solutions would be labeled 1 N and 0.1 N. Recall that the gram-equivalent weight of a compound is that weight which contains 1.008 gm of replaceable hydrogen or its equivalent in terms of chemical reaction. This means that a definite volume of any acid will react exactly with an equal volume of any base, if the normalities of the two solutions are the same. It also means that definite volumes of all 0.1 N oxidizing agents will react with the same volume of all 0.1 N reducing agents.

(f) Specific gravity

The specific gravity of a liquid is the weight in grams of 1 ml at ordinary temperatures. It is really a figure that compares the liquid with water (which has a specific gravity of 1). Thus when we say that concentrated HCl has a specific gravity of 1.19, we mean that concentrated HCl is 1.19 times as heavy as water. If H_2SO_4 is added to water in increasing amounts the specific gravity of the solution increases, and it is possible to work out a table showing the relation between specific gravity and concentration. All handbooks contain such tables for the common chemical compounds. In industry where solutions are made up in large quantities, it is customary to mix the components of the solution until the specific gravity comes up to the value corresponding to the concentration desired. In such cases the specific gravity is determined by suspending a hydrometer in the solution vat or bath.

Another method for measuring the density of a liquid or solution is the Twaddell system. The figures are expressed as degrees, each degree being equal to 0.005 gm, which is added to 1.000, the specific gravity of water. For example, a specific gravity of 1.005 is the same as 1^{o}; a specific gravity of 1.025 is the same as 5^{o} Tw, etc. To convert degrees Twaddell to specific gravity, simply multiply by 0.005 and add 1.000.

A third method for expressing the density of liquids is the Baumé system. Many hydrometers are provided with both Baumé and specific gravity scales. A handbook should be consulted for tables showing the relation between these two systems and the method of converting one into the other.

REAGENTS

The word reagent is applied to many solutions found in laboratories. It is a rather vague term that tells little about the concentration of the solution. In general, a reagent is a solution for testing, identifying, measuring, or preparing substances. Thus we speak of Schweitzer's reagent, Schiff's reagent, and Millon's reagent. All laboratories have dilute solutions of the common acids and bases known as reagents (reagent HCl or reagent NaOH). These reagent acids and bases will be made up approximately the same in different laboratories, but it must be clearly understood that reagent HCl does not designate a definite concentration. In some laboratories it may be a 15% solution and in others an 18% solution. In some laboratories all the common acids and bases are 6 M (six molar).

The student will find it a great convenience to know the concentration of these reagent acids and bases, either in per cent or grams per liter. It is often necessary to prepare a dilute solution from one that is more concentrated. For example, suppose you wish to make a 5% solution of HNO_3. You can make it by diluting any HNO_3 solution that is stronger than 5%, but you must know the concentration of the stronger solution. You will find two such solutions available, reagent HNO_3 (which may be 18%) and concentrated HNO_3, 1 liter of which contains 990 gm HNO_3. It would be much easier to make small quantities of 5% HNO_3 by diluting the reagent rather than the concentrated HNO_3.

The student should fill in the accompanying chart, have it checked by the instructor, and make a copy of it on a small card that can be kept in the laboratory locker for ready reference. The chart tells an abbreviated story of how the reagents are prepared. With the exception of NaOH, they are all made by measuring out a certain volume of concentrated material (as purchased), and diluting it to a definite volume. The chart gives the two volumes. It also tells how much of each compound is contained in 1 liter of the starting material (the concentrated form). It will be found most useful if the concentrations of the reagents are expressed in grams per liter. The approximate per cent strength of the reagents can be obtained by dividing this number by 10.

The Reagent Acids and Bases

Volume of Starting Material	Diluted up to	Weight of Compound in 1 liter of Starting Material	Concentration of Reagent, gm/l
H_2SO_4 1.1 liters concentrated	8 liters	1760 gm	
HNO_3 7.5 liters concentrated	40 liters	990	
Acetic 5 liters glacial	20 liters	1000	
HCl 12.5 liters	40 liters	specific gravity of 1.19 is a 38% solution	
NH_4OH 17.5 liters	40 liters	640 gm NH_4OH	
NaOH 15 lb solid	40 liters		

The figures printed in the first two columns are those used in a typical college laboratory. If the reagents are made up differently in a particular college, the instructor may dictate the proper figures for insertion in the blank spaces provided.

DILUTING SOLUTIONS

We have learned that laboratories are provided with reagent acids and bases but that it is often necessary to use solutions which are more dilute. For example, a solution that contains 1.5 gm/l HNO_3 is required. Suppose that reagent HNO_3 contains 185 gm/l and you wish to use it to make the 1.5 gm/l solution. This involves the use of an inverse proportion, in which two figures are volumes and two figures are grams per liter. The grams per liter figures are fixed, 185 and 1.5, but only one of the volumes is fixed; the other is to be calculated. Which is which depends on the situation. You may wish to prepare 4 liters of the 1.5 gm/l solution; if so, the volume of the 185 gm/l solution must be calculated; or you may wish to start with 50 ml of reagent HNO_3 and dilute it until it is a 1.5 gm/l solution; in this instance the volume of the diluted solution must be calculated. Suppose you wish to make 4 liters of the 1.5 gm/l solution. All that is necessary is to substitute the proper figures in a general inverse proportion involving volumes and grams.

$$V_1 : V_2 = gm_2 : gm_1$$

The sub 1 and sub 2 may refer to either solution; make your own choice. Let the sub 1 figures refer to reagent HNO_3 and the sub 2 figures refer to the 1.5 gm/l solution.

Then

$$V_1 : 4 = 1.5 : 185$$

$$V_1 = 0.0324 \text{ liter}$$

Therefore you would measure out 0.0324 liter (32.4 ml) of reagent HNO_3 and add enough water to make 4000 ml.

Let us take the other example, i.e., how much 1.5 gm/l HNO_3 solution would be made starting with 50 ml reagent HNO_3? The figures in the general inverse proportion would become

$$50 : V_2 = 1.5 : 185$$

$$V_2 = 6166.6 \text{ ml}$$

which means that, if you start with 50 ml reagent HNO_3 and add enough water to make 6166.6 ml total volume, you will have a solution that contains 1.5 gm HNO_3 per liter.

The method of dealing with percentage figures rather than grams per liter is approximately the same, except that some error will be introduced when dilute solutions are stronger than 10 or 12%. The general proportion is

$$V_1 : V_2 = \%_2 : \%_1$$

USE AND CARE OF THE LABORATORY

Reagents

A well-organized laboratory will have reagents arranged in a way that will be convenient for all students, but different teachers will have different ideas about the plan. The student should become acquainted with this plan as soon as possible.

As far as possible, all reagents and solutions will be labeled to show the concentration; some will be marked in per cent concentration and others as grams per liter. If a soda ash solution is made up with 10 gram soda ash in 1 liter of solution it may be labeled 10/1 or 1%, either of which will designate the concentration. Ordinary reagent acids and bases should be labeled with a capital R, e.g., H_2SO_4 R, HCl R, etc. The strength of such reagents can be ascertained by referring to the chart on page 4.

All reagent bottles should be kept in their proper place. Do not take bottles to your own table and leave them there. The efficiency of the whole laboratory is quite dependent on any student's being able to find a reagent where it is supposed to be.

If too much reagent is taken from a stock bottle or if some reagent is left over from an experiment, do not put it back into the bottle without asking the teacher about it. It is too easy to make a mistake, and if one reagent is contaminated with another a very bad situation is created. There probably will be some instances in which you will be directed to return unused reagent to the stock bottle. Be sure to follow such directions, because there will be some good reason for it.

When the directions call for the use of a solution of different concentration from that provided in the laboratory, you must make it up by diluting some stronger solution of definite strength (see page 4).

The top of your desk should be kept as neat as convenient. If something is spilled on the table or on the floor, it must be cleaned up at once. It is up to you to keep your particular portion of the laboratory clean. Purses, textbooks, etc., should not be kept on top of the laboratory table.

The only materials that may be put into the sinks are those that can be washed down with water. Anything else, matches, labels, pieces of yarn, bulky precipitates, litmus paper, etc., must be put into waste pails. At times, extra pails will be provided for waste that is to be disposed of in a special way.

When you leave the laboratory, wash off the top of the desk with a sponge and dry it as much as you can with the sponge. Look around your section of the laboratory and see that it is left neat.

The Laboratory Work

Following this introduction you will find the laboratory work divided into seven sections. Section I covers work on cellulose (cotton and rayon); Section II deals with wool; Section III has some interesting work on water; Section IV deals with soap; Section V contains work on silk; Section VI consists of a study of the methods for the identification of fibers; and Section VII gives the methods for the preparation of all reagents and solutions, together with a list of apparatus required.

There is no prescribed amount of work to be done in any one laboratory period. Do what you can in the time available, and do not try to cover more ground than you can absorb and digest.

One absolutely essential requirement is that you read over and learn the text material that precedes definite laboratory directions. There is no greater waste of time than doing work in any laboratory without knowing what you are doing. While you are working at your desk you will be under observation by your instructor and will be questioned about what you are doing. Your laboratory grade will be based mostly on the impression you make as a result of these observations and questions. It is not enough that you get certain results unless you understand the reasons for them or the use to which they may be put. It is hoped that this course will be an intellectual exercise rather than a mere feat of memory.

In the Table of Contents you will find a list of all laboratory experiments, so that you may know where to find definite directions. You will save much of your laboratory time if you will read over ahead of time what comes next in the laboratory work.

As you come to blank spaces in the laboratory directions, where questions are to be answered or observations made, fill in the blanks at once, <u>in the laboratory</u>, unless otherwise directed. The answering of these questions is very important <u>because they are</u> designed to call your attention to the proper observations to be made or the proper conclusion to be drawn. They will help to fix significant points in your mind, and you will find that through them you will learn more textile chemistry. Around them a large share of the examination questions will be built.

Most of the materials you work with, if not destroyed during an experiment, will be saved and mounted in the spaces provided in the book. For your convenience in keeping a record of samples, they will be given numbers. These numbers run consecutively through each section. For example, the samples obtained in the study of cellulose are numbered I-1, I-2, I-3, etc.; the samples of wool are numbered II-1, II-2, etc. These numbers are printed in the vacant spaces where the samples are to be mounted. Label your sample with the proper number as soon as you have an opportunity, and do not attempt to remember them by position, or order, or their location in your locker, or in any way except by number. However, do not carry the number idea to an extreme. The number on a sample is merely an abbreviated method of labeling until the sample is ready to be mounted in your book. For example, I-5 is a strip of cotton muslin that has been boiled with 0.5% HCl for 5 minutes and dried without washing. It will be in your locker and on top of your desk along with a number of similar samples. To avoid getting it confused with the others it must be labeled, and it is much simpler to label it I-5 than to tell in words on the label just what it is. But the number 5 has no further significance. The important thing about that sample is that it has been treated with dilute HCl under certain conditions. When handling that sample your thought should be, "This is my dilute HCl acid sample," and <u>not</u>, "This is my number 5." Samples may be mounted in your book outside the laboratory period.

Very little benefit can be derived from laboratory work without a good background and knowledge of the subject being studied in the laboratory. The main purpose of laboratory work is to give the student a chance to see and handle things, to actually observe how they behave under various conditions. The laboratory work in this book is designed to illustrate the fundamental properties of textile materials and the more important of the operations performed in the textile industry.

It often happens that laboratory work will progress ahead of lectures or textbook assignments. If this occurs, the student should read the textbook discussion on the subject before doing the experiments. The student is strongly urged to make full use of the index in Introduction to Textile Chemistry (I. T. C.) so that he can refer to the pages where the subject is discussed. When definite references to I. T. C. are given, the student should refresh his memory by reading the designated pages.

QUESTIONS

1. Define solute and solvent.

2. What is the difference between a solution and a liquid such as alcohol?

3. What is meant by a saturated solution? A concentrated solution? Are there instances in which they could be the same thing?

4. What is the effect of temperature on the solubility of a substance such as sugar?

5. What is meant by each of the following labels that one might find on bottles in a laboratory?

(a) NaCl, 7% solution
(b) 0.05 M H_2SO_4
(c) Bleach liquor 4° Tw
(d) NaOH 10/1
(e) 0.15 N HCl
(f) HNO_3 R
(g) HNO_3 concentrated
(h) $SnCl_4$, specific gravity 1.04

6. How would you make 600 ml 2% HNO_3 starting with a solution that is 11%?

7. How much 1.5% HCl could you make from 75 ml 18% HCl?

8. How would you prepare 2 liters of 0.5 M HCl starting with concentrated HCl, which contains 38% HCl and has a specific gravity of 1.2?

9. Consult the chart on page 4 and tell how you could make 1 liter each of 3% NaOH, 4% H_2SO_4, and 3.2% NH_4OH, starting in each instance with the reagent.

10. How would you make a 3.7% solution of table salt?

SECTION I

The Chemistry of Cellulose

THE EFFECT OF HEAT ON COTTON

1. (a) IN ABSENCE OF AIR: DRY DISTILLATION (I. T. C., page 168)

Put a small amount (about 2 ml) of absorbent cotton in the bottom of a dry test tube. Place a piece of wet blue litmus paper across the top of the tube. Heat the bottom of the tube with a small flame until the litmus paper changes color. Note the physical change in the cotton and any gases produced by the dry distillation.

Are the gases acid or alkaline? ____________ What is the main gas in the mixture? ____________

(b) IN PRESENCE OF AIR: BURNING.

Bring the end of a piece of cotton yarn into the side of a small Bunsen flame. Does cotton burn rapidly or slowly, char, or form a bead? ____________

SOLVENTS FOR CELLULOSE

2. CUPRAMMONIUM (I. T. C., page 131)

Fill a wide-mouth bottle about half full of Schweitzer's reagent and add about 1 gram of absorbent cotton, a little at a time, working each amount with a glass rod until it is thoroughly impregnated with the liquid. Stopper the bottle tightly and set it aside until the next laboratory period.

How does it look then? ____________

____

Put some reagent H_2SO_4 into a beaker and pour a little of the cellulose dispersion into it. What happens? ____________

Pour some more of the dispersion into 100 ml distilled water. What happens? ____________

____

Would a similar thing happen if you diluted a solution of sugar in the same way? ____________

What is it that keeps the cotton dispersed? ____________

What would result if this cellulose solution were forced through fine openings in a spinneret under the surface of H_2SO_4? ____________

This would be cuprammonium rayon (Bemberg).

DO NOT pour the rest of the solution into the sink, but pour it into a pail or large bottle provided for this purpose.

HYDROCELLULOSE

3. THE EFFECT OF ACIDS ON COTTON (I. T. C., page 133 and 172)

Before starting work on this experiment, which is a long one, you must read over the entire directions and the discussion of hydrolysis, so that you will understand what you are going to do and the purpose of it and will be able to work intelligently. The reading should be done outside the laboratory, so that when you are ready to start the experiment you can come into the laboratory and proceed without loss of time.

It is more interesting to do this experiment with more than one kind of cotton goods, and perhaps four or five qualities of cloth will be provided. One brand may be assigned to one group of students and other brands to other groups. Be sure to record the name of the material assigned to you.

This material will be handed out in the form of warpway strips, about 1½ by 7 in., which will be enough strips for the entire experiment. It probably is more practical to hand out all the strips at one time, but this does not mean that all students must work with them at the same time. If you are not ready to start the experiment, you should take the strips away with you when you leave, so that they will not be exposed to any acid fumes in the laboratory. When you are ready to start the work, bring all of them to the laboratory and proceed as directed.

The sizing must be removed from the goods because it will interfere with the scorching test to be made later. The sizing can be removed by boiling the strips in 0.01% HCl solution for about 45 minutes. The strips must not be allowed to come into contact with air during this boiling. This is a general rule that must be carefully followed. The effect of a reagent on textile materials is one thing, but the effect of the reagent plus air may be entirely different. The strips must be kept from floating on the surface of the boiling liquid. Rinse the strips thoroughly in four or five changes of distilled water. Decide how much 0.01% HCl you will need, and then check the following statement with the teacher. I will take_____ml reagent HCl and add_____ml water to make_____ml 0.01% HCl.

The teacher may desize the strips beforehand and thus save considerable laboratory time for the students.

The effect of four acids will be studied, two mineral and two organic -- HCl, H_2SO_4, CH_3COOH, and $H_2C_2O_4$ (oxalic). Two concentrations of each acid will be used, 0.5% solutions and concentrated acids. Concentrated HCl contains about 38% HCl and 62% water; concentrated H_2SO_4 and CH_3COOH contain no water; and concentrated oxalic acid contains about 8% acid. (Oxalic acid is a solid, and an 8% solution is almost saturated.) These acids will be used under two different sets of conditions -- cloth will be treated with the concentrated acids in the cold for 5 minutes and then rinsed very thoroughly; the dilute acid treatment will be at the boiling point for 5 minutes and the cloth will be dried without rinsing.

The 0.5% solutions will be made by taking 10 ml of reagent

HCl and adding __________________ml water to it. (See page 5.)

H_2SO_4 and adding __________________ml water to it.

CH_3COOH and adding __________________ml water to it.

Have these figures checked.

The 0.5% oxalic acid will be found already prepared.

PROCEDURE AND PRECAUTIONS

EFFECT OF CONCENTRATED ACIDS

Fold the strip of cloth, put it in a small beaker, add enough acid to cover it, and hold it down with a glass rod until it is saturated. After 5 minutes, rinse it well, as directed below.

Rinsing the Strips

Pour the entire contents of the small beaker into your largest beaker filled with tap water; set it under the faucet at once; and let water run on it for 10 minutes. This is done with all the acids except concentrated H_2SO_4, which must not be poured into water. With this acid, lift out the strip with forceps or a pair of glass rods, drop it into a large beaker filled with water, and then let water run on it.

The object to be attained is the removal of all acid before the cloth is dried, so that the acid does not continue to attack the cellulose. What we wish to determine is the effect of a 5-minute treatment of cotton cloth with concentrated acid, and not the effect of small amounts of acid allowed to dry on the cloth.

Marking the Strips

If you wish to rinse more than one strip in the same large beaker you may cut notches in the end of the strips before putting them into the acid. Any method you wish to use will be all right, as long as it differentiates the strips. You cannot depend on pencil or ink marking.

Drying the Strips

Make a clothesline with some cotton yarn and hang the rinsed strips on it. These rinsed strips must not be left in the laboratory. Wet cloth left in the laboratory absorbs acid vapors from the air and is weakened. This, of course, would give results that are out of line. Take the strips with you when you leave the laboratory, but in so doing, wrap them so they will not touch each other. After they are thoroughly dried this detail is not important, but as long as they are damp they must not touch each other. Do not bring them back to the laboratory until you are ready to make the strength tests. If a strip has been attacked so much that it cannot be handled and has no strength at all, simply record it as "destroyed."

Numbering the Strips

As soon as the strips have been rinsed, put stickers on them with the proper numbers -- HCl = I-1, H_2SO_4 = I-2, CH_3COOH = I-3, $H_2C_2O_4$ = I-4.

EFFECT OF BOILING DILUTE ACIDS

Put a test strip into some 0.5% acid and boil it for 5 minutes. During this time the cloth must be entirely submerged. The effect of hot acid plus air is not the effect of acid. The presence of air introduces an oxidation factor which acts in the same direction as hydrolysis; that is, it weakens cotton, so that if you permit this your results will be wrong. Use plenty of acid. It may be necessary to hold down the strip with a glass rod. At any rate you must keep it below the surface of the boiling solution.

The Boiling

The rate of boiling should be slow; keep it just at the boiling point. As it boils, water will evaporate and the solution will become stronger. Therefore, you may have to add a little distilled water occasionally to keep the total volume approximately constant.

Drying the Strips

The cloth in this part of the experiment is not to be rinsed; the acid is allowed to dry on it. At the end of the 5-minute boiling, simply lift out the strip, squeeze out the excess solution, and hang the strip up to dry. Acid of this strength will not hurt your hands and so you should wring out the piece of cloth as much as you can with your fingers. If one of the four pieces is not wrung out as much as the other three, there obviously will be more acid left in it. This extra acid will attack the cellulose as it dries, and the result will be too much hydrolysis along with too much loss in strength. Try to squeeze out all the strips alike. These strips, as before, must not be left in the laboratory but taken home and kept there until you are ready to make the strength tests. While they are wet they must not touch each other.

Numbering the Strips

Before hanging up the strips to dry, put stickers on them with the proper numbers: HCl = I-5, H_2SO_4 = I-6, CH_3COOH = I-7, and $H_2C_2O_4$ = I-8.

Cut off a 2-in. piece from each of samples 1 to 8. Be sure to mark these pieces with the correct number and save them until you are ready to do Experiments 4 and 5. Then they can be cut in two, and one half used for Experiment 4 and the other half for Experiment 5. These two experiments may be done before testing the tensile strength of the main pieces.

DETERMINATION OF TENSILE STRENGTH OF CLOTH

This will be done on the Scott tensile strength machine. The strips for testing on this machine must be prepared ahead of time as instructed below.

Preparation of Strength Test Strips

The main strip that you have left is about 1.5 in. wide and about 5 in. long. It must be trimmed down until it is exactly 1 in. wide, and the length left as it is. Small variations in length are unimportant, but the width must be very exact. We cannot rip off a little from each side of the strip because the ripping would strain the threads along each edge, and the observed strength would be too low. Nor can we cut the pieces into strips 1 in. wide, because it would be impossible to do this without damaging some of the outer edge threads. The correct procedure for preparing these test strips is to cut them down to a width of about 1.25 in. and then pull the threads with your fingers the rest of the way. The result is a miniature rug having a solid center exactly 1 in. wide and a fringe (of the filling yarns) along the sides of it. Do not cut off this fringe because the interlacing of warp and filling yarns affects the strength of the warp, and it is the warp strength that we are determining.

Variations in the length of the test strips are not important, as the only requirement is that it be long enough to be gripped by the jaws of the testing machine. The length that you will have (about 5 in.) is satisfactory. On the other hand, the width of the solid centers must be exactly 1 in. and be measured with a good ruler (not with a tape measure, or yardstick). We wish to know how much pull is required to break a piece of cloth 1 in. wide. This means that in some instances we will test 80 threads, but in others we may test only 60 threads. The number of threads per inch depends on the construction of the cloth. If the cloth has 80 threads per inch, it would not be fair to test only 77 of them. The measuring of this 1-in. width must be done as carefully as possible.

Not only do we want to determine the breaking strength of a piece of cloth 1 in. wide, but we want to know the breaking strength per thread. This means that we must count the threads in 1 in. of the warp. This can be done after the tensile strength has been determined; cut a small piece across the end of the strip (warp threads) and pull out and count the threads in the 1 in. width.

If one is doing very careful work with the strength of cotton goods, one must pay attention to the moisture content of the cotton at the time the tensile strength is determined (the relations among moisture content, humidity, and strength are discussed in I. T. C., page 169). Cotton differs from wool, silk, and rayon in that it is stronger when damp. Most textiles are weaker when damp. This increase in the strength of cotton is not a small matter, e.g., cotton is 30% stronger when conditioned at 70% R.H. than when conditioned at 30% R.H. This means that all cotton strength tests to be used for comparing various cloths must be made on strips that have been allowed to stand in an atmosphere of constant humidity. For comparison purposes, it makes little difference what the humidity is as long as it remains constant. For the purpose of this experiment the humidity of the ordinary laboratory will remain sufficiently constant, and strength tests may be made if the strips have been allowed to condition in the humidity that is normal for a particular time of year. However, it would not be fair to have some strips conditioned in the extra dry air of some dormitories and others in a laboratory where steam baths are operating. These factors must be seriously kept in mind when the results of strength tests are to be used for comparing cotton cloths. Cotton is usually conditioned for research purposes at a relative humidity of 65%. Some laboratories are equipped with entire rooms maintained at a constant humidity.

When working in a small laboratory or when a small quantity of cotton must be conditioned, the material may be stored in desiccators containing sulfuric acid of some definite strength. Wilson[1] shows the relation between the concentration of H_2SO_4 and the relative humidity of the air in con-

[1] Ind. Eng. Chem., 13, 326 (1921).

tact with it. He gives figures for four different temperatures, one of which is quoted in the following table. A temperature of 25° C is only a little above ordinary room temperature, and it is a sort of constant temperature used in research work.

Relation between Relative Humidity and
Concentration of H_2SO_4 at 25° C

% H_2SO_4	R.H.	% H_2SO_4	R.H.
0	100	40	56.8
10	96.1	45	46.8
20	88.5	50	36.8
25	82.9	60	17.2
30	75.6	70	5.2
35	66.8		

These figures may be used to draw a curve by plotting concentrations against relative humidity. From this curve one can determine what concentration of H_2SO_4 should be used to give any desired humidity. Most of the work done with textiles is done at a relative humidity of 65% or 72%. If one wishes to use this method for conditioning samples, simple make up the proper H_2SO_4 solution, put it in the bottom of a desiccator, and cover with a perforated plate. Be sure that the plate and the sides of the desiccator are wiped free from acid. Samples stored in this desiccator for 8 hours will have reached the moisture equilibrium obtained in the relative humidity of the desiccator.

If a tensile strength machine is not available, it is of course impossible to get exact figures. However, we feel that the experiment is still worth doing. One can get a very rough idea of strength by breaking the strip (not tearing it) between the hands. The main purpose of the experiment is to show the effect of acids on cotton in a relative way, and this can be approximated by breaking with the hands. In this method the thread strength cannot be determined.

Use of the Tensile Strength Machine

In principle, when a strip of cloth is tested, it is clamped vertically between two jaws. The bottom jaw is attached to a stretching screw which moves down when operated by a motor. The top jaw is attached to a weight-raising device and a scale which reads in pounds. When a strip is clamped between the jaws and the stretching screw moves down, it pulls on the strip of cloth, which in turn lifts the weight until the cloth breaks. As soon as this happens, the weight is no longer lifted and the scale records the number of pounds that were required to break the strip. When using the machine, perform the following operations in the order listed.

Put the strip between the jaws vertically and clamp the top jaw, being sure that the strip is hanging perpendicularly. Stand directly in front of it and line it up so that it hangs straight.

Attached to the weight arm are several little "dogs" that click along a ratchet as the weight arm is moved out. When the machine stops, these dogs drop down into the ratchet notches and hold the arm so that it will not swing back. These dogs can be lifted up so they will not touch the ratchet, but at the start of the test they must be down.

Set the machine so that it reads zero.

Clamp the strip with the bottom jaw. This must be done so that as nearly as possible all the threads in the one inch are under equal tension. That is, do not have one side tight and the other side slack, for then when the machine starts pulling it will pull on only some of the threads and will therefore break them sooner than it should. We want a pull on all the threads at the same time.

Start the motor. It may be allowed to run all the time you are using the machine, but must be turned off when you leave it.

Look at the pointer and see that it is still at zero and see that the dogs are down in the ratchet.

Pull the throttle lever forward as far as it will go (about 8 in.) and release it at once. Let it fly back.

Put your hand on the reversing bar and be ready to push down on it as soon as the cloth breaks. This will reverse the stretching screw and move the lower jaw up to its original position, ready for another test.

Read the scale before taking out the strip.

Record the reading and sample number.

Put the machine back so that it reads zero. To do this use both hands. You will find the weight arm is heavy. Hold this weight arm with one hand and lift up the dogs with the other hand. Keep them up until the arm is brought to its zero position. This is important. These dogs are the only thing about the machine that can be harmed easily. Their sharp edges must not be damaged by being jammed against the ratchet while you are moving the weight arm.

Remove the strip and save it.

Points to be kept in mind in order to avoid poor results:

1. The test strip must hang straight up and down.
2. All threads in the strip must be under equal tension when the test is started.
3. The jaws must be clamped tightly to avoid slipping.
4. After the strip has been pulled and found to be slipping through the jaws, it is not at all suitable for retesting because it has already been under too much strain.

Mounting the Samples

Cut a section from each strip to show how it broke -- in small scattered spots, straight across, with a tearing action, etc. Mount these samples on the next page.

Recording Results

The instructor will furnish you with the original strength of each material, which will have been determined by averaging the results of ten or more separate tests.

When you have determined the tensile strength of each of your test strips, record the figures in the proper place on the chart on the blackboard. When the figures from the entire class have been recorded the instructor will calculate the average of each set, and you will record these averages in the table below. Calculate the per cent loss in strength caused by each treatment for each material and record the figures.

Effect of Acids on Cotton Cloth
(Averages of Class)

Names of Cloth								
Original strength	Strip	Thread	Strip	Thread	Strip	Thread	Strip	Thread
Treatment	Tensile Strength	Per Cent Loss	Tensile Strength	Per Cent Loss	Tensile Strength	Per Cent Loss	Tensile Strength	Per Cent Loss
Concentrated HCl								
H_2SO_4								
HOAc								
Oxalic								
Dilute HCl								
H_2SO_4								
HOAc								
Oxalic								

Samples of ______________________________ treated 5 minutes with acid

Strength of original: strip__________; thread__________.

With Concentrated Acids, Washed Well before Drying.

I-1 I-2 I-3 I-4

	HCl	H_2SO_4	CH_3COOH	$H_2C_2O_4$
Strip strength				
Thread strength				
% loss in T.S.				

With 0.5% Acids, Dried without Washing

I-5 I-6 I-7 I-8

	HCl	H_2SO_4	CH_3COOH	$H_2C_2O_4$
Strip strength				
Thread strength				
% loss in T.S.				

TESTS FOR HYDROCELLULOSE (I. T. C., page 135 and 174)

When cotton cloth is exposed to the action of acids, the initial effect is the partial hydrolysis of the surface of the cloth. This results in a sort of surface film or layer of modified cellulose known as hydrocellulose. If the action is prolonged the hydrolysis progresses until the cloth is completely destroyed, but if the action of acids is confined to a short period of time only the surface is affected. However, even this small surface hydrolysis may be sufficient to cause some loss in strength.

We are therefore interested in ways of showing the presence of this modified cellulose on the surface of a cloth. In order to do this, we may take advantage of either physical or chemical properties of hydrocellulose.

One important property of hydrocellulose is the fact that it is more sensitive to heat than unmodified cellulose and will therefore scorch at a lower temperature. If a small amount of hydrolysis makes cotton scorch more easily, then cotton hydrolyzed to a greater extent should show a darker scorch with the same amount of heat. We shall use this scorching test in Experiment 4 to show the relative extents of hydrolysis produced in Experiment 3.

When cellulose is hydrolyzed by the action of acids the long chains of the high polymer are broken into shorter chains, and aldehyde groups are formed at such points of cleavage. These aldehyde groups have reducing properties like certain reducing sugars. As hydrolysis progresses, more reducing groups will be formed, and therefore the reducing power of the hydrocellulose will be increased. This reducing power can be measured by boiling the material with Fehling's solution, because when Fehling's solution is reduced it yields cuprous oxide (Cu_2O), a reddish brown solid. When modified cotton cloth is boiled in this reagent, the depth of color on the cloth is a measure of the relative extent of hydrolysis. We shall use this test in Experiment 5.

4. THE SCORCHING TEST

Place a small piece of the original cloth together with small pieces of acid-treated cloth (from Experiment 3) on a sheet of white paper. These pieces should have no labels or stickers on them. When the test is ended some of the pieces may be so dark that you cannot see numbers written on them. It is suggested that you arrange them in some particular order, by number, so that you will know which is which at the end of the heating. When you remove them from the paper you must mark them in some way so they will not get mixed until they are mounted. The same numbers, 1 to 8, may be used. Cover the samples with a sheet of paper and heat them with an electric iron until the original cotton begins to scorch. In this way, all the pieces will receive the same amount of heat, and so the different amounts of scorching will measure the relative amounts of hydrolysis. You must keep the iron in constant motion and not let it stand in any one spot. Move it over the entire surface of the top paper. If this precaution is not observed, some of the pieces will be heated more than others. Remove the iron frequently and raise the top paper to see whether the original cloth is beginning to scorch.

Note that we do not know the exact temperature to which these pieces have been heated. We can use the original cotton as a sort of thermometer. The temperature required to scorch the original cloth is fairly definite and can be closely reproduced by various students.

Mount the samples in the second column of the chart on page 17 in decreasing order of their scorch color; that is, put the darkest one at the top and then graduate the samples down to the lightest color at the bottom. Then fill in the first column to match the second column, using the particular acid with which each sample has been treated.

5. THE FEHLING'S SOLUTION TEST

Hydrocellulose has the property of reducing Fehling's solution. This is due to the splitting of the cellulose molecular chains to form shorter chains that have aldehyde groups at the ends. As hydrolysis progresses, the number of these aldehyde groups will increase, and hence the reducing power will increase. This whole matter should be reviewed thoroughly after the structure of cellulose has been studied and the mechanism of degradation discussed.

Fehling's solution is an alkaline solution of cupric oxide, CuO. It consists of two parts, (A) a solution of copper sulfate, and (B) a solution containing sodium hydroxide and Rochelle salt (sodium potassium tartrate). Whenever Fehling's solution is used in a test, equal volumes of the two solutions, A and B, are mixed. A complex combination of copper with the tartrate ion is kept in solution by the sodium hydroxide, but the reagent actually amounts to a solution of cupric oxide, CuO.

If a substance with reducing property is added to boiling Fehling's solution, the cupric oxide is reduced to cuprous oxide, Cu_2O. The latter is a reddish brown solid that is insoluble in the alkaline reaction mixture and will therefore precipitate out. The amount of Cu_2O precipitating is a measure of the amount of reduction and therefore a reliable indication of the amount of reducing agent.

When a piece of cloth having a partially hydrolyzed surface (hydrocellulose) is boiled with dilute Fehling's solution, the precipitated Cu_2O sticks to the cloth, giving it a definite color. Now if hydrolysis of cellulose yields compounds having reducing property and the further the hydrolysis progresses, the greater the reducing power of the product, then when this test is carried out, darker colors will be produced on those samples that have been hydrolyzed to the greater extent. This test then gives us a means not only for detecting the presence of hydrocellulose, but also for estimating the relative amount of it, and we shall use the test on the pieces of acid-treated cotton cloth that were cut off and saved in Experiment 3.

The Procedure

Mix 25 ml each of the two parts of Fehling's solution in a 400 ml beaker. Add 100 ml water and bring it to a boil. Drop a piece of 0.5% acid-treated cotton into the boiling solution and continue boiling gently for 5 minutes. Remove the piece to a beaker and rinse it with four changes of hot distilled water. Dry it. If the pieces are taken in a definite order, you can keep the particular ones in mind until they are rinsed. Then put small stickers on them with the proper numbers, so they will not get mixed before they are mounted. The same numbers, 1 to 8, may still be used. The other three dilute acid-treated samples may be tested in the same beaker of Fehling's solution. If you wish, you may boil samples 5 to 8 with Fehling's solution at the same time, providing they are notched in some way, so you can identify them.

Start with fresh Fehling's solution when you test the concentrated acid-treated pieces. Carry out the test in the same way as described above.

Mount the samples on page 17 in decreasing order of color; that is, put the darkest one at the top and then graduate them down the column to the lightest one at the bottom. Beside each sample write the acid used in making it and give its strength, e.g., concentrated HCl or 0.5% oxalic. These acids should arrange themselves in the same order found in the other two columns on the page.

What have you done to the Fehling's solution? ____________________

What happens to the CuO? ____________________ What is it on the cloth that brings about this reaction? ____________________

Which sample has the darkest color? ____________________

What does this tell you? ____________________

____

Testing for Hydrocellulose

Scorching Test		Fehling's Solution Test	
Acid and Concentration	Sample	Acid and Concentration	Sample

6. VEGETABLE PARCHMENT (I. T. C., page 175)

Paper may be parchmentized by the action of strong sulfuric acid for a short time, followed by a thorough washing.

Put some H_2SO_4 (66% by volume) into a beaker. Take half a piece of filter paper, hold it at the tip end, and dip it into the acid for 5 seconds. Lift it out and plunge it into a large beaker filled with water. Let water run on it until it is washed free from acid. It should not show a red color when blue litmus paper is pressed against it. Number it I-9. While it is still wet, compare it with a piece of wet, untreated, filter paper as to the following factors:

Tensile strength ____________________

Tearing strength ____________________

Feel of the surface ____________________

Its appearance when looked through toward the light ____________________

Dry I-9 by ironing it with a medium hot iron between papers. When dry, compare it with ordinary filter paper as follows:

Feel and appearance of surface ____________________

After folding each one several times ____________________

I-9

PARCHMENTIZED FILTER PAPER

The chemical action that takes place is not well understood. One author claims that the pores in the paper become filled with impervious hydrocellulose, which gives it properties similar to parchment. Another author claims that a thin film of hydrocellulose is formed on the surface during the 5-second treatment with strong acid and that when this film comes into contact with large amounts of water it is changed into a substance like amyloid, which gives the surface a parchment-like quality.

QUESTIONS

1. Can cotton be hydrolyzed in an acid medium? In an alkaline medium?
2. What simple test (using no chemicals) will detect the presence of hydrocellulose on cotton?
3. Describe the probable mechanism of the reaction of acid on cotton yarn.
4. What type of acid harms cotton the most? The least?
5. If a cotton cloth is spotted with a dilute acid (1 or 2% H_2SO_4), why should it be rinsed out at once instead of waiting two days?
6. Why does hydrocellulose reduce Fehling's solution?
7. Suppose a hole is discovered in a cotton cloth; how could you tell whether the damage had been caused by (a) a sharp instrument, (b) a tearing or gouging action, or (c) the action of acid?
8. What is the chemistry of the action of Fehling's solution on hydrocellulose?
9. How does the tensile strength of cotton vary with its moisture content?
10. How is paper parchmentized?

ESTERS OF CELLULOSE

7. PREPARATION OF CELLULOSE NITRATES (I. T. C., page 148)

Mix 25 ml concentrated HNO_3 with 35 ml concentrated H_2SO_4 in a 150 ml beaker. Adjust the temperature to 35° C. Take six sheets of filter paper (a quite pure form of cellulose) and crush them in your hands to make them wrinkled and soft. Then tear them into small bits. Add these pieces of paper to the mixed acids, a few at a time, and immediately push them below the surface with a glass rod. After about one-third of the paper has been added, take the temperature of the acids. Sometimes the paper will contain enough moisture to raise the temperature of the bath when it comes into contact with the concentrated sulfuric acid. Do not let the temperature go much above 35° C. When all the paper has been added, let the mixture stand for 1 hour. During this time the temperature should be kept at about 35° C. You will do this, not by heating the beaker on a wire gauze with a burner, but by keeping it in a water bath which is maintained at 35° C. For this purpose use your largest beaker with water in it sufficient to come up to the level of the nitration mixture when the small beaker is placed inside the larger one. Heat the water bath to 35° C and then reduce the flame so that it will keep the water at that temperature. Keep the thermometer in the water and read it occasionally.

At the end of an hour, decant the mixed acids into the sink; rapidly fill the beaker with tap water and pour its contents into your largest beaker, which has been filled with water. Wash the solid several times by decantation, and then dry it. This washing must be done before leaving the laboratory, because hydrolysis will take place if free acid is left on the product. If there is not quite enough time, you may reduce the time of nitration. Make the following observations on the dried product:

Color compared with original__________________________. The feel compared with the original:

______________________________________. Does it have a fibrous structure?____________________

Is it soluble in water?______________________________ Burn a small pile of pieces on a wire

gauze and compare with the speed of burning some untreated paper.__________________________

____________________________ Fill a test tube one-third full of ether-alcohol (40:60) mixture.

Add several pieces of nitrated cellulose and work with a glass rod. Cork it and let it stand. What

happens?____

Does it all dissolve?____________________________ If some of it does not dissolve, what might the

insoluble portion be?____

Pour some of this solution into the palm of your hand and blow on it until the liquid evaporates.

What is the result?____

8. PREPARATION OF CELLULOSE ACETATE (I. T. C., page 150)

(This preparation should be started at such a time that it can be completed within about 48 hours.)

In general, cellulose acetate is prepared by acetylating cotton with acetic anhydride in the presence of zinc chloride or sulfuric acid in a glacial acetic acid medium. The purpose of $ZnCl_2$ or H_2SO_4 is to act as a sort of starter, which attacks the surface of the cotton, thus activating it so that acetic anhydride can acetylate it more easily. The purpose of glacial acetic acid is to furnish a liquid medium in which the reaction can take place and in which the cellulose acetate will be distributed.

According to the usual procedure, cotton is impregnated with a solution of zinc chloride or sulfuric acid in glacial acetic acid. It is allowed to stand for a short time to allow the zinc chloride to start its action, and then the real acylating agent, acetic anhydride, is added. We shall use sulfuric acid as the starter, and you will find glacial acetic acid containing 7.5 ml concentrated H_2SO_4 per liter available.

Put 40 ml glacial acetic acid containing concentrated H_2SO_4 into a 250 ml beaker. Weigh 5 gm absorbent cotton on a semiquantitative balance and add it to the beaker in small portions. (Weigh the cotton accurately because you will weigh the cellulose acetate at the end and calculate the per cent yield you obtain.) After each addition, push down the cotton with a glass rod until all the fibers are saturated. Toward the end, the additions will not be easy and will require considerable handling, but more cotton must not be added until that already present is completely saturated with the sulfuric acid solution. Remember that sulfuric acid is going to act as a starter and therefore it must come into contact with all the cotton fibers. During this part of the preparation the temperature must not be allowed to rise too much, for if it does some acid hydrolysis of cotton will occur, and this is not desirable. The temperature should be kept under 30° C so that if the beaker feels slightly warm in your hand the temperature is too high, and the beaker should be placed in a bath of cold water.

After all the cotton has been added cover the beaker with a watch glass and let it stand for 10 to 15 minutes. Place the beaker in a bath of cold water so as to control the temperature during acylation. Add 40 ml acetic anhydride in about 5 ml portions, working it into the cotton after each addition. After all the acetic anhydride has been added stir the reaction mixture for 2 or 3 minutes, put your name on the beaker, cover it, and leave it on your table.

Teacher: The beakers containing the acetylation mixture must be checked occasionally. If the temperature goes up too much there will be excessive hydrolysis of the cellulose, and a poor quality acetate will result. It is not necessary to measure the temperature. The color of the reaction mixture is a good indicator. If the reaction is going too fast or if the temperature is too high, the reaction mixture will become brown. If this happens, the beaker should be moved to a cooler place. On the other hand, if the cotton does not swell and soften after a few hours the beaker should be moved to a slightly warmer place. It may be necessary to stir the mixtures.

When the student returns at the next laboratory period, he is to examine the contents of the beaker and answer the following questions:

When you left the mixture on your table what did it look like? ______________________

______________ What does it look like about 48 hours later? ______________________

____ Tell definitely what is in the

beaker now. ____

Cellulose acetate is soluble in acetic acid of about 60% or stronger, but when the solvent is diluted more than that the acetate will coagulate and be precipitated. We shall therefore pour the reaction mixture into a large amount of water. However, the mixture may be too thick to be poured. If this is true of your mixture, dilute it, not with water, but with glacial acetic acid, stirring in the acid until the mixture is thin enough to be poured.

Pour the reaction mixture into about 400 ml distilled water. Add it in a thin stream or in small portions with constant and vigorous stirring. If the mixture is not added slowly and stirred, the acetate will coagulate in lumps which will occlude acetic acid so that it will be very difficult to wash the cellulose acetate free from acid. After the transfer has been completed add water to the smaller beaker so as to coagulate the acetate on the sides of the beaker. From this point on use care to avoid any loss of solid cellulose acetate.

Wash the cellulose acetate until it is free from acid (litmus paper test). This can be done by decanting the solution through a Buchner funnel attached to a filter pump. Add water to the solid, stir, and decant again. In the subsequent washings use your hand to mix and squeeze the solid acetate. Continue this until the solid is free from acid, and then transfer all of it to the funnel and dry it as much as you can with suction. Transfer it to a large watch glass, label with your name, and allow to dry. Several days' drying may be necessary. If an oven is available, the teacher may put the samples of acetate in it to hasten the drying. The acetate should not be weighed until it is completely dry. Then weigh the dry cellulose acetate.

Weight of dry acetate ______________________ gm

Weight of original cotton ______________________ gm

Gain in weight ______________________ gm

Per cent gain in weight ______________________ %

Turn your product in to the instructor.

Refer to I. T. C., page 151, and make the following calculations:

5 gm cotton should yield ________ gm of the monoacetate.

5 gm cotton should yield ________ gm of the diacetate.

5 gm cotton should yield ________ gm of the triacetate.

Assuming that you did not lose any of the solid acetate, what per cent yield did you get if your product is all monoacetate? ________ all diacetate? ________ all triacetate? ________

The per cent acetic acid in the monoacetate is ________

The per cent acetic acid in the diacetate is ________

The per cent acetic acid in the triacetate is ________

What do you think your product is? ________

Answer the following questions dealing with this preparation:

1. What is the purpose of the H_2SO_4? ________
2. What is the purpose of acetic anhydride? ________
3. What is the purpose of acetic acid? ________
4. What does freshly coagulated cellulose acetate look like? ________
5. After being dried, what does it look like? ________
6. Is your preparation a primary or secondary acetate? ________
7. Why is the secondary acetate more desirable for rayon manufacture? ________
8. How is cellulose acetate coagulated from an acetic acid solution? ________
9. During this preparation, how might some acid hydrolysis take place? ________
10. How many pounds of acetate rayon could theoretically be made from 100 lbs of cotton? ________
11. Is acetate rayon a regenerated cellulose? ________
12. Should chloroform or acetone be used to remove grease spots from acetate rayon? ________
13. Why? ________
14. To what class of organic compounds does acetate rayon belong? ________

THE OXIDATION OF CELLULOSE (I. T. C., page 136 and 175)

In this experiment you will expose cotton cloth to bleach liquor under two conditions, out of contact with air and in contact with air. The bleach liquor is strong enough to overbleach the cloth very much, so you may observe the damage and the properties of such overbleached cotton. You will study methods for detecting its presence with Fehling's solution and methylene blue and also its partial solubility on NaOH.

9. THE PRODUCTION OF OXYCELLULOSE ON COTTON

Put 100 ml bleach liquor (prepared as directed on page 73) into a 250 ml beaker. Hang a strip of muslin in it (use one of the strips that are about 1.5 x 7 in.) so that it lies across the bottom of the beaker, comes up along the side and hangs over the top. Paste this free end to the outside of the beaker with a sticker. Label the beaker with your name, cover it with a watch glass, and let it stand until the next laboratory period. This interval should not be longer than 48 hours.

Remove the strip and cut a notch in the top end so that you will know which portion of the strip was not exposed to the oxidizing agent. Rinse in running water for about 5 minutes. Immerse in a dilute solution of sodium bisulfite, $NaHSO_3$, for 5 minutes (dissolve about 1/4 teaspoon of $NaHSO_3$ in 100 ml water). Sodium bisulfite is an anti-chlor that will destroy any residual bleach. Rinse in running water, immerse in 5% HCl for 2 minutes, and rinse again until free from acid (litmus paper test). Cut this strip of cloth lengthwise. One of the narrow strips will be I-10 and the other I-11. Save I-10 for Experiment 10, and I-11 for Experiment 11.

Would you expect some bleach liquor to be drawn up into the upper part of the strip by capillary action?__________ Would you expect some oxidation of cotton in the upper part of the strip?__________ In what portion of the cloth, above the surface of the liquid, would you expect the highest concentration of calcium hypochlorite?__________ How does ordinary air activate bleach liquor?________________ Does the oxygen of the air oxidize cotton?__________ Will activated bleach liquor oxidize cotton?__________ Will the cotton below the surface be oxidized?__________ In what portion of the cloth would you predict the most oxycellulose would be formed?________________

10. DETECTION OF OXYCELLULOSE BY FEHLING'S SOLUTION

Put 25 ml each of Fehling's solution A and B into a 400 ml beaker. Add 100 ml water and bring to a boil. Immerse I-10 in this solution and continue boiling gently for 5 minutes. Remove the strip and rinse in running water.

Which <u>end</u> of the strip is the darker color?________________ Why?________________ __________ Where is the color still darker?____________________ Why is it darker than the portion that was submerged in the bleach liquor?____________________

Test the strength of the strip at different places along its length by pulling it with your fingers.

Where is the strip weakest?______________________________

Where is it strongest?________________________ What is the connection between strength and amount of Cu_2O deposited?____________________________

Mount the sample below.

I-10

Submerged in bleach	At surface of bleach	Not submerged in bleach

Cotton Muslin, Bleached and Tested with Fehling's Solution

This experiment illustrates how we can demonstrate the existence of oxycellulose on cotton and can also determine relatively how much is present. This same analysis may be made quantitatively to determine the copper number of a sample of cotton, which is an exact measure of the reducing capacity of the cotton and an important value in deciding how far oxidation has progressed. The determination of copper number should not be attempted by students with no training in the technique of quantitative analysis.

THE COPPER NUMBER OF OXIDIZED COTTON

The quantitative value that measures the ability of oxidized cellulose to reduce alkaline copper solutions is known as the copper number or copper index and is numerically equal to the number of grams of reduced copper formed by the action of 100 gm of cellulosic material. There are several methods for determining this value, differing in such points as time, temperature, concentration, and type of alkali used. A critical study of these methods led Clibbens and Geake[1] to select the Braidy method as the best. It has the advantages that (a) blank determinations carried out in the absence of cellulose give values close to zero, (b) pure cellulose gives a very low value, (c) only slight modifications in the cellulose give larger increases in the value than can be obtained by other methods, and (d) the results are reproducible.

THE DETERMINATION OF THE BRAIDY COPPER NUMBER

Solutions Required:

Copper Solution:	100 gm $CuSO_4 \cdot 5H_2O$ in 1 liter
Alkali:	50 gm $NaHCO_3$ and 250 gm Na_2CO_3 (crystalline) in 1 liter
Ferric Alum:	100 gm ferric ammonium sulfate and 140 ml concentrated H_2SO_4 in 1 liter
Permanganate:	A 0.04 N solution of $KMnO_4$

The Reduction

Cut dry cotton material into small pieces, weigh exactly 2.5 gm and put it into a small glass-stoppered Erlenmeyer flask. Immerse the flask up to its neck in a constant level bath of boiling water. Immediately before use, measure 5 ml of the copper solution with a pipette into a small beaker and add 95 ml of alkali from a graduate. Bring this mixture to a boil and pour it into the hot Erlenmeyer flask containing the cotton being tested. Use a glass rod to distribute the cotton through the liquid and allow bubbles of air to escape. Put in the glass stopper, immerse the flask in a boiling water bath, and heat for 3 hours. The flask should be full of liquid so that no air space is left at the top.

Determination of the Reduced Copper

At the end of 3 hours, filter the contents of the flask by decantation and suction through a Gooch crucible provided with a thin asbestos mat. Wash (by decantation) 3 times with hot Na_2CO_3 (1%) and finally transfer the pieces of cloth and Cu_2O to the Gooch. Discard the filtrates collected in the suction flask, and provide the flask with a large test tube that will collect the next washings. Wash the contents of the Gooch with hot ferric alum solution, using 2 portions of 10-15 ml each, and finally wash with hot H_2SO_4 (about 2 N). Transfer the combined ferric alum and H_2SO_4 filtrates quantitatively to a suitable size flask and titrate with 0.04 N $KMnO_4$, using a calibrated 10 ml burette.

The reduced copper on the cotton material will reduce an equivalent amount of ferric iron to ferrous iron. When this is titrated with $KMnO_4$, the amount required will be equivalent to the ferrous iron present and therefore indirectly equivalent to the amount of reduced copper formed by the action of oxidized cotton on the alkaline copper solution.

[1] J. Textile Inst., 15, T27-38 (1924).

$$5Cu_2O + 5Fe_2(SO_4)_3 + 5H_2SO_4 = 10CuSO_4 + 10FeSO_4 + 5H_2O$$

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 2MnSO_4 + K_2SO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

1 ml 0.04 N $KMnO_4$ is equivalent to 0.0025 gm reduced copper.

The copper number is the grams of reduced copper formed by 100 gm of cotton. This 100 gm is 40 times the weight of sample used in the determination. Therefore, each milliliter of 0.04 N $KMnO_4$ used in the titration means a copper number of 0.1 (40 times 0.0025).

For a detailed discussion of the Braidy copper number, the reader is referred to the article by Clibbens and Geake mentioned above, and to Heyes[2] for a micro method requiring only 0.25 gm of material for testing. A modified Fehling's solution for this test is discussed by Staud and Gray[3].

ABSORPTION OF BASIC DYES (I. T. C., page 143)

The increased absorption of basic dyes exhibited by oxidized cellulose seems to be associated somewhat with the acid groups, probably because the COOH group reacts with the positively charged base of the basic dyestuff. At any rate, after the oxidation of cellulose begins, its ability to absorb basic dyes, such as methylene blue, is increased. If localized overbleaching has taken place, the overbleached areas will dye a darker shade with methylene blue, so that the depth of color is a measure of the extent of oxidation, a qualitative demonstration of which you will make in the following experiment.

11. DETECTION OF OXYCELLULOSE BY METHYLENE BLUE

Put I-11 into a 250 ml beaker and add enough methylene blue (0.1%) to cover it well. Heat to about 85° C and keep it there about 10 minutes. Remove the strip and rinse well with water. What causes some parts to be dyed a darker color than others?

____

What caused the excessive oxidation at the area dyed the darkest color? ____________________

____.

I-11

Submerged in bleach	At surface of bleach	Not submerged in bleach

Cotton Muslin Bleached and Tested with Methylene Blue

THE METHYLENE BLUE NUMBER OF OXIDIZED COTTON

The determination of this value should not be attempted by students with no training in the technique of quantitative analysis.

Raw, unbleached cotton has the property of absorbing methylene blue, a basic dyestuff. This absorption is due to impurities such as protein and pectic matter, and if cotton is carefully scoured and bleached its ability to absorb this dye should be reduced, for pure cellulose has a quite small and fairly constant absorption. If this absorption could be put on a quantitative basis so that the

[2] J. Soc. Chem. Ind., 47, T90-92 (1928).
[3] Ind. Eng. Chem., 17, 741 (1925); 19, 854 (1927).

amount of dye absorbed could be definitely expressed, we should have a method for following the progress of purification of cotton during bleaching and ultimately for measuring the success of the bleaching operation.

Such a method has been perfected and gives us what is known as the methylene blue absorption number. This methylene blue number is defined as the number of millimoles of methylene blue hydrochloride absorbed by 100 gm of dry cotton.

Methylene blue is absorbed not only by the impurities in raw cotton but also by the oxidized portions containing COOH groups resulting from oxidation (oxycellulose). This fact has long been used as a basis for measuring the extent of oxidation and becomes very important in connection with the bleaching of cotton, because bleaching is an oxidation process, and too much bleaching can be detected by determining the methylene blue number.

Briefly stated, the method for determining this value consists of treating a weighed amount of dry cotton with a solution of dyestuff or known strength and subsequently determining how much dye is left in solution. In practice a number of precautions and limitations must be observed, and these will be mentioned in the following paragraphs.

The concentration of the dyestuff solution used should be 0.4 millimole per liter. This is made by diluting a stock solution containing 10 millimoles per liter. Methylene blue hydrochloride has the formula $C_{16}H_{18}N_3SCl$, with a molecular weight of 320. Thus 10 millimoles would be 3.2 gm. The stock solution is made by dissolving exactly this weight of dyestuff and making the solution up to exactly 1 liter. When this solution is diluted so as to contain 0.4 millimole per liter, one obtains the solution to be used in the actual determination of the methylene blue number.

An amount of dry cotton of about 1.5 to 2.0 gm is accurately weighed, placed in a 75 ml bottle and covered with 50 ml methylene blue solution (0.4 millimole) measured with a pipette. The stopper is painted with paraffin and the bottle wired in a shaking machine and shaken for 18 hours. Some of the solution is then transferred to a colorimeter tube, and the amount of dyestuff in it determined by comparing the color with that of a dye solution of known strength. This is best done in a Kober-Klett or similar colorimeter. In using an instrument of this type, a solution of known strength is placed in one cylinder and the unknown solution in another cylinder. These two solutions are viewed by the operator who, by means of glass plungers, can look through different amounts of the solution, and by adjusting these plungers, can match the depth of color in the two cylinders and get them exactly alike. It is generally assumed in colorimetric analysis that the concentrations of two solutions showing equal color intensity, when viewed in the colorimeter, are inversely proportional to the lengths of columns of solution traversed by the light in reaching the eye of the observer. That is, if one column of blue solution is 20 mm long and another column is 10 mm long and they both show the same color intensity, then the second one is twice as strong as the first one. These lengths are measured in the colorimeter and if the concentration of one solution is known, that of the other can be calculated by an inverse proportion. In the use of methylene blue solutions, however, this calculation can be made only if the two solutions are of about the same strength. Therefore, in the determination of the methylene blue number we use a solution containing 0.2 millimole per liter of the dyestuff as the standard for comparison, and we adjust the weight of cotton being tested so that it will absorb about 1/2 the dyestuff shaken with it. If 1/2 the dye is absorbed from the 0.4 millimole solution, it will then contain 0.2 millimole per liter. The first weight of cotton used in the test may be too large or too small; if so, more tests must be carried out until the residual solution contains approximately 0.2 millimole of dyestuff per liter. The limits of variation allowed are as follows: if the standard reads 20 mm, the unknown solution must be somewhere between 17 and 23 mm when the two colors are of equal intensity.

The values obtained by the above method are accurate and reproducible, but may be interpreted and conclusions drawn from them, only if the following points are kept in mind.

1. The origin of the raw material is a factor. Normally, bleached Egyptian cotton, especially Sakel cotton, has a higher methylene blue number than American cotton. The values for Sakel are about twice as large as for American cotton (0.92 as against 0.45 to 0.50).

2. Cotton that has been poorly scoured before bleaching will have a high methylene blue number, which is not reduced by further bleaching.

3. The alkalinity of the ash in the cotton goods is a determining factor. An increase in ash alkalinity results in an increase in the methylene blue number, so that for an accurate study, the disturbing effect of variations in ash alkalinity should be eliminated by washing all materials with dilute acid before making the determination.

4. The bleaching medium affects the value. Cottons bleached in an alkaline medium have a higher value than those bleached in an acid medium. Two such samples in which the same amount of oxidation was known to have taken place gave values of 2.15 and 0.91. This is to be expected, as it is well known that aldehyde groups are much more easily oxidized in an alkaline medium. This would yield an oxycellulose containing more COOH groups and therefore a higher methylene blue number.

5. The methylene blue number for cottons bleached in an acid medium is fairly constant. Over a range of oxidations equivalent to a consumption of 0 to 0.17% oxygen, the methylene blue numbers varied from 0.70 to 0.80. When an acid bleach is used, the reaction of hydrolysis enters in. As this is a splitting action resulting in the formation of aldehyde groups, the copper number should increase (see the accompanying chart). But the aldehyde groups are not so easily oxidized in an acid medium, and therefore the methylene blue number remains about constant.

6. Variations in the hydrogen ion concentration of the bleach affect the amount of absorption.[4] The relation between methylene blue number and the pH of the bleach is shown by the following figures, taken from Birtwell, Clibbens, and Ridge.[5] They are the results of bleaching sea island cotton in sodium hypochlorite solutions of different acidities. The amount of oxygen consumed was the same in each case.

pH of Bleach	Copper Number	Methylene Blue Number
13.0	0.43	1.83
12.0	0.62	2.15
11.2	0.52	2.23
10.2	0.63	2.96
9.0	1.20	2.90
7.0	2.54	1.50
4.6	3.88	1.14
2.7	3.71	0.90
1.0	2.10	0.96

DIFFERENCE BETWEEN HYDROCELLULOSE AND OXYCELLULOSE

The accompanying table shows that there are two types of oxidized cotton, one with a high methylene blue number (formed in alkaline oxidizing mixtures) and one with a high copper number (produced in acid oxidizing mixtures). (See I. T. C., page 143.) The cotton with the high methylene blue number has a high carboxyl group content, and the cotton with the high copper number has a high reducing group content. Now when cellulose is hydrolyzed in acid medium, the COOH group content is low. Krajcinovic[6] has proposed a method for distinguishing between hydrocellulose and oxycellulose of the first type mentioned above; the method is based on the fact that this type of oxycellulose has a higher COOH group content than hydrocellulose. The principle underlying this test is that COOH groups (of the nonreducing type of oxycellulose) will form addition compounds with aromatic amines and diamines, which can be diazotized and coupled to form colored compounds. Modified cellulose that has a small COOH group content will not do this; at least it will yield only a small amount of color. It is obvious that any method based on the amount of COOH group could not distinguish between hydrocellulose and an oxycellulose that had been formed in an alkaline medium. The Krajcinovic test is illustrated in the following experiment.

12. THE KRAJCINOVIC TEST

Moisten 0.5 gm each of hydrolyzed and oxidized cotton with 2 ml 0.1 M solution of benzidine in alcohol ($H_2N\text{-}C_6H_4\text{-}C_6H_4\text{-}NH_2$). Let stand 2 minutes and then rinse with water. Diazotize by immersing the sample in a mixture of 15 ml HCl (3% solution) and 5 ml $NaNO_2$ (3% solution, which should not be made up too far in advance). Let stand 3 minutes and rinse with water. Add 2 ml β-naphthol (a 0.1 M solution in alkali). Let stand 5 minutes. Rinse and observe the color. Mount the sample. The hydrolyzed sample is I-12, and the oxidized one is I-13.

[4] For a further and complete discussion of methylene blue absorption, the reader is referred to:
Birtwell, Clibbens, and Geake, J. Textile Inst., 14, T297-313 (1923).
Birtwell, Clibbens, and Ridge, J. Textile Inst., 16, T13-52 (1925).
Clibbens and Geake, J. Textile Inst., 17, T127-144 (1926).

[5] J. Textile Inst., 16, T32 (1925).
[6] J. Textile Inst., 38, T11 (1947).

The Krajcinovic Test

I-12 I-13

Hydrocellulose Oxycellulose

Teacher: See page 73 for preparation of hydrolyzed and oxidized cotton for this experiment.

13. DETERMINATION OF STRENGTH OF BLEACH LIQUOR (I. T. C., page 180)

This determination is based on the fact that hypochlorites will react with iodide ion in acid medium to liberate iodine. This is an oxidation reaction in which iodine is oxidized from the iodide ion to the neutral iodine atom. Write equation to show the reaction of NaOCl with HI to form I_2.

____

The amount of iodine in a solution can be determined by titrating it with a standard solution of sodium thiosulfate.

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

The addition of thiosulfate is continued until the I_2 color has disappeared. If we know the exact amount of $Na_2S_2O_3$ used in this titration we can calculate how much I_2 was liberated by the action of NaOCl, and from this the amount of hypochlorite in an unknown bleach. However, bleach liquors are not evaluated in terms of hypochlorite ion but in terms of available chlorine. The term available chlorine does not really have anything to do with chlorine that can be utilized but is a manner of expressing the oxidizing power of bleach. One atom of chlorine as it is found in a hypochlorite is equivalent to two atoms of iodine (as shown in the equation filled in on the solid line above) and therefore is equivalent to one oxygen. However, the calculations are made on the basis of an equivalent weight of 35.5 for chlorine.

The determination of available chlorine involves the use of burettes. As some small laboratories do not have burettes, an optional method (Method B), in which burettes are not needed, is described.

It is suggested that the determination of available chlorine be made on three kinds of bleach -- concentrated bleach as purchased by the laundry, the laundry bleach after it has been diluted and is ready to add to the wash wheel, and household bleach such as Clorox or Roman Cleanser.

Method A

Withdraw a 10 ml sample of bleach liquor with a pipette and carefully transfer it to a 100 ml volumetric flask. Fill the flask exactly to the mark with distilled water, stopper with a cork, and mix thoroughly by up-ending the flask several times.

Withdraw 10 ml of this dilute bleach with a pipette and transfer it to a small Erlenmeyer flask.

What fraction of the original sample of bleach does this represent?__________ Add 20 ml water, 5 ml KI (20% solution), and 5 ml glacial acetic acid to the flask. Cork and let stand 5 minutes.

What do you see?______________________________ This color is due to what?________________

Prepare a burette by putting a thin layer of grease on the stopcock and clean the burette thoroughly. It is not necessary to let it dry; simply rinse it twice with the solution you are going to use in it. Fill the burette with 0.1 N $Na_2S_2O_3$ (be sure that the tip below the stopcock is filled with the solution). It is not necessary that the top of the column of liquid be exactly at the zero reading. Record the exact reading in the chart on page 28.

Add the $Na_2S_2O_3$ to the flask slowly, while whirling the flask a little, until the iodine color has become a light brown. The object of this titration is to reach a point at which the iodine has just been destroyed by the thiosulfate. Theoretically, the thiosulfate might be added until the iodine color disappears, but such an end point is very elusive because it is difficult to tell the exact point at which the color disappears. The end point can be made much more sensitive by adding a little starch solution, which forms an intense blue color with only small amounts of iodine.

Add 1 ml freshly prepared starch solution and continue the addition of $Na_2S_2O_3$, drop by drop, stopping just as the blue color disappears. Record the burette reading.

Run another titration on a 10 ml sample of the diluted bleach.

Name of bleach ____________________

	First Titration	Second Titration
Last reading	____________	____________
First reading	____________	____________
Ml $Na_2S_2O_3$ used	____________	____________

1 ml $Na_2S_2O_3$ used = ________gm chlorine

If the two titrations are close enough to satisfy the teacher, take an average of them and use this figure in the following calculations.

Total gm Cl in 10 ml diluted bleach ________

Total gm Cl in 10 ml original bleach________

Assume that the specific gravity of the original bleach is 1.0; what is the weight of 10 ml of it?

________This weight of bleach contains how much available chlorine?________gm. Calculate the per cent available chlorine in the bleach.________

Method B

This method does not require the use of pipettes or burettes. It is not so accurate as Method A, but we find that it serves the purpose of demonstrating the differences among the three kinds of bleach and is good enough for laundry control purposes.

Measure 1 tablespoon (T) of the bleach liquor as accurately as possible and transfer to a standard size cup. Fill the cup with water and stir carefully until well mixed. If some of the solution is spilled, another mixture must be prepared. One standard cup contains 8 liquid oz, which is equivalent to 16 T.

Carefully measure and transfer 1 T of the diluted bleach to a 150 ml beaker. This is equivalent to what fraction of the original spoonful?________ Add 20 ml water, 5 ml KI (20% solution), and 5 ml glacial acetic acid. Mix with a glass rod and let stand 5 minutes (leave the rod in the beaker).

The iodine, which is liberated and is shown by its brown color, is to be destroyed by adding a 1.0 N $Na_2S_2O_3$ solution drop by drop; count the drops required to destroy the color of the iodine. These drops can be added from a medicine dropper or a piece of glass tubing drawn out to a tip like a pipette.

Add 1.0 N $Na_2S_2O_3$, stirring slowly just until the iodine color is destroyed. (Starch may be used as described in Method A, if desired.) Count the drops and record on page 29.

Titrate a second T of the diluted bleach in the same manner. If the teacher is satisfied with the two results, take an average and use it to calculate the strength of the bleach liquor.

Name of bleach ________________.

Number of drops used in first titration________; number of drops used in the second titration ________. If we assume that the average drop is 0.05 ml, then 1 drop of 1.0 N $Na_2S_2O_3$ will equal 0.00178 gm chlorine. Calculate the number of grams Cl in 1 T diluted bleach________; in 1 T of original bleach________. Assuming that the original bleach has a specific gravity of 1.0, what is the weight of 1 T of it?________gm. This weight contains how much available chlorine? ________gm. Calculate the per cent available chlorine in the bleach________%.

Refer to I. T. C., page 180, and answer the following questions: I found laundry bleach, as purchased, to contain________% available chlorine. If I wished to make 20 gallons of a 1% bleach I would____

What weight of chlorine in a bleach is generally used by a laundry for a 100-lb load of wash? __________What volume of a 1% bleach would this require?________________

I found the per cent available chlorine in the diluted laundry bleach to be________%. Does this check with the strength of bleach that a washroom foreman will usually add to the wash wheel? __________What is the usual strength?__________How many quarts will he usually add for a 100-lb load?__________How many grams of chlorine would this contain?__________On this basis, how many liquid ounces of the bleach you tested would recommend for an ordinary load of about 8 lb in a home laundry bleaching operation?________________

I found household bleach to contain________% chlorine. One T is 1/2 ounce. If your washing machine holds 12 gallons and you add 1 T of household bleach for each gallon of water, how many ounces of bleach are you adding?________How many grams of available chlorine would you be adding?________The average load is about 8 lb. How much chlorine would you be adding per pound of wash?________How much per 100 lb of wash?________How much does the laundry use for 100 lb of wash?________If you wish to use laundry bleaching formulas in the home, how much, in ounces, tablespoons, or teaspoons, of household bleach would you recommend for a load?________________

QUESTIONS

1. Can cotton be oxidized in acid medium? In alkaline medium?

2. When cotton is bleached with hypochlorites, why does the reaction proceed more rapidly when exposed to air than when submerged in bleach liquor?

3. What is bleaching powder? What would be the result of adding excess Na_2CO_3 to a solution of calcium hypochlorite? Equations and names.

4. Would the above solution be acid, neutral, or alkaline?

5. Why should bleach liquor be stored out of contact with air?

6. In what two ways could overbleached areas on a cotton cloth be detected? Which do you think is the more satisfactory?

7. What is meant by copper number? Methylene blue number?

8. Are these values always good criteria of excessive oxidation? Discuss the effect of pH of the bleaching bath.

9. How did you make these tests in a qualitative way?

10. By what test can the difference between hydrocellulose and oxycellulose be shown?

11. With what type of oxycellulose would this test not be reliable?

12. Make a brief statement of the chemical reactions on which the determination of strength of bleach liquor is based. Give equations also.

13. What is meant by available chlorine?

14. Why is starch used in a titration involving the disappearance of iodine?

THE ACTION OF ALKALIES ON COTTON (I. T. C., page 189)

14. ACTION OF DILUTE AND STRONG NaOH ON COTTON

Measure two 5-yd lengths of cotton yarn with a yardstick. (A No. 6 knitting cotton is suitable.) These should be measured carefully because they will be measured again after the alkali treatment to determine the amount of shrinkage. Fold them into small skeins. One will be I-14 and the other I-15. They may be tied in some way so as to identify them.

Make 200 ml of 5% NaOH by diluting the reagent NaOH. Put I-14 into this solution. Put I-15 into some 23% NaOH. Leave each of them for 5 minutes. Describe how the two skeins behave when they are immersed in the alkali.

I-14 ____________________

I-15 ____________________

After 5 minutes remove the skeins and rinse them in running water for 10 minutes. RETURN THE 23% NaOH TO THE STOCK BOTTLE. Remove the skeins from the running water. Do they

feel slippery? __________ Why? __________ It is difficult to remove all alkali by rinsing with water, and so we shall do it with acid. Immerse the skeins in some 1% acetic acid and stir for 5 minutes; rinse again for 10 minutes; squeeze out and dry.

At the next laboratory period, measure the length of each skein and fill in the following chart.

Shrinkage of Cotton with Alkali

	Original Length	Length after Treatment With		Per Cent Shrinkage
		5% NaOH	23% NaOH	
I-14	______	______	______	______
I-15	______	______	______	______

Mount about 4-in. samples of the original yarn, I-14, and I-15. Save the rest of I-15.

Original	I-14 With 5% NaOH	I-15 With 23% NaOH

Cotton Treated with Sodium Hydroxide

Which one was mercerized?________ Does it have an increased luster?________

Will it be found stronger than the original?________ Which one will be dyed a darker color with direct cotton dyes?________ Which one showed more shrinkage?________

________ Make brief but clear statements about the effect of 5% and 23% NaOH on cotton yarn.

____

____

____

15. MERCERIZING UNDER TENSION

Measure 5 yd of cotton yarn and wrap it neatly and tightly around a heavy wire square. This square is made of heavy fence wire bent to make a frame about 4 or 5 in. square. The ends are twisted together so they will not slip. This makes a rigid frame on which yarn can be wrapped and which will prevent shrinkage of the yarn when it is mercerized. Tie the ends of the yarn securely and immerse the frame in enough 23% NaOH to cover the frame and yarn.

How does the yarn behave?________

How does it seem to change in appearance?________

Would it act the same way if immersed in 5% NaOH?________

After about 5 minutes remove the frame without taking off the yarn. Wash and rinse it as directed in Experiment 14. RETURN THE 23% NaOH TO THE STOCK BOTTLE. Remove the yarn from the frame. If sufficient rinsing has been given the yarn it will not feel slippery. If these conditions have not been attained, rinse the yarn with more 1% acetic acid and then with more water.

This is I-16. Does it have an increased luster?________ Should it be stronger than it was?________ Mount a small sample of I-16 and save the rest.

I-16

A Sample of Cotton Mercerized under Tension

16. STRENGTH OF MERCERIZED COTTON

Determine the tensile strength of unmercerized yarn (the original yarn), yarn mercerized without tension (I-15) and yarn mercerized with tension (I-16). Do this whenever the tensile strength machine is available. It may even be done after Experiment 17 has been performed.

To test the tensile strength of yarns, remove the clamp jaws from the testing machine and put spools in place of them. Wind the yarn around these spools and tie it with a knot that will not slip. Use the entire length of yarn, which should be enough for two or three turns around the spools. Operate the machine as directed on page 12. When recording the tensile strength in the accompanying table, reduce it to one turn, that is, if you have used three turns around the spools, divide the found strength by three. Save all the yarns after testing. Record your results in the following table.

Strength of Cotton Knitting Yarn

	Pounds	Change in Strength, %
The original yarn	________	
Yarn mercerized without tension (I-15 or I-18)	________	________
Yarn mercerized with tension (I-16 or I-19)	________	________

17. DYEING MERCERIZED COTTON

You will dye the yarns left from Experiment 14 and 15, that is, the original cotton yarn and the yarns that have been mercerized in two ways. If you have not been able to use the tensile strength machine you may dye them anyway, and then test their strength later. Dyeing will not change their strength.

Fold these yarns into small skeins and tie them in some way so you can identify them. Prepare the dye bath:

300 ml distilled water
25 ml Benzopurpurin 4B (2/1)

Wet out the skeins, immerse them in the cold dye bath, raise it to the boil, and continue boiling gently for 20 minutes. Wash the yarn in running water until no more color is removed. Number the dyed yarns as follows:

Unmercerized yarn is I-17
Yarn mercerized without tension is I-18
Yarn mercerized with tension is I-19

Cut off small samples for mounting and, if the tensile strength has not already been determined, save the rest for this test. If the strength has been tested, discard them.[7]

I-17 Unmercerized	I-18 Mercerized without tension	I-19 Mercerized with tension

Cotton Yarn Dyed with Benzopurpurin 4B

CHEMICAL TEST FOR MERCERIZED COTTON

In making this test use short pieces of mercerized cotton yarn along with some unmercerized yarn. Make proper allowance for any difference in size of the two yarns. The properties of mercerized cotton and ordinary cotton differ merely in degree. They are so much alike that it is difficult to tell the difference. In general, cotton is more active after it has been mercerized, and the increased activity is a basis for this chemical test, which is concerned with the absorption of iodine solutions.

18. THE HUBNER TEST FOR MERCERIZED COTTON

This test is based on the ability of cotton to form a color with iodine in the presence of strong solutions of zinc chloride. Mercerized cotton is more active than ordinary cotton and therefore is attacked by $ZnCl_2$ first and yields a darker color with iodine. You are acquainted with the fact that starch turns blue when iodine is added to it, and for this reason the yarns being tested must be free from any starch sizing. To insure this the test pieces must each be boiled for 10 minutes in three changes of distilled water before they are ready to test.

After samples of mercerized and unmercerized cotton have been desized, they should be frayed out so as to loosen the individual fibers. Wet out the sample with water, blot slightly between filter papers, and spread out on a white plate or a glass plate with white paper under it. Add a few drops of $ZnCl_2$-I_2 reagent (page 74). Mercerized cotton will form a deep reddish violet color, whereas unmercerized cotton will be only slightly stained. It often happens that the color of the solution is so dark that the color effect on the fibers cannot be detected. If this occurs the fibers should be transferred to a beaker of distilled water. Note that the color rinses off cotton very quickly but is retained by mercerized cotton much longer. Other swollen celluloses (viscose and cuprammonium rayon) show the same behavior as mercerized cotton when subjected to this test.

[7] For those wishing extensive information on the mercerization of cotton, a fine review of the literature will be found in an article by Clibbens, J. Textile Inst., 14, T217-249 (1923), and a still more detailed discussion in Marsh's Mercerizing, D. Van Nostrand Company, 1942.

SECTION
II

The Chemistry of Wool

19. COMPARISON OF RAW WOOLS

Examine two samples of wool in the grease. (If possible, a fine and a coarse wool should be provided for this purpose.) Mount sample of each wool, with its name, and under the samples write all the physical properties you can determine by your examination, keeping in mind the fact that you are comparing the wools.

	II-1	II-2
Name	______________________	______________________
Properties	______________________	______________________
	______________________	______________________
	______________________	______________________
	______________________	______________________

ELEMENTS IN WOOL

20. TESTS FOR NITROGEN AND SULFUR IN WOOL

(a) Nitrogen by Dry Distillation

Place a few short pieces of wool yarn in a test tube. Hang a piece of wet red litmus paper across the top of the tube and heat the bottom of the tube until the wool distills. Note the change in color of litmus paper.

When wool distills does it produce an acid or alkaline gas? ______________________

What is probably the only gas you know which is of this type? ______________________

What is the formula for this gas? ______________ This proves that wool contains what element?

____

(b) Nitrogen by Wet Reaction

Put a few pieces of wool yarn in a small beaker and cover with reagent NaOH. Put a piece of wet red litmus paper on the underside of a small watch glass and cover the beaker with it. Boil gently for 4 to 5 minutes. Save the solution for Experiment 20 (d). What happens to the litmus paper?____________________What gas is evolved from a hot solution of wool in NaOH?________________ Therefore wool contains what element?________________

(c) Sulfur by Dry Distillation

Place a few pieces of wool yarn in the bottom of a test tube and cover the top of it with a piece of filter paper dipped in lead acetate, $Pb(C_2H_3O_2)_2$. Heat the tube until the wool distills. Note the change on the lead acetate paper. The color is due to a deposit of lead sulfide on the paper. If only a thin layer is deposited it will have a silvery appearance, but if there is a larger deposit it will be black, as you know.

What ion will react with lead ion to make lead sulfide?________________

What gas contains this ion?____________________Since this gas is evolved when wool is distilled, it proves the presence of what element in wool?________________

(d) Sulfur by Wet Reaction

Use the alkaline solution of wool made in Experiment 20 (b). Pour some of it into a test tube and carefully pour some lead acetate solution down the side of the tube. You will note that black and white precipitates are formed, producing a gray mixture. There are two ions in the alkaline solution that will react with lead ion, hydroxide and sulfide.

Which one will give a black precipitate?____________________Write equations for the formation of both precipitates.____________________________________

____

IMPURITIES IN RAW WOOL

21. WOOL GREASE

Put some raw wool into a small, wide-mouthed bottle until it is about 1/3 full. Add CCl_4 until the wool is well covered and then stir with a glass rod for about 5 minutes. What does CCl_4 do to wool grease?____________________

Pour off the solution onto a large watch glass and evaporate the solvent by heating over a beaker of boiling water. Squeeze out the wool and save for Experiment 22.

Examine the wool grease left after evaporating the CCl_4. How does it feel?________________ ____________________ What color is it?________________Add 5 ml distilled water to it and rub with your fingers. Is it soluble?________________ Does it emulsify?______ Now add 5 ml soap solution and rub it again. Does the grease emulsify more easily than with plain water?________________ Would you use water or soap solution to remove wool grease from raw wool?________________________

22. WOOL SWEAT

Are there impurities left on the wool after the CCl_4 treatment?________________

What two names are applied to this impurity? ____________________

Is it soluble in water? ____________

Put the wool from Experiment 21 into a small beaker, add 30 ml distilled water, and boil gently for 2 or 3 minutes. Filter into a small casserole or evaporating dish and evaporate just to dryness. Note color of the solid.

Heat the dry solid and note the color change that takes place. Continue heating with a very hot flame until the residue in the casserole is white. Let cool and then carefully add 5 ml reagent HCl and see if any effervescence occurs.

What class of inorganic salts will effervesce when treated with strong acids? ____________

When suint is subjected to high temperature, what is the final product? ____________

This tells us something about the components of wool sweat, because organic compounds will char when heated. Furthermore, when sodium or potassium salts of higher fatty acids are heated they char, and then if heated more they decompose and form carbonates, Na_2CO_3 or K_2CO_3. Did you find that this was the behavior of the solid suint in the casserole? ____________

You therefore conclude that wool sweat contains what type of compound? ____________

Make statement regarding the solubility (and insolubility) of wool grease and wool sweat in water and in CCl_4. Wool grease is ____________________

Wool sweat is ____________________

23. DETERMINATION OF SCOURING LOSS

Weigh 4 to 5 gm of ____________ wool on the semiquantitative balance. This need not be exactly 4 or 5 gm, but whatever it is must be known exactly, e.g., it might weigh 4.57 gm or 5.13 gm. If possible, estimate the third decimal place in the weight. Avoid small bunches of loose fibers, for it is easy to lose them during the handling of the wool in this experiment. A good procedure is to weigh a bunch of wool on the rough scales, so that you know it is somewhere near the amount desired, and then simply put it on the finer balance and weigh it accurately.

Prepare three scouring baths as follows:

Bath No.	Volume of Soap (5/1)	Volume of Soda Ash (10/1)	Volume of Distilled Water
1	30 ml	20 ml	65 ml
2	15	10	90
3	5	5	105

Put the weighed wool into bath 1 at 50° C. Work it with your hands, avoiding too much squeezing. Simply move it about in the bath or lift it up and then let it drop back into the bath. Continue for 15 minutes.

Transfer the wool to bath 2, also at 50° C. Be sure to get <u>all</u> the wool and squeeze it lightly before putting it in the second bath. (Baths 1 and 2 are to be saved for the next experiment.) Handle the wool in bath 2 the same as you did in 1. Then transfer it to bath 3 at 50° C and again scour it. Remove the clean wool and rinse it in three or four changes of distilled water. Do not lose any of the fibers during this rinsing. Spread out the wool and let it dry until the next laboratory period, when you will weigh it accurately on the semiquantitative balance.

Weight before scouring________________gm

Weight after scouring________________gm

Loss in weight________________gm

II-3

Per cent loss in weight________________%

Is your wool sample a low, high, or medium scouring wool?________________

Has your wool been felted during scouring? ________________ How much water is in each scouring bath?________________

Sample of Scoured________________Wool.

Weight of soap in bath 1________________ 2________________ 3________________

Weight of Na_2CO_3 in bath 1________________ 2________________ 3________________

Assume that you wish to wash a 1-lb wool sweater in the same way that you scoured this small amount of wool. (Assume that the small sample weighed 5 gm.) For this purpose you have available solid soap, solid soda ash, and water. Tell how you would make up the three baths, expressing the amounts in ounces and gallons.

1 ounce = 28.36 grams
1 pound = 453.76 grams
1 gallon = 3.785 liters

I would make up the baths as follows:

1 ________________ oz soap ________________ oz soda ________________ gal water

2 ________________ oz soap ________________ oz soda ________________ gal water

3 ________________ oz soap ________________ oz soda ________________ gal water

24. THE WASTE SCOURING LIQUORS

Combine the first two baths left from Experiment 23 and let this represent an industrial waste liquor. It contains certain substances in real solution and other substances in emulsion form.

In solution it contains________________

In emulsion it contains________________

(a) The Lime Magma

Fill a large test tube 1/3 full of this liquor and add about 25 ml saturated $CaSO_4$ solution. Shake it thoroughly and let it stand. Note the lime magma that rises to the top.

What insoluble compound is formed when soap reacts with calcium ions?________________

when soda ash reacts with calcium ions?________________What substances will be found in the lime magma?________________

(b) The Acid Magma

Fill a large test tube about 1/3 full of the waste scouring liquor and add 25 ml reagent H_2SO_4. Mix thoroughly and let stand. Note the acid magma which forms at the top.

How does H_2SO_4 react with soap?________________

How does it react with soda ash? ____________________

What substances will be found in the acid magma? ____________________

What would be formed if the lime magma were treated with H_2SO_4? ____________________

____

25. DETERMINATION OF MOISTURE IN WOOL

Weigh 5 gm raw wool accurately on the semiquantitative balance. Place it on a large watch glass that has your name on a sticker. Leave it on top of your desk. It will be placed in an oven at 105° C for the proper length of time, cooled in a desiccator, and handed to you at the next laboratory period. This bone-dry wool must be weighed at once before it begins to absorb moisture from the air.

Name of the wool ____________________

Air-dry weight __________ gm

Bone-dry weight __________ gm

Grams moisture __________

Per cent moisture in the wool is ________ %.

Allowing a regain of 16%, calculate the conditioned weight of a 1000-lb batch of this particular air-dry wool. Show your calculations below.

26. THE ACTION OF ACIDS ON WOOL

You will treat 4 or 5 pieces of wool yarn with acids

H_2SO_4 HCl HNO_3 CH_3COOH

of two strengths and under varying conditions. One strength of acid will be concentrated, and the other a 10% solution. (This latter you will make up yourself from the reagent.) The conditions will be "cold," "boiling," "dried with rinsing," and "dried without rinsing."

Note:

(a) The time of each treatment will be about 3 minutes.

(b) The yarn treated with concentrated acids requires just enough acid to cover it, and if it is to be dried without rinsing it must be well squeezed out with glass rods and blotted with filter paper before drying.

(c) The yarn to be boiled must be well covered with the acid, using not less than 100 ml of it, and the boiling should not be too vigorous. We do not want to get the effect of boiling acid plus air but of the acid alone. The material must therefore be kept below the surface of the reagents used. The combined action of air and reagent is usually entirely different from the action of the reagent alone.

(d) When the yarn is being dried, the various batches must be placed far enough apart so that the acid from one batch does not get on its neighbor.

(e) In numbering, keep the same order of acids given above, e.g., for the first treatment, H_2SO_4 = II-4, HCl = II-5, HNO_3 = II-6, and CH_3COOH = II-7. Then for the second treatment H_2SO_4 = II-8, HCl = II-9, HNO_3 = II-10, and CH_3COOH = II-11.

(f) Make the proper calculations for making up the 10% acids from the reagents and record them in the following table. Have them checked before using them in the tests.

I will use	________	ml reagent H_2SO_4 plus	________	ml H_2O to make	________	ml 10% acid
	________	HCl	________		________	
	________	HNO_3	________		________	
	________	CH_3COOH	________		________	

The Treatments:

(a) Cold concentrated acid, dried without rinsing (II-4 to II-7)
(b) Cold concentrated acid, dried after rinsing (II-8 to II-11)
(c) Cold 10% acid, dried without rinsing (II-12 to II-15)
(d) Boiling 10% acid, dried without rinsing (II-16 to II-19)
(e) Boiling 10% acid, dried after rinsing (II-20 to II-23)

Mount the samples on the squares on page 40.

Do you consider that wool is very sensitive to dilute acids?__________Which acid harms it the least?__________Are mineral acids more harmful to wool than organic acids?__________

27. ABSORPTION OF DILUTE ACIDS BY WOOL (I. T. C., page 268)

What basic group does wool contain?______________ Due to its presence, wool will absorb acids from dilute solutions and part of this acid cannot be rinsed out. This means that the acidified wool will have some properties that are different from ordinary wool.

Among such properties is its ability to react with, and be dyed by, acid dyes. We shall use this fact to prove that acidified wool is different. That is, we shall use the acid dyestuff as a sort of indicator. Acid dyes are salts of color acids. Since these complex organic color acids are weak acids, if we treat their salts with a strong acid such as H_2SO_4 we shall liberate the weaker color acid, which is then available for dyeing wool. Therefore, up to a certain point, the more acid there is on the wool, the darker it will be dyed by an acid dye. If wool has no acid on it, it will merely be stained and much of the color will wash out afterwards.

Prepare two skeins of wool yarn about 2 yd long.

Boil one of the skeins in 300 ml distilled water for 5 minutes. Boil the other skein for 5 minutes in 300 ml of 2% H_2SO_4 solution. In the subsequent handling of these skeins every precaution must be taken so that no acid whatever comes into contact with the first skein. It might come from your hands, from a graduate, from beakers, or from glass rods or other sources. You must use care in avoiding this. The acidified skein should be lightly rinsed before dyeing it. The other need not be.

Prepare two dye baths, each containing

25 ml acid dye (2/1); use an acid violet or croceine scarlet
275 ml distilled water

Enter one skein in each bath, bring to a soft boil, and continue for about 20 minutes, turning the skeins occasionally. After a few minutes note the color of the baths.

Which bath has lost more color? ______________________ Which wool is absorbing more dyestuff? ______________________ Remove the skeins and wash in separate beakers under running water. Mount them on page 41.

II-4	II-5	II-6	II-7
H_2SO_4	HCl	HNO_3	CH_3COOH

Cold Concentrated Acid, Dried without Rinsing

II-8	II-9	II-10	II-11
H_2SO_4	HCl	HNO_3	CH_3COOH

Cold Concentrated Acid, Dried after Rinsing

II-12	II-13	II-14	II-15
H_2SO_4	HCl	HNO_3	CH_3COOH

Cold 10% Acid, Dried without Rinsing

II-16	II-17	II-18	II-19
H_2SO_4	HCl	HNO_3	CH_3COOH

Boiling 10% Acid, Dried without Rinsing

II-20	II-21	II-22	II-23
H_2SO_4	HCl	HNO_3	CH_3COOH

Boiling 10% Acid, Dried after Rinsing

II-24 II-25

Ordinary Wool Acidified Wool

Both are dyed with ____

DIFFERENTIATING REACTIONS

28. NEGATIVE TESTS FOR WOOL

Cold concentrated HCl will not dissolve wool or cotton but will dissolve silk in a short time.

Loewe's reagent (alkaline copper solution) will not dissolve wool or cotton but will dissolve silk when warmed in it.

These two tests may be used for distinguishing among these fibers. The following experiments show additional tests that may be used for the same purpose.

29. MILLON'S TEST

This is one of the simplest and best tests for distinguishing between animal and vegetable fibers. Silk, wool, and hair are all quickly and definitely identified by it. The material to be tested is moistened with the reagent, allowed to stand a short time, and the color noted. Do this with wool and cotton. Use only a few drops of reagent for each test.

Wool produces a ________________ color. What does cotton do? ________________________________

Even when animal fibers have been dyed they will yield colors which show a change toward the red. Suppose a union has a cotton warp and the filling is composed of two wool yarns shot together, with six cotton yarns between them. Could you use the Millon test and show not only that the material contains some wool, but also roughly the proportion of wool in it? __________ How would you judge the proportion of wool? ____

____

30. PICRIC ACID

Picric acid, trinitrophenol, is an acid dyestuff that furnishes its own acid for dyeing animal fibers.

Put a few pieces of wool and cotton yarns, together with a small piece of silk, into a medium size beaker. Add picric acid (5/1) sufficient to cover them well, and boil gently for 3 minutes. Wash well and dry. Mount samples on page 42.

II-26 II-27 II-28

Wool Silk Cotton

Dyed with Picric Acid

31. ALKALINE LEAD ACETATE AND PICRIC ACID TEST

Mix 1 part of alkaline lead acetate solution with 3 parts of picric acid (5/1) in a large test tube. Enter some wool, silk, and cotton. Warm in a hot water bath (not boiling) until the wool has definitely changed color. Pour the contents of the test tube into a beaker, decant the liquid, and wash the yarns with water. Then add some dilute acetic acid (reagent diluted 20 times). Let stand a few minutes and again wash thoroughly. Mount the yarns.

What causes the wool to have the color it has? ____________________

What causes the silk to have the color it has? ____________________

II-29 II-30 II-31

Wool Silk Cotton

All Treated with Alkaline Lead Acetate and Picric Acid

From these results do you think silk and cotton contain any sulfur? ____________________

The reagent used in this test is quite strongly alkaline. What do you think would happen to the wool yarns if they were left too long in the hot reagent? ____________________

A piece of knit goods is supposed to be all wool. If you test a piece of it in the above manner, what results would you obtain that would make you report that the material is part cotton?

____

____

32. CHLORINATION OF WOOL (I. T. C., page 278)

Wet out a 3-gm skein of wool yarn and immerse it in 100 ml of 1.5% HCl for 5 minutes. Remove the wool, squeeze out well, and immerse in 100 ml bleach liquor, $Ca(OCl)_2$. Let stand for 1 hour with occasional stirring. Note the feel of the wool. After 1 hour remove the wool, squeeze out the excess bleach liquor, and immerse in a bath of 0.5% HCl. Let stand 5 minutes and then wash thoroughly in running water. Does it still have the odor of chlorine? If so, treat with an antichlor, that is, immerse it in a 2% sodium bisulfite solution for 5 minutes, wash thoroughly, and dry.

The preceding treatment has been planned to produce an overchlorination of the wool, so that you may see the bad effects of such overtreatment. Mount a few strands of this wool as II-32 and save the rest for the next two experiments.

II-32

Overchlorinated Wool

Describe the physical properties of this wool as compared with the original wool. Mention such things as size, fluffiness, elasticity, feel, strength.

Could calcium hypochlorite be used to bleach wool? ____________________

33. DYEING CHLORINATED WOOL

Prepare two dye baths, each containing

15 ml acid dye (acid violet, acid navy blue, or croceine scarlet)
10 ml glauber's salt (50/1)
100 ml distilled water

Make up a half skein of ordinary wool and dye it in one bath (II-33). In the other bath dye one-half of the wool left from Experiment 32(II-34). Heat the baths to about 60° C and then enter the wool. Work for a few minutes and then lift the skeins and add 5 ml H_2SO_4 (10/1) to each bath. Enter the skeins again and boil gently for 15 minutes. If the level of the dyebath goes down during this boiling, add some distilled water to it. After 15 minutes boiling, lift the skeins and add 5 ml more H_2SO_4 to each bath. Continue boiling for 5 minutes longer. Wash the skeins, dry, and mount them.

II-33 II-34

Ordinary Wool Chlorinated Wool

Both dyed with______________________________

In which bath did the color exhaust more quickly?____

Which wool is dyed darker?________________________Is it dyed evenly or is it more or less spotted?

___________________________If a cloth is woven from chlorinated wool and portions of the yarn have been overchlorinated, what results would you expect to obtain when the cloth is dyed with an acid dye?____

34. CHLORINATED WOOL AND FELTING

Make a felting bath by mixing

100 ml soap solution (5/1)
100 ml soda ash solution (10/1)

Make up a half skein of ordinary wool (II-35) and put in the bath, together with the rest of the chlorinated yarn made in Experiment 32. Heat the bath as hot as your hands will stand and then scour the yarn thoroughly by rubbing it between your hands. Treat it as though it were very dirty and you were trying to get it clean. The object is to get it felted if possible, so that the more vigorously you handle it, the better it will be. Continue scouring for 5 or 6 minutes. Rinse the wool in two or three changes of distilled water and then under running water.

II-35 II-36

Ordinary wool felted Chlorinated wool felted

Take some of each yarn and try to open it up and separate it into its individual plies. Which one can be separated more easily in this way?________________________________

Which kind of wool felts the more easily?________________________________

Compare ordinary wool with chlorinated wool in the following ways:

Color________________________________

Felting property________________________________

Strength________________________________

Elasticity________________________________

Dyeing with acid dyes________________________________

QUESTIONS

1. How would you demonstrate the presence of nitrogen in wool?
2. Why is wool soluble in hot NaOH?
3. After it has dissolved in NaOH, in what form is the sulfur found? How can you prove it?
4. How can wool sweat be separated from wool grease? What is another name for each one?
5. Which is soluble in water?
6. How can the other one be removed from wool?
7. What chemical compounds are found in each one?
8. What is meant by a high scouring wool?
9. About how much does it lose when scoured?
10. What is a lime magma? How is it made? What does it look like? What does it contain?
11. Is wool more sensitive to acids or to alkalies?
12. Tell how wool reacts with each of the following and indicate whether or not the reagent would be of any use for distinguishing between animal and vegetable fibers:
    (a) concentrated HCl
    (b) hot picric acid
    (c) Loewe's reagent
    (d) alkaline lead acetate and picric acid
    (e) boiling 5% KOH
    (f) Millon's reagent
13. Why should it ever be desirable to chlorinate wool?
14. How is wool chlorinated? Give steps in the process.
15. Why is overchlorinated wool undesirable?
16. How does chlorinated wool compare with untreated wool in regard to dyeing with acid dyes and in felting property?
17. How does overchlorinated wool look and feel?

SECTION
III

Laboratory Examination of Hard Water (I. T. C., page 87)

35. TESTS FOR IONS

Evaporate about 100 ml hard water to about 1/2 to 1/3 of its volume. Filter. This is the stock solution that you will test. The concentration of ions has been increased by reducing the volume. Even so you must bear in mind that the concentration of ions is very small. When you make tests for ions do not expect to get large amounts of precipitates. In some instances it may be only a cloudiness.

(a) Test for Calcium. Add a few drops NH_4Cl and then a few drops of ammonium oxalate, $(NH_4)_2C_2O_4$ to 10 ml stock solution. Mix and let stand. Calcium oxalate will precipitate if there are Ca ions in the water. Save.

(b) Test for Magnesium. Use the mixture obtained in (a). Filter and treat filtrate with 1 ml NH_4OH and a few drops of Na_2HPO_4 solution. Mix and let stand. A white crystalline precipitate shows the presence of Mg ions in water.

(c) Test for Chloride. To 5 ml stock solution add a few drops HNO_3, mix, and then add a few drops $AgNO_3$. A white precipitate indicates Cl ion. It might also indicate bromide or iodide.

(d) Test for Sulfate. To 5 ml stock solution add a few drops HCl, mix, and then add a few drops $BaCl_2$. A white precipitate shows the presence of SO_4 ions.

Make a statement about the ions you found present. ______________________________

____

____

Total Hardness by Soap Method

When soap is added to hard water a certain amount of the soap is destroyed, that is, precipitated in the form of insoluble calcium or magnesium soaps. In order for soap to act as a detergent it must be in solution, and therefore the soap that is precipitated by the hardness of the water is not available for cleaning purposes. Another way to say the same thing is that when solutions of soap are shaken they will form a suds or lather that will stand up for several minutes without breaking, but if the soap is precipitated (insoluble calcium and magnesium soaps) no suds will be produced. Thus if a few drops of soap solution are added to some distilled water and the mixture is shaken, a suds will be formed at once and it will stand up for a few minutes. However, if the same amount of soap solution is added to hard water it will be precipitated, after which shaking will not form a suds. If the soap solution is added in small portions, a point will be reached when all of the hardness of the water will have been precipitated along with soap. In other words, the soap will have softened the water. The next few drops of added soap solution will remain in solution, and when shaken will form a good suds. Thus the amount of soap solution required to form a good suds with hard water, over and above that required to form a suds with distilled water, is a direct measure of the hardness in the water.

If the soap solution has been standardized so that each milliliter is equivalent to a definite amount of $CaCO_3$, then the amount required to form a suds with a definite volume of hard water can be converted into terms of parts per million of $CaCO_3$ for the hard water being tested. This method for determining hardness is not precisely accurate but for all practical purposes it is good enough, and its simplicity makes it one of the best methods for the layman. It does not tell whether the hardness is calcium or magnesium hardness, and whether it is temporary or permanent, but it does evaluate the water in terms of its soap-destroying power, which is the main factor most consumers are interested in. The directions for making up the standard soap solution will be found on page 48.

36. DETERMINATION OF SUDSING FACTOR

Pipette 50 ml freshly boiled and cooled distilled water into an 8-oz bottle. Add 2 drops standard soap solution from a burette, stopper the bottle, and shake vigorously. Continue the addition of soap solution, drop by drop, with vigorous shaking between additions, until a suds is formed that will stand up for 5 minutes without breaking. After the bottle is shaken, it should be placed on its side to give the largest surface possible. Make two or more such tests and average the volumes of soap solutions used. This is the sudsing factor, which is __________ ml soap solution.

37. DETERMINATION OF SOAP-DESTROYING POWER OF WATER

Pipette 50 ml hard water into an 8-oz bottle. Add standard soap solution from a 25 ml burette, as described previously, until a 5-minute suds is formed. At first the soap solution may be added in 0.5 ml portions, but as the end point is approached the additions should be decreased to about 2 drops each. Record the volume of soap solution. Sometimes the presence of excessive amounts of magnesium salts in the water will make this end point a false one. In order to check this after a 5-minute suds has been produced, add a few more drops of soap solution and shake. If the suds disappears or breaks more quickly, the first end point was a false one and the addition of soap solution should be continued until the true end point is reached. Subtract the sudsing factor from the volume of soap solution used. This is the amount of soap used for the hardness in 50 ml hard water, and since each milliliter of soap solution is equivalent to 1 mg $CaCO_3$ the number of milliliters used is equal to the hardness in 50 ml water expressed as milligrams of $CaCO_3$. If this is the amount in 50 ml, then the hardness in 1 liter will be 20 times this number.

Example:

Hard water tested	50 ml
Soap solution used	6.4 ml
Sudsing factor	.4 ml
Soap solution for hardness	6.0 ml

6 x 20 = 120 ppm $CaCO_3$ hardness

The size of the sample of hard water must be adjusted so that the volume of soap solution required will not be more than 7.5 ml. The reason for this is that the addition of alcohol to water changes its surfaces tension, and, since surface tension is connected with the formation of a suds, the amount of alcohol must be kept low; this means a small volume of soap solution. If more than 7.5 ml standard soap solution is required, another sample of the water should be tested; e.g., pipette 25 ml of hard water into the 8-oz bottle and add enough distilled water to bring the volume up to 50 ml. Test with soap solution as before. When calculating the parts per million hardness, remember that this time you have used only 25 ml water instead of 50 ml as in the first test.

Determine the hardness of the sample of water assigned to you and record results below.

Hard water __________

Volume tested		__________ ml
Volume of distilled water		__________ ml
Strength of soap solution	1 ml =	__________ mg $CaCO_3$
Volume of soap used		__________ ml
Sudsing factor		__________ ml
Volume soap for hardness		__________ ml
Total hardness of water		__________ ppm $CaCO_3$

The same procedure can be used for evaluating the sudsing power of soaps. (See page 52.) If solutions of various soaps are added to a standard hard water, it will be found that the amount of soap required to produce a good suds will vary considerably among different soaps.

Preparation of Standard Soap Solution (ml = 1 mg $CaCO_3$)

Roughly weigh 100 gm powdered castile soap or any other high-grade soap (Ivory or Lux). Transfer to a 2-liter beaker, add 1 liter 80% alcohol, and stir on a steam bath for 30 minutes. Cover and let stand overnight. Filter or decant the solution. This is a stock soap solution to be diluted so that 1 ml will be equivalent to 1 mg $CaCO_3$ after titrating it against a standard hard water.

Determine the sudsing factor of the stock soap solution. This is the same thing as a blank, that is, the volume of soap solution required to form a suds with distilled water. Pipette 50 ml freshly boiled and cooled distilled water into an 8-oz bottle. Add 1 drop of stock soap solution from a burette, stopper, and shake. Continue the addition of soap solution, drop by drop, with vigorous shaking between additions, until a suds is formed which will last 5 minutes without breaking. After the bottle is shaken, it should be placed on its side to give the largest surface possible. Record the volume of soap solution used. Repeat. If the volume used in the second test varies more than 0.2 ml from the first volume, make a third test. The average of these volumes is the sudsing factor for 50 ml distilled water.

Pipette 25 ml standard hard water (1 ml = 1 mg $CaCO_3$) into an 8-oz bottle and add 25 ml freshly boiled and cooled distilled water. Add the stock soap solution from a burette in small portions and record the volume required to form a 5-minute suds. Subtract the sudsing factor from this. The result is the volume of soap solution equivalent to 0.025 gm $CaCO_3$. If we want a soap solution such that 1 ml = 1 mg $CaCO_3$, 1 liter will be equivalent to 1 gm $CaCO_3$. This is 40 times 0.025. Therefore, the volume of stock soap solution required to titrate 25 ml standard hard water (to a 5-minute suds end point) multiplied by 40 is the volume of stock soap solution which should be diluted with 80% alcohol to 1 liter in order to make the standard soap solution, 1 ml = 1 mg $CaCO_3$.

Preparation of Standard Hard Water, 1000 ppm $CaCO_3$

Accurately weigh 0.5 gm pure calcium carbonate and transfer to a 150 ml beaker. Add reagent HCl drop by drop until the $CaCO_3$ is dissolved. After each addition allow time for effervescence to subside so that there is a minimum of foaming. Add about 50 ml freshly boiled distilled water and make just slightly alkaline with NH_4OH (litmus). Transfer quantitatively to a 500 ml volumetric flask, cool to room temperature if necessary, and make up to the mark with freshly boiled and cooled distilled water. Each milliliter of this solution will equal 1 mg $CaCO_3$; that is, its hardness will be 1000 ppm (1000 mg or 1 gm/l) $CaCO_3$.

This solution may be used to standardize soap solutions or it may be diluted to make a hard water of any desired hardness.

38. REMOVAL OF TEMPORARY HARDNESS BY HEAT

Start with 400 ml hard water measured with a graduate. Boil gently until it has evaporated from 1/3 to 1/2. Let cool and then add enough distilled water to bring the volume back to 400 ml. (If the water is cloudy it should be filtered before making up to 400 ml.) Mix well and determine the hardness by the soap method.

Volume tested	____________	ml
Volume distilled water	____________	ml
Strength soap solution	1 ml = ____________	mg $CaCO_3$/l
Volume soap used	____________	ml
Sudsing factor	____________	ml
Volume soap for hardness	____________	ml
Total hardness of water	____________	ppm $CaCO_3$

39. ALKALINITY OF WATER

Refer to I. T. C., page 89, for a discussion of the types of alkalinity that may be found in hard water. At this point we are concerned with the quantitative determination of alkalinity, and we are going to titrate water with 0.02 N H_2SO_4, using two indicators, phenolphthalein and methyl orange. Phenolphthalein turns red in solutions of hydroxides and normal carbonates, but it is not colored by solutions of bicarbonates. Methyl orange is yellow in any of these alkalies, and when the alkalies are just destroyed by being titrated with an acid, the color is orange. In acid solutions it is red.

If a red color is produced when phenolphthalein is added to hard water, it tells us that the alkalinity is due to either hydroxide or carbonate or both. Let us assume that both are present and that we titrate the water until the red color just disappears. At that time the following reactions will have taken place:

$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2HOH$$

$$2\,MgCO_3 + H_2SO_4 = Mg(HCO_3)_2 + MgSO_4$$

It is seen that all of the OH alkalinity has been neutralized, but only one-half of the CO_3 alkalinity has been neutralized. The other half is in the form of bicarbonate which is still titratable but does not show the alkaline color with phenolphthalein. If methyl orange is added to the above mixture, it will show its alkaline color, yellow, and the bicarbonate can be titrated by adding more H_2SO_4 until a little red shows up in the yellow.

$$Mg(HCO_3)_2 + H_2SO_4 = MgSO_4 + H_2CO_3$$

From the preceding brief discussion you can see that, if we titrate hard water with H_2SO_4 to a phenolphthalein end point and then to a methyl orange end point, we shall have figures from which each of the types of alkalinity in the water can be calculated.

Laboratory Directions

Pipette 100 ml hard water into an Erlenmeyer flask and add 4 drops phenolphthalein indicator. If the water becomes pink, titrate with 0.02 N H_2SO_4 until the pink color just disappears. Record the volume of acid used. Add 2 drops methyl orange indicator and continue titrating with H_2SO_4 until the first appearance of some red in the yellow. Record the volume of acid used. It is much easier to determine these end points if the indicators are added to 100 ml distilled water and the color of the reaction flask is compared with the distilled water flask. In order to simplify the method for calculating alkalinity from these titration figures, we shall designate the volume of acid for the phenolphthalein end point by P and the <u>total</u> volume of acid used by MO.

Calculations

Remember that you have tested 100 ml of hard water, but the results must be expressed in parts per million $CaCO_3$ (milligrams per liter), and hence all titration values must be multiplied by 10. The molecular weight of $CaCO_3$ is 100 and its equivalent weight is 50. A 0.02 N solution of $CaCO_3$ would contain 1 gm per liter, and 1 ml would contain 0.001 gm or 1 mg. Thus each milliliter of 0.02 N H_2SO_4 equals 1 mg $CaCO_3$. Remember that OH and HCO_3 types of alkalinity cannot exist together, and so if there is any OH there cannot be any HCO_3, and if there is HCO_3 then OH must be absent. To decide which one is present compare F and MO; if P is greater than 0.5 MO then OH is present, and if P is less than 0.5 MO then HCO_3 is present. The balance of the alkalinity in either instance will be normal CO_3 unless P = O, in which case all of the alkalinity will be HCO_3.

Let us convert these relationships into equations, all of which are based on two equations.

$$MO - P = 1/2\ CO_3 + HCO_3 \text{ (if any)} \qquad (1)$$

$$P = 1/2\ CO_3 + OH \text{ (if any)} \qquad (2)$$

Suppose HCO_3 is absent; then $P > 0.5$ MO.

From equation 1,

$$0.5\ CO_3 = MO - P$$

Substitute in equation 2 and get

$$P = MO - P + OH$$

$$OH = 2P - MO$$

$$CO_3 = 2(MO - P)$$

Suppose OH is absent; then $P < 0.5\ MO$.

From equation 2,

$$0.5\ CO_3 = P$$

Substitute in equation 1 and get

$$MO - P = P + HCO_3$$

$$HCO_3 = MO - 2P$$

$$CO_3 = 2P$$

If 100 ml water has been titrated, all the calculated values for alkalinity must be multiplied by 10. These calculations may be clarified by consulting the following chart, in which six different waters are compared. In each case 100 ml water was titrated with 0.02 N H_2SO_4 (1 ml = 1 mg $CaCO_3$), and the volumes used are given under P and MO. The last three columns show the alkalinities in parts per million $CaCO_3$.

Water	P	MO	OH	CO_3	HCO_3
1	10	18	20	160	0
2	13	19	70	120	0
3	14	25	30	220	0
4	6	18	0	120	60
5	3	20	0	60	140
6	2	22	0	40	180

Determine the alkalinity of waters assigned to you and record results below in a table like the preceding one.

QUESTIONS

1. How does most well water differ from river water? What makes water hard?

2. How can you show the presence of Ca and Mg ions in hard water?

3. Why does hard water destroy soap?

4. What principles and procedures underlie the determination of total hardness in water by the soap method? What is meant by sudsing factor?

5. What are the objections to the use of hard water in ordinary laundering?

6. Tell briefly how a standard hard water is prepared. How is the hardness of this water expressed?

7. Tell briefly how a standard soap solution for determining hardness is prepared. How would this solution be labeled?

8. A 25 ml sample of hard water is tested by the soap method, using 7.1 ml of standard soap solution (1 ml = 1 mg $CaCO_3$); sudsing factor is 0.4 ml. Calculate the hardness of the water in parts per million $CaCO_3$. Would this be considered a low, medium, or quite hard water?

9. We wish to prepare a soap solution such that 1 ml = 1 mg $CaCO_3$. We have available a standard hard water (1000 ppm $CaCO_3$) and a stock soap solution, 5.2 ml of which is required to form a 5-minute suds with 25 ml of the water (plus 25 ml distilled water). Tell what you would do to make the desired standard soap solution.

10. Phenolphthalein is added to 100 ml hard water and no color change is seen. What does this tell you? If methyl orange were then added and a yellow color obtained, what would you conclude?

11. Why is it not possible for OH ions and HCO_3 ions to exist side by side?

SECTION IV

Laboratory Tests on Soap (I. T. C., Chapter 3)

40. LIBERATION OF FATTY ACIDS

Put 10 ml soap solution (5/1) into a test tube. Add 3 to 5 ml reagent H_2SO_4 and mix well without shaking too much. Where does the layer of fatty acids separate? ________________ Is it all liquid or partly solid? ____________________ Can you make scme statements about the fats that might have been used to make this particular soap? ____

____

____

41. REACTION WITH HARD WATER

Put 25 ml soap solution (5/1) into a shall beaker and add 25 ml saturated $CaSO_4$. Stir and let stand. Describe the appearance of the insoluble calcium soap. ______________________________

____

Equation for reaction:

____

42. EMULSIONS WITH SOAP (I. T. C., page 72)

Put a few drops of oil (a fairly heavy mineral oil) into a test tube. Add 10 ml water and shake. Is the oil emulsified? ______________ To a little fresh oil add 10 ml soap solution (5/1). Shake. Is the oil emulsified? ______________ Why is soap a good emulsifying agent? ________________________

____

43. SUDSING POWER OF SOAP

You have learned that suds formation is important in connection with the detergent action of soap; even though it alone would not be the deciding criterion of soap quality, yet with other factors being equal the soap that forms the best suds will also clean the best.

In the following experiment you will use equal volumes of tap water (hard water) and you will find that varying amounts of the five commercial soaps will be required to produce suds when shaken with it. This will show that more of one soap than another will be required to produce a suds. But sudsing power can also be viewed in a different way. What ions does hard water contain that will react with soap and precipitate it? ____

Do you think the soap thus precipitated would take any part in forming a suds?________________

Do you think it would take any part in cleaning?________________ Do you think that every time you use soap with hard water you waste some of the soap?____________________ Do you think that some soaps might be more wasteful than others?____________________

From the results of this experiment you will calculate what weight of each of the five soaps will be wasted by 1 gallon of hard water. This does not mean that the soap which wastes the most is the poorest cleaner, but only that it will require more of it to do the job of cleaning.

The plan of this experiment will be to use an alcoholic solution of soap, which by itself will not form any suds when shaken but when added to water will do so. A uniform amount (20 ml) of tap water will be used in each test, and 80 ml of distilled water will be added to it. This is the standard volume to be tested (100 ml). The distilled water, containing no hardness, will not precipitate any soap but is added merely to bring the total volume up to a convenient workable one. If a less hard water were to be used perhaps 40 ml of it might be taken for the test; if so only 60 ml of distilled water would be added. Or if a quite hard water were to be used in the test, only 10 ml of it would be taken and 90 ml of distilled water would be added to it. These volumes are supposed to be juggled so that not more than 10 ml of alcoholic soap solution is ever used to produce a suds. The reason for this is that, if too much alcoholic soap solution is used, too much alcohol will be introduced into the mixture and it will change the surface tension of the solution so as to reduce the suds-forming ability.

Tap water and distilled water (volume 100 ml) are placed in an 8-oz bottle, and an alcoholic soap solution is run in until, after shaking, a suds is formed that will stand up for 2 minutes without breaking.

Preparation of the Alcoholic Soap Solution

Dissolve, by stirring, 5 gm commercial soap in 500 ml warm distilled water. This is to be diluted with alcohol, but to get a fair comparison among several soaps we must not add so much alcohol that some of the builders will be precipitated. We must determine what alcohol-water mixture is the proper one.

Remove 20 ml of this soap solution (graduated cylinder) and add alcohol to it until a filterable precipitate begins to form. The alcohol may be added from a graduated cylinder so that the required volume will be known. Suppose this volume is 50 ml. A mixture of 20 ml water and 50 ml alcohol is about a 72% alcohol mixture. If this is the proper mixture for this particular soap, then if we wish to make a 5/1 solution we would dissolve 5 gm soap in 280 ml warm distilled water and add 720 ml alcohol. Some soaps may require only 40 ml alcohol for the 20 ml sample, others 60 ml, etc. Calculate the percentage alcohol for the one that requires the smallest volume of alcohol and use this mixture for making up all the solutions. After the solutions are prepared let them stand for a day or so and then filter off any small amounts of precipitated solids.

The Procedure and Technique

Clean your burette, rinse with distilled water, and let it drain. Add a little alcoholic soap solution of the particular soap you are testing. Rinse the burette with this solution and discard it. Fill the burette with soap solution and put a bunch of filter paper in the top of it in order to prevent evaporation. If some evaporation takes place, would it change the strength of the soap solution?________________ Would it become stronger or weaker?______________________________

Using a pipette, introduce 20 ml of tap water into an 8-oz bottle. An ordinary 250 ml glass-stoppered reagent bottle is satisfactory. Add 80 ml distilled water, measured with a graduate. Do you think a few milliliters, more or less, of distilled water would affect the results?

______________________ Record the burette reading on the chart below. Now let 2 ml soap solution run into the bottle, stopper it, and shake vigorously. A suds probably will not form. Add 2 ml more soap and shake again. Continue these additions in 2 ml portions until a suds does form. Then place the bottle on its side and watch the suds. If it breaks within 2 minutes, more soap must be added. From this point add smaller amounts of soap in each portion. The final reading is taken when the suds stands up for two minutes. Record the final reading. The volume of soap solution used in this way is only an approximate value but should be close to the real one.

Clean the bottle and repeat the test, recording the figures as before. This time the solution may be added in larger portions, for you already know about how much of it will be required. When you have added within about 1 ml of the previous volume of soap solution, start adding it at the rate of only about 2 drops at a time. About 5 minutes' time should be taken out at this point. That is, there is a certain time factor involved in the precipitation of soap by the hardness in water. Therefore, before actually finishing the titration, shake the bottle for about five minutes and then continue adding soap solution until the end point is reached. The end point in this test can be obtained within 2 drops, that is, at one point the suds will not stand for 2 minutes, and then by adding only two more drops of soap solution, a suds will form which will not break under 2 minutes. If this volume of soap solution checks with the first titration, no further test need be made. If the titrations do not check within 0.2 ml, then a third titration must be made and the results calculated from the average of the best two.

Suds Titrations

	#1	#2	#3
Final reading	________	________	________
First reading	________	________	________
Volume soap used	________	________	________

The average that I shall use in my calculations is________ml soap. This soap solution contains________gm soap per milliliter. The weight of soap wasted by 20 ml tap water is______gm. If there are 3,785 ml in a gallon, how much soap is wasted by 1 gallon water ?________gm. Convert this into ounces. ________oz. (1 oz = 28.36 gm.)

Determine this value for each soap assigned to you.

The teacher may decide what soaps and how many each student will test. Some interesting summaries may be obtained if each student hands in the results for each soap tested. The teacher may then average these figures for each soap and give them to the class, after which the student should record them in the following chart.

Soap Wasted by 1 Gallon Water (Total hardness of water is ppm $CaCO_3$)	
Brand of Soap	Ounces Wasted
1	
2	
3	
4	
5	

44. DETERMINATION OF TOTAL FREE ALKALINITY IN SOAP (I. T. C., page 68)

Preparation of the Solution to be Titrated

Accurately weigh an amount of soap of about 5 gm. Carefully transfer it to a medium size beaker and add about 125 ml distilled water. This is merely to dissolve the soap and need not be measured accurately. Warm, with stirring, until the soap dissolves and then carefully transfer the solution to a 250-ml volumetric flask, avoiding spilling any of the solution. Rinse the beaker 3 times with 5 ml portions of distilled water to be sure of getting all of the soap solution out of it. Add these rinsings to the flask.

Next add to the flask 80 ml of a saturated salt brine, adding about 5 ml at a time and whirling the contents of the flask after each addition. What is the precipitate that forms? ________________

________________ The reason for adding the salt in small amounts and the whirling is to prevent some of the free caustic or carbonate alkalinity from being wrapped up in the precipitate and thus not being found when the solution is titrated. After the salt brine has been added, add about 1 t of solid salt, and whirl again for a few minutes. On the neck of each volumetric flask there is an etched ring. When the flask is filled up to this mark, it will contain exactly 250 ml of solution. Add enough distilled water to your flask to fill it to this mark and then add 5 ml more water (measured in a 10 ml graduate). Cork the flask and mix the contents thoroughly by turning it upside down and shaking it several times. The extra volume of water is added to compensate for the volume occupied by the precipitate present. This precipitate looks as if it would occupy a larger volume than 5 ml, but if you were to filter it off and dry it, you would find that its volume is about 5 ml. The flask and contents may be corked and set aside until the next laboratory period if necessary.

Filter the contents of the flask into a dry Erlenmeyer flask and consider where, and in what form, the three kinds of alkalinity are.

Combined alkalinity is in the ________________________ in the form of ____________.

Caustic alkalinity is in the ________________________ in the form of ____________.

Carbonate alkalinity is in the ________________________ in the form of ____________.

Discard the precipitate into a special waste pail provided. Do not put it in the sink or in the usual waste pail. Cork the filtrate and save it for titration.

Technique of Titrations and Calculations

Put 50 ml of the soap solution to be titrated into a medium size beaker and add about 100 ml distilled water. The solution will be measured with a 50 ml pipette which must be rinsed once with a little of the soap solution to be measured in it. (After using the pipette it should be rinsed at once with distilled water and placed upright on some filter paper to drain.) After adding a few drops of the proper indicator to the beaker containing the soap solution, you are ready to make the titration. The amount of indicator used depends on your vision. If you think you can more easily see the color change with a deeper color, then use more indicator.

Slowly add some of the acid from the burette and do not stir the solution until you see what is happening to the color. If the color changes from the alkaline color to the acid color in the one spot where the acid has been added, stir the mixture and see if the color of the entire solution goes back to the alkaline color. If it does, add more acid and continue until the exact halfway color is formed. Save the solution. Some of these titrations may require 18 to 20 ml of acid, but others may require none or perhaps only a few drops of acid. When the halfway color is obtained, read the burette as accurately as you can and record it in the following chart. This first determination will probably not be accurate, but it will be close to the real value. A second titration is then made, using another 50 ml sample of the solution being tested. This second titration may be carried out much faster than the first one, because you may add almost the previous volume of acid without waiting. The solution saved from the first titration is now placed beside the one you are working with, and by comparing the colors in the two beakers you will be able to obtain a more exact end point. Take the reading and record it. If the volume of acid used in the second titration agrees with that used in the first, your determination is completed, but if the two volumes differ by more than 0.2 ml, a third titration must be made. The two which check best are used in making the calculations.

Titrate 50 ml of the solution prepared for free alkali determination, with HCl (approximately 0.1 N), using methyl orange as the indicator.

The color of methyl orange in acid solutions is ________________, and in alkaline solutions it is ________________. When I add it to my solution the color is ____________, which tells me ________________________. Strength of HCl used, in terms of Na_2O is 1 ml = ________ gm Na_2O.

Record of Titrations

No.	Volume Solution Titrated	Grams Soap Titrated	Burette Readings	Volume Acid Used	Grams Na_2O Found	Per Cent Na_2O in the Solid Soap	Average Per Cent Na_2O to be Reported
1			b*				
			a*				
2			b				
			a				
3			b				
			a				

*a = first burette reading; b = second burette reading.

45. DETERMINATION OF FREE CAUSTIC ALKALINITY

Accurately weigh an amount of soap of about 5 gm. Dissolve and transfer as described in the first part of Experiment 44. Add 35 ml $BaCl_2$ (15% solution), 5 ml at a time, whirling as in Experiment 44.

What kinds of alkalinity will be precipitated by Ba ions?________________

What kind of alkalinity is left in solution?________________

After the soap solution has been transferred to the volumetric flask, fill the flask up to the mark with distilled water, add 5 ml more water, and mix well as previously instructed. Filter and discard the precipitate in a special waste pail. Cork the filtrate and save it for titration. Use the same technique as described in Experiment 44.

Titrate 50 ml of the solution with HCl (approximately 0.1 N), using phenolphthalein as the indicator.

The color of phenolphthalein in alkalies is________________, and in acids it is ____________. When I add it to my solution the color is________________, which tells me________________________. Strength of HCl used, in terms of Na_2O, is 1 ml = __________gm Na_2O.

Record of Titrations

No.	Volume Solution Titrated	Grams Soap Titrated	Burette Readings	Volume Acid Used	Grams Na_2O Found	Per Cent Na_2O in the Solid Soap	Average Per Cent Na_2O to be Reported
1			b*				
			a*				
2			b				
			a				
3			b				
			a				

*a = first burette reading; b = second reading.

46. DETERMINATION OF FREE CARBONATE ALKALINITY

The total free alkalinity in my soap is__________% Na_2O. This alkalinity is composed of free ______________________________and free______________________________. I found the free caustic to be______________________________% Na_2O and therefore the free carbonate alkalinity is______________________________% Na_2O.

47. DETERMINATION OF TOTAL ALKALINITY IN SOAP

Accurately weigh an amount of soap of about 5 gm and dissolve and transfer it as instructed in the first part of Experiment 44. Fill the flask up to the mark with distilled water, but do not add extra water. Thoroughly mix the contents of the flask as described before. The alkalinity in this solution is a mixture of all three kinds. If the flask is set aside until the next laboratory period, it will probably gel. If it does, place it in a bath of water and heat the water until the soap gel melts and you get a solution again. Do not heat it any more than necessary.

Titrate 50 ml of this solution with H_2SO_4 (approximately 0.2 N), using methyl orange as the indicator. What is the halfway color of methyl orange?______________________________This is the most difficult titration you will make, because as acid is added the fatty acids of the soap will be liberated and form an oily emulsion in the titration beaker. This makes it very difficult to see the color of the indicator, and it is all the more necessary to save the first titration mixture as a guide or comparison for the second titration. The only thing to do is to keep trying until you get two results that agree. Strength of H_2SO_4 used in terms of Na_2O (1 ml =__________gm Na_2O).

Record of Titrations

No.	Volume Solution Titrated	Grams Soap Titrated	Burette Readings	Volume Acid Used	Grams Na_2O Found	Per Cent Na_2O in the Solid Soap	Average Per Cent Na_2O to be Reported
1			b				
			a				
2			b				
			a				
3			b				
			a				

48. DETERMINATION OF COMBINED ALKALINITY

I found the total alkalinity of my soap to be__________% Na_2O and the total free alkalinity to be __________% Na_2O, which leaves the combined alkalinity equal to % Na_2O.

Summary of Soap Analysis

If the preceding quantitative determinations have been made, they should be summarized. Students should post their results in some convenient place and the instructor should scrutinize them, rejecting those that are out of line and averaging the rest. The student should then record the averages for the particular soap he has analyzed in the space on page 58. The Na_2O percentages should then be converted into the terms in the third column.

Alkalinity of ____________________ Soap

Total	________ % Na_2O	
Free	________	
Combined	________	________ % $C_{15}H_{31}COONa$
Free caustic	________	________ % $NaOH$
Free carbonate	________	________ % Na_2CO_3

49. METALLIC SOAPS FOR WATERPROOFING

Put a piece of muslin (about 4 to 5 in. square) into a beaker and cover it with a solution of aluminum acetate. Squeeze it with your fingers so that the cloth becomes thoroughly saturated with the solution. Do this about every 5 minutes for 20 minutes, then squeeze out the excess liquid and return the aluminum acetate to the stock bottle. Immerse the impregnated cloth in a dilute soap solution (dilute the 5/1 stock solution about 3 times). Let it stand with occasional turning for about 20 minutes, then squeeze out, rinse twice in distilled water, and dry (IV-1).

When dry, let some water run on it. How does it behave? ____

____

Make a small pocket or bag with the piece of cloth, fill it with water, and watch it. How does it behave? ____

____ Hold the piece of cloth up to the light and compare it with some untreated muslin. What is the difference? ______________

____

____

IV-1

Waterproofed Cotton

QUESTIONS

1. Write a chemical formula that might represent soap. Why isn't soap a homogeneous pure chemical compound?

2. How can the fatty acids be liberated from soap? What do they look like? Is this a pure acid or a mixture? Is the specific gravity smaller or greater than 1.0?

3. What do you see happen when soap solution is mixed with hard water? What causes this? Write equations.

4. Why is a certain amount of soap wasted when used with hard water?

5. Can soap be used to soften water? Explain. Why isn't this good common practice?

6. What is meant by soap builder?

7. Is soap a true salt? Justify your answer.

8. What happens when a saturated salt brine is added to a soap solution? What stays in solution?

9. What kinds of alkalinity does a commercial soap contain? To what may each be due?

10. What is precipitated when a solution of commercial soap is treated with $BaCl_2$? What stays in solution?

11. What indicator is used when titrating the total alkalinity of a soap?

12. Do soaps have different sudsing characteristics? How can this be determined?

SECTION
V

Laboratory Work on Silk

50. TIN WEIGHTING OF SILK (I. T. C., page 298)

You will be provided with pieces of white unweighted crepe which you will weight as directed below.

Take enough pieces so they will weigh 1.5 to 2.0 gm, and weigh them accurately to the third decimal place. Immerse them in a cold solution of $SnCl_4$ (sp gr = 1.275) for 30 minutes. RETURN THE $SnCl_4$ TO THE STOCK BOTTLE. Put the pieces into a large beaker, hold them down with a glass rod, and wash them under running water for 10 minutes. Squeeze them well and immerse in a solution of Na_2HPO_4 (sp gr = 1.04) at 60° C for 10 minutes. RETURN THE SODIUM PHOSPHATE SOLUTION TO THE STOCK BOTTLE. Wash the pieces as before, spread them out on filter paper, and let them dry until the next period. These will be V-1, and the original unweighted silk V-2. Weigh the treated pieces accurately.

Weight after one weighting __________ gm

Original weight __________ gm

Gain in weight __________ gm = __________ % gain

Take these same pieces and put them through the same weighting operations as before. Dry and weigh.

Weight after second weighting __________ gm

Original weight __________ gm

Gain in weight __________ gm = __________ % gain in two weightings

Give the pieces a third weighting. Same directions as before. After this third weighting, before drying them, immerse the pieces in a solution of sodium silicate (sp gr = 1.03) at 60° C for 10 minutes. Rinse them well, and dry until the next laboratory period. Weigh.

Weight after third weighting __________ gm

Original weight __________ gm

Gain in weight __________ gm = __________ % gain in three weightings

SUMMARY OF TIN WEIGHTING OF SILK

Per cent of original weight added in one weighting is __________ %

in two weightings __________ %

in three weightings __________ %

<u>The Burning Test on Weighted Silk</u>

Use pieces about 1 in. square. Put a piece of the original unweighted silk on a wire gauze and burn it with a Bunsen burner. Burn a piece of your weighted silk in the same way. Describe how they burn:

Unweighted silk____

Weighted silk ____

____

Mount samples below.

V-1 V-2

Tin Weighted Silk Unweighted Silk

TESTS ON SILK

51. HYDROLYSIS WITH ALKALIES

Refer to Experiment 20, page 35. If silk is a protein like wool, would you expect it to dissolve in hot NaOH?____________ If lead acetate were added to this solution, would you expect to get a black precipitate?____________ Why?____________________________

Put two pieces of silk, together with some cotton and rayon yarns, into a beaker and cover them with reagent NaOH. Heat to boiling and continue for about 3 minutes.

What happens to the silk?________________________to the cotton?____________ to the rayon?____________________________What would happen to wool under similar conditions?__________________________ Decant a little of this solution into a test tube and add 0.5 ml lead acetate solution. The result is__________________.

What would you get if wool protein had been dissolved in this solution?________________

Given a quantity of unknown fibers that might be wool, silk, or cotton (but not a mixture), how would you tell which one it is?____________________________________

____

Could you detect the presence of silk, mixed with wool, by treating with NaOH and lead acetate?

____

52. MILLON'S TEST

Test a piece of silk with Millon's reagent, as described in Experiment 29. A_____color is formed. Is it the same color you got with wool?______________Test pieces of cotton and rayon yarns with the same reagent. Can you distinguish between animal and vegetable fibers by means of Millon's reagent? ____________________ How? ____

____

53. COLD CONCENTRATED HCl

Pour some concentrated HCl on a large watch glass. Take small yarns or individual fibers of silk, wool, cotton, and rayon and slide them beneath the surface of the acid. Tell how each behaves:

Silk ____

Wool ____

Cotton ____

Rayon ____

In all the preceding tests, wild silks will behave like ordinary mulberry silk except to a lesser degree. Wild silk is much more resistant to all reagents than cultivated silk.

54. BOILING OFF SILK WITH SOAP SOLUTION (I. T. C., page 292)

Weigh one small bunch of raw silk (V-3). This should weigh about 0.5 gm, but the weighings must be made as carefully as possible to the third decimal place. This weighed sample should be prepared at the laboratory period before you actually degum it, so that the entire period is available for boiling off. A second bunch of raw silk (V-4) which is not weighed, will be boiled off in the present experiment along with V-3, and then saved for Experiment 55. These bunches of silk must be tied (using some of the silk itself) so that they will not snarl or tangle too much in the degumming bath, and they must be tied so that they can be identified because they will be heated in the same bath.

The weight of V-3 is __________ gm.

Put V-3 and V-4 into a 150 ml beaker and add 100 ml soap solution (5/1). This soap should be a pure olive oil soap. This will be heated for 1½ hours at about 95° C but not with a direct flame. Instead, place the beaker in a large casserole or beaker and surround it with water. Heat the casserole and keep the water boiling gently for 1½ hours. You will have to add small amounts of water to the casserole from time to time to take the place of water that evaporates. Several times during the period, work the silk gently with a glass rod. Do not tangle it any more than you can help.

Lift the samples of boiled-off silk and, without squeezing them, drop them into a beaker of distilled water. Now is the best time to separate them if they have become tangled. The soap left on them will lubricate them enough so they can be pulled apart. After separating, rinse them separately in three changes of distilled water and try to get rid of as much soap as possible. Then put them all in one large beaker and let water run on them for 5 minutes. The sample that has been weighed must of course be handled so that none of the silk is lost. Finally squeeze the samples separately, open them up, and spread them out to dry until the next laboratory period. Weigh V-3 accurately.

Weight of V-3 before boiling-off __________ gm

After boiling-off __________ gm

Loss in weight __________ gm = __________ % loss

Mount V-3 together with some raw silk (in the gum).

V-3

Raw Silk Degummed Silk

Describe the differences between the raw silk and the boiled-off silk. ____________________

____

____

____

55. SCROOPING DEGUMMED SILK

After certain treatments silk yarns or fabrics, when crushed, produce a crunching sound and have a sort of raspy feel. This property is known as "scroop." It is not inherent in the fiber itself but is produced by the action of organic acids on degummed silk and is in part responsible for the rustling sound associated with the wearing of silk garments. Other fibers can also be scrooped but to a much smaller extent. The mechanism of scrooping is not known, but it seems possible to produce it by the action of almost any organic acid.

Scroop your V-4 by steeping it for 10 minutes in a bath of 0.5% tartaric acid at about 30° C. Remove the sample, squeeze out the excess liquor, and dry it without washing.

V-4

Scrooped Silk

Compare the feel of the scrooped silk with the degummed silk (V-3). Describe the difference.

____

____

____

SECTION VI

The Identification of Fibers

In this age of competition, superadvertising, Fair Trade Practice Rules, government specifications, fads, and styles, an elementary knowledge of the methods used for the identification of fibers in textile materials is essential for the student (in this field). It may be necessary to identify the individual fibers in a loose mixture of fibers, in single or ply yarns, in knit goods, or in woven fabrics. It is assumed that the analyst has some knowledge of the physical and chemical properties of fibers, of what fibers might be expected in certain types of goods, of the common blends of fibers that are found in yarns, of the construction of certain cloths with different warp and filling yarns, of various resin finishing treatments, and perhaps even the item of cost.

If a piece of cloth is to be analyzed for fiber content, it must first be examined in a preliminary way to give some idea of the possibilities; such things as decorative stripes, colored patterns, occasional novelty yarns, a warp much stronger than the filling, and uses to which the material is to be put are important indications of fiber content. It must be understood that, in woven goods, there may be only one kind of fiber in both warp and filling; there may be a warp of one fiber and a filling of another fiber; some yarns may be two- or three-ply, in which one ply may be different from the others; fibers may be mixed or blended before spinning, so that there may be more than one kind of fiber in one yarn or in one ply of a yarn.

It seems obvious that the first thing to do is to take the material apart, separate it into warp and filling yarns and into the plies of each, or perhaps untwist them into the individual fibers. The appearance of the fibers should be examined carefully for fineness, length, and luster. For example, if a yarn is composed of long filaments, all of the short staple fibers are eliminated without further testing. The converse of this is not necessarily true, because of the increasingly wide use of rayon staple fiber, staple nylon, and spun silk. One must not be misled by certain degrees of luster nor by crimp in fibers, since these may be produced artificially. However, much information may be gained by this picking-apart investigation.

The identification of fibers may be approached in two broad ways, (a) by a microscopical examination and (b) by the use of chemical reagents, solvents, and stains. Each has its advantages. In general, the use of the microscope is perhaps the better for an ultimate identification, and yet in some instances the results should be confirmed by chemical methods. In a similar way testing by chemicals has its limitations and may reach a point beyond which differentiation is not possible. In this laboratory manual we shall get along without a microscope, since we shall be concerned with only some of the major fibers.

For detailed discussions of the use of the microscope in textile analysis, the reader is referred to Schwarz, Textiles and the Microscope, McGraw-Hill Book Company, 1934; von Bergen and Krauss, Textile Fiber Atlas, American Wool Handbook Company, 1942; American Society for Testing Materials (ASTM) Standards, 1944, pages 1932-1950; Matthews and Mauersberger, Textile Fibers, John Wiley & Sons, Inc., 5th Edition, 1947, pages 998-1039.

If more detailed information on the general subject of textile testing and analysis is desired, the author recommends the following texts: Matthews and Mauersberger, Textile Fibers, John Wiley & Sons, Inc., 5th Edition, 1947, pages 977-1096, Trotman and Trotman, Textile Analysis, J. B. Lippincott & Company, 1932; Skinkle, Textile Testing, Chemical Publishing Company, 1940; ASTM Standards; and the Year Book of the American Association of Textile Chemists and Colorists, 1944.

Various general methods or schemes for the systematic identification of textile fibers have been proposed by different associations or agencies. These schemes are complete and workable; they differ from each other to some extent but on the whole are quite similar and accomplish the same purpose. The three most important of these plans have been proposed by the AATC and C in "Methods of Fiber Identification and Quantitative Separation," in the 1942 Year Book; by the ASTM "Tentative Methods for Identification of Fibers in Textiles," in the 1942 ASTM Standards; and by the Textile Institute (England) as proposed by a special committee and reported in the Journal of the Textile Institute, 32, S1-30 (1941).

The method we shall follow is somewhat simpler than these, because we shall cover a smaller range of possibilities. It consists of the picking-apart preliminary study already mentioned, followed by burning tests and then by chemical solvent and reagent treatment.

At times it may be necessary to draw a conclusion from the formation of a color. Whether this will be practical depends on the condition of the material being tested. For example, wool turns black when warmed in alkaline lead acetate solution, but if the wool is already dyed dark brown, no change in color would be observed. However, if fibers are dyed some light shade, the test could be made with lead acetate to see if any of the fibers turn black. Thus it may be necessary to strip dyes from goods before making tests (see later). As another example, cotton and mercerized cotton can be differentiated by testing with a $ZnCl_2$-I_2 reagent, as a result of which mercerized cotton will take on a blue color which does not wash out easily, but the color on cotton can be washed out quickly. It is well known that starch and iodine form a blue color and therefore the test would be of no value if the unknown cloth were sized with starch. Therefore, before making such a test all finishing material must be removed. The presence of oils or fats may interfere with some tests. They can be removed by the proper organic solvents.

It is obviously necessary that textile materials be clean before they are tested for fiber content. Most finishes and sizes can be removed by boiling the goods in three 15-minute changes of distilled water. The rubber coating on some yarns can be removed by immersing in three changes of benzene. The small amount of fatty material left on some textiles can be removed by dipping in ether or 95% alochol. If it is necessary to strip dyes, such preparations as Rongalite, Formopon, or Protolin may be used. These various combinations of sulfoxylates with formaldehyde are good reducing agents. The stripping is done in slightly acid baths at about 60° C.

LABORATORY WORK ON FIBER ANALYSIS

Procure a sample of textile material from the teacher. Record its number or devise some other means for identifying it. Carry out the tests outlined on the following pages until you are satisfied that you have conclusively identified the fibers in the sample. Fill in the accompanying blank, or one similar to it, and hand in for checking. Note that the first part of the report deals with the general character of the material and preliminary observations, together with conclusions that may be drawn from them. The second part shows the results of burning tests. The third covers the use of chemical reagents and solvents. As far as grading in a regular way is concerned, emphasis will be placed on proper conclusions and the elimination of unnecessary tests, as determined by preceding observations.

FIBER ANALYSIS

Mount Sample here

mple No.__________ Date__________________________ Student's name______________________________

Description of sample ____

____

Probable use____

Type of weave____

Printed or woven pattern ____

	Warp	Filling
Threads per inch	....	....
Fine or heavy count	....	....
Ply	....	....
S or Z twist in singles	....	....
S or Z twist in folding	....	....
Decorative stripe	....	....
Different fibers in design yarns	....	....
Burning tests indicate what?	....	....
	....	....
	....	....

Chemical tests made:

Tests made	On what	Observations	Conclusions

Final report on sample: State fibers identified in all yarns.

BURNING TEST

The behavior of various textile fibers when introduced into a Bunsen flame or the flame of a burning match may give considerable information regarding the identity of fibers. Some experience is necessary if correct conclusions are to be drawn from such burning tests, and it is suggested that the student make burning tests on all known fibers available in the laboratory. The burning test is made on single fibers or fine count yarns known to be composed of only one kind of fiber. The best procedure is to hold the fiber with a pair of forceps or tweezers and bring the end of the fiber up to the side of the flame (not over the top of it). Do not put it entirely into the flame.

Various observations are to be made. These have to do with the manner of burning and the appearance of the fiber after burning. Some of these observations are:

1. Does the fiber actually burn rapidly with a flame?
2. Does it burn slowly with very little flame?
3. As the fiber is brought into the flame, does it seem to burn and then extinguish itself?
4. Does the fiber appear to melt and shrink away from the flame?
5. Does it seem not to burn at all?
6. Does the fiber retain its original shape or structure and does this burned structure have any strength?
7. Is a bead formed on the end of the fiber and is this bead hard or crunchy?
8. Does burning result in an almost complete destruction of the fiber, leaving a very small amount of shapeless ash?
9. Is there an odor associated with the burning, such as burning feathers or hair, burning paper, or acetic acid?

These burning tests should be repeated by the student until a reasonable amount of expertness is attained. The behavior of textile fibers when subjected to this burning test is shown below. The names of the fibers are given first, followed by the expected results of the burning test.

1. Glass and asbestos fibers (mineral fibers). These fibers are noncombustible, although glass fibers may melt.

2. Weighted silk. Burns slowly with little flame and leaves a charred material that has the same size and shape as the original. This can be demonstrated by placing a small piece of weighted silk cloth on a wire gauze and burning it with a Bunsen flame. All the yarns in the piece can still be seen, and sometimes it is possible to pick up the piece and handle it. However, if it is rubbed between the fingers it will fall apart and will be found to consist of a shapeless powder.

3. Nylon, Vinyon, and Saran (Velon). These man-made filaments are self-extinguishing. As they are brought into the flame they melt and shrink away from it, leaving a hard bead at the end of each filament. Odors have been noticed when these materials are burned, but they are quite difficult to detect and describe.

4. Animal, casein, zein and soybean fibers. All these fibers are protein and give an odor of burning hair or feathers. They burn slowly (as compared with cotton) and leave beads on the fibers.

5. Acetate rayon. This rayon burns more rapidly than wool or silk but more slowly than other rayons or cotton. It is difficult to judge the rate of burning, but a bead is formed that is brittle and crunchy compared with the hard beads formed by other fibers. Sometimes the odor of acetic acid can be detected.

6. Cellulosic fibers and regenerated rayons. These materials burn rapidly with a real flame and form no bead. There is only a very small amount of shapeless ash left. It is often possible to detect the odor of burning paper.

CONCLUSIONS FROM BURNING TESTS

As previously stated, a fair amount of experience is required in order to draw the proper conclusions from burning tests. However, the tests will probably give conclusive evidence of mineral fibers and the man-made synthetic fibers. Furthermore, they will give a strong indication as to whether the fiber is animal or vegetable, but this should be confirmed by additional tests. It must be remembered that a resin-treated cotton or rayon or a protein-coated vegetable fiber will exhibit different burning characteristics from those of untreated fibers. Furthermore, one may encounter yarns in which have been blended wool and cotton or wool and rayon or rayon and casein fiber or spun silk and rayon.

For the rest of this discussion we shall eliminate the mineral fibers and weighted silk and confine our study to the behavior of animal, vegetable, and man-made fibers. We shall divide all of these into two large groups, based on their solubility or insolubility in boiling 5% KOH. Each group will then be subdivided by the use of chemical reagents until the unknown fibers are finally identified.

THE KOH TREATMENT

Boil the unknown material in a suitable volume of 5% KOH in a covered beaker for 5 to 10 minutes. Bring the solution to a boil and then reduce the flame so that it does not boil too vigorously or foam too much.

If the unknown material is a piece of cloth, a small part of it should be unraveled to separate it into warp and filling yarns. Treat each batch of yarns separately with the KOH. The yarns must be kept submerged in the boiling liquid.

During the boiling period, observe whether or not all or only part of the fibers dissolve; also note if there is an excessive swelling of fibers. Remove undissolved fibers from the solution, rinse with water and then with acetic acid (1%) and then again with water, label, and save. You may find some use for them later.

THE KOH-SOLUBLE FIBERS

These fibers are of course not really soluble in boiling KOH, but are hydrolyzed by the hot alkali and converted into water-soluble split products. They must therefore be natural or man-made protein fibers. Thus this group will consist of wool, hairs, silks (mulberry or wild), zein, casein, and soybean fibers.

Two other reagents may be used for placing an unknown fiber in this group. They are boiling picric acid and Millon's reagent. You have already learned (page 41) that protein fibers are dyed yellow with picric acid and are colored red by Millon's reagent. The use of such color tests, however, is limited because many samples to be identified are already dyed medium to dark shades. Furthermore, it is possible that wrong conclusions may be drawn if filaments or fibers are coated with resins or proteins.

The KOH-soluble fibers can be divided into two subgroups in two ways. One method is based on the reaction with alkaline lead acetate, which would divide them into sulfur-free fibers and sulfur-containing fibers. The other method is based on solubility in concentrated HCl.

The procedure with the first method is to immerse the fibers in a solution of alkaline lead acetate (page 42) in a test tube and place the tube in a bath of water at about 80° C. If the fibers contain sulfur they will be blackened, due to the formation of lead sulfide on the surface of the fibers. This test will be of little value unless the fibers are white or are dyed a light shade.

The concentrated HCl test is made by sliding single fibers into some concentrated HCl on a watch glass and observing whether or not they dissolve. Mulberry silk will dissolve quickly, but wild silks require a much longer time to dissolve. Wool, hairs, and casein fiber do not dissolve in cold concentrated HCl. This test can be used for either white or dyed fibers.

We can summarize the subdividing of the KOH-soluble group of fibers as follows:

The lead acetate test:

(a) blackened--wool and hairs
(b) not blackened--silks, casein, and zein.

The concentrated HCl test:

(a) soluble--silks
(b) insoluble--wool, hairs, casein, and zein.

If the lead acetate test is used, we must then be able to distinguish between wool and hairs or between silk and casein fiber. No chemical test or reagent will differentiate between wool and the various hair fibers. One must resort to the microscope.

Silk and casein fiber can be differentiated as follows: immerse the fibers in cold concentrated HNO_3 and watch the behavior (pay no attention to any color change). Casein fiber appears to be unaffected and will retain its original structure. On the other hand, silk shows considerable swelling (transversely) and shrinking (longitudinally), so that a complete change in structure is observed and one gets the impression of complete disintegration.

It may be of interest to distinguish between wool and casein fiber, since they are frequently blended together. This can be done by taking advantage of the fact that casein, when dyed with methylene blue, will retain the blue color much longer than wool. The fiber surface is first activated with alkali and then dyed in the cold.

Immerse the fibers in 10% NaOH at room temperature for 5 minutes; remove and rinse well. Immerse the fibers in a 0.1% solution of methylene blue and stir for 10 minutes at room temperature. Remove and rinse well. Watch the color; note that casein fiber will be dyed blue, whereas wool will be only slightly stained or not at all.

THE KOH-INSOLUBLE FIBERS

We shall list the fibers of this group in three divisions, for reasons that will soon be apparent:

(a) Acetate rayon and Vinyon
(b) Nylon
(c) Natural cellulosic fibers, mercerized cotton, regenerated rayons, and Saran (Velon).

Division (a). Fibers are soluble in warm acetone. Put fibers in a small test tube, cover with acetone, and place in a water bath at 30 to 35° C for 10 to 15 minutes. Acetone is flammable; keep away from open flames. This treatment will dissolve acetate rayon and Vinyon, but the other fibers will not be dissolved. If the unknown fibers are found to dissolve in warm acetone, it will be necessary to distinguish between acetate rayon and Vinyon, as follows: put the fibers in a small test tube and cover with glacial acetic acid, cork, and shake gently for 5 to 10 minutes. Acetate rayon will dissolve, but Vinyon will not.

Division (b). Nylon can be separated or distinguished from Division (c) fibers by means of phenol (carbolic acid), in which nylon is soluble. Put some 90% phenol into a small beaker, immerse fibers, and stir with a glass rod for 10 minutes. Nylon will dissolve, whereas the others will not. CAUTION: Phenol is very corrosive to the skin and will cause bad burns. You may get it on your skin from the cork in the bottle, from the outside of the bottle, from the beaker, or from the stirring rod. If such contact occurs, wash skin thoroughly in running water and then soak in a dilute solution of sodium bicarbonate.

Division (c). At this point we have cellulose, modified cellulose fibers, and Saran. We shall say nothing more about Saran; it is not affected by any of the reagents that will be used; and because of the physical nature of Saran filaments, they would never be confused with cotton, linen, rayon, etc. Division (c) fibers can be divided into two parts in two different ways, each one based on color reactions. These tests are therefore limited to white goods or materials from which the dyes have been stripped.

The Phloroglucinol Test

This test distinguishes between cellulosic materials having a high lignin content and those with none (or smaller amounts). To the first class belong such fibers as jute and hemp and materials (such as paper) that may contain wood pulp. The other fibers in Division (c) are free from lignins.

Put some fibers on a white spot plate (or a glass plate with a white paper under it) and moisten with a few drops of phloroglucinol reagent (page 73). The lignocelluloses, such as jute, hemp, and wood pulp, will be colored red. The other fibers will be unstained. The difference between jute and hemp must be determined microscopically.

The difference between cellulose and lignocellulose can be detected also by Texchrome dye. A drop of the dye is applied to damp fibers, allowed to stand 2 to 3 minutes, and then washed thoroughly. Cotton and linen will be stained a light blue, and jute and hemp a dark brown.

The $ZnCl_2$-I_2 Test

This test will distinguish between swollen and unswollen cellulosic fibers. The $ZnCl_2$-I_2 test is based on the fact that swollen cellulose (mercerized cotton and regenerated rayons) will absorb iodine (and be colored by it) more easily and will retain it longer than cotton, linen, ramie, etc. The most important part of the test is the relative time the color is retained while the stained sample is being rinsed.

The sample to be tested should be wet out with water and then squeezed between filter papers so that it is left damp. The material must be entirely free from starch finishing materials (page 65). Place some of the damp fibers on a white spot plate (or a glass plate with a white paper under it), add a few drops of $ZnCl_2$-I_2 reagent, and let stand about 3 minutes. Mercerized cotton and other swollen celluloses (rayons) will be colored a reddish purple, whereas unswollen cellulose fibers will be only slightly stained. If it is difficult to judge the color, transfer the fibers to a beaker of distilled water and move them about slowly. Unswollen cellulose will lose color almost immediately, whereas swollen cellulose will retain the blue color for some time. This is purely a relative matter, because all the fibers will be decolorized if they are washed long enough. The difference between rayon and mercerized cotton can be judged by luster.

The difference between viscose and cuprammonium rayon can be detected by the use of Texchrome dye. Texchrome is a combination of dyes which yields significantly different colors with most of the major textile fibers. Wet out the sample to be tested, press between filter papers, and then spot with one drop of Texchrome. Let stand 2 to 3 minutes and then wash thoroughly. A lavender color is produced on viscose and a dark blue on cuprammonium.

There is no chemical test by which cotton can be distinguished from linen. The use of the microscope is of course the best method, but other methods have been recommended. For the details of these see Herzog's "The Determination of Cotton and Linen," Bulletin 5, Series 8, Teachers College, Columbia University.

One simple and fairly reliable test to show whether a fiber is cotton or linen is based on the twisting behavior of the fiber while it is drying. Separate one fiber from the yarn, dip one end of it in water, and hold that end toward you while it dries. Watch the direction in which the fiber twists. The free end of a flax fiber will rotate to the right (clockwise), and a cotton fiber will rotate to the left (counterclockwise).

The preceding discussion of the identification of fibers is condensed in the accompanying chart.

IDENTIFICATION OF FIBERS

Burning Test	Structure Unchanged	Mineral	Rubbing: no effect			
		Weighted silk	Rubbing: changed to a shapeless ash			
	Structure Changed	KOH-soluble: wool, hairs, silk, casein	Lead acetate test	Blackened: wool, hairs	Use microscope	
				Not blackened: casein, silk	Concentrated HNO_3	Structure retained: casein
						Disintegrated: silk
			Concentrated HCl test	Soluble: silk		
				Insoluble: wool, hairs, casein	Methylene blue	Not colored: wool, hair
						Blue: casein
		KOH-insoluble: acetate, Vinyon, nylon, cotton, linen, ramie, hemp, jute, mercerized, cotton, rayons	Acetone	Soluble: acetate Vinyon	Glacial HOAc	Soluble: acetate
						Insoluble: Vinyon
			Phenol	Soluble: nylon		
			Phloroglucinol	Red color: hemp, jute		
				Not colored: cotton, linen, ramie, mercerized cotton, rayons		
			$ZnCl_2$-I_2 reagent	Blue color: mercerized cotton, rayons		
				Not colored: cotton, linen, ramie, hemp, jute		

SECTION

VII

Preparation of Solutions and Reagents. Apparatus Required

The following reagents, solutions, and materials will be required for the laboratory work outlined in this book. The probability is that all the experiments will not be assigned, so that each instructor must decide what work is to be done and then list the reagents and materials that will be required. It is assumed that all laboratories will have a stock of concentrated acids, ordinary reagent strength acids and bases, organic solvents, etc., so that the amount of these to be used is not important.

The preparation of reagent acids and bases is very flexible. The directions given below are merely suggestions and may be changed according to the discretion of any teacher.

ORDINARY CONCENTRATED AND REAGENT ACIDS AND BASES

Concentrated HCl
H_2SO_4
HNO_3

Glacial Acetic Acid

Reagents

HCl	2.5 liters concentrated made up to 8 liters
HNO_3	1.5 liters concentrated made up to 8 liters
H_2SO_4	1.1 liters concentrated made up to 8 liters
Acetic	2.0 liters glacial made up to 8 liters
NaOH	3.0 lb in 8 liters
NH_4OH	3.5 liters concentrated made up to 8 liters

VOLUMETRIC STANDARD SOLUTIONS

H_2SO_4 0.2 N approximately 27 ml concentrated H_2SO_4 made up to 5 liters and then standardized

H_2SO_4 0.02 N use 1/10 of above amount

HCl 0.1 N approximately 38.5 ml concentrated HCl made up to 5 liters and then standardized

Reagents

Acetic anhydride

Acetone

Acid navy blue, 2/1

Acid violet, 2/1

Alcohol, grain 95%

Alkaline lead acetate: Dissolve 30 gm basic lead acetate in 500 ml water. Dissolve 30 gm NaOH in 500 ml water. Mix the two solutions and filter through cotton if necessary.

Aluminum acetate: Dissolve 90 gm $Al_2(SO_4)_3$ in 300 ml water. Dissolve 140 gm lead acetate in 400 ml water. Mix the two solutions and make up to 1 liter. Filter.

Ammonium chloride, 50/1

Ammonium oxalate, 50/1

Barium chloride, 150/1

Benzidine: Dissolve 1.85 gm in 100 ml alcohol.

Bensopurpurin 4B, 2/1

Bleach liquor: Put about 20 gm commercial bleaching powder into a mortar. Work water into it with a pestle, adding the water in small portions to make a smooth cream. Add more water while stirring and finally transfer it to a wide-mouthed bottle and add enough water to make a little over a liter. Let settle and decant through filter paper before using. The solution should be stored in a cool dark place.

Calcium sulfate, saturated solution

Carbon tetrachloride

Chloroform

Croceine scarlet, 2/1

Disodium phosphate, $Na_2HPO_4 \cdot 12H_2O$, sp gr 1.04

Ether-Alcohol, 400 ml ether, 600 ml alcohol

Fehling's solution
A. 70 gm $CuSO_4$ in 1 liter
B. 100 gm NaOH and 346 gm sodium potassium tartrate in 1 liter

Glacial acetic acid + 7.5 ml concentrated H_2SO_4 per liter

Glauber's salt, 50 gm $Na_2SO_4 \cdot 10H_2O$ per liter

Hydrocellulose (for Experiment 12): Immerse washed cotton cloth in a 3% solution of H_2SO_4 for 2 hours at 70° C. Rinse well until no red color is formed on blue litmus paper when pressed on the cloth.

Lead acetate, 50/1

Loewe's reagent: Dissolve 10 gm crystalline $CuSO_4$ in 100 ml water. Add 5 ml glycerin. Add reagent NaOH, stirring until the precipitate, which forms at first, is dissolved. Let stand overnight and filter. If a precipitate forms during storage, filter before using.

Methylene blue, 0.1%, 1 gm/1

Methyl orange indicator, 1 gm per 100 ml water; put in dropping bottle

Millon's reagent: Put 2 ml mercury into 20 ml concentrated HNO_3 and stir until dissolved. If the solution is turbid add a little more acid. This reagent is not very stable. Make up only enough to last about 1 month.

β-Naphthol: Dissolve 10 gm in 1 liter 5% NaOH.

Oil: any dark lubricating oil

Oxalic acid, 0.5%, 5 gm/1

Oxalic acid, saturated solution

Oxycellulose (for Experiment 12): Immerse washed cotton cloth in a 1% $KMnO_4$ solution for 62 hours at room temperature. Rinse well and immerse in 2% $NaHSO_3$ solution until white. Rinse thoroughly and dry.

Phenol (90%): CAUTION (See page 69). Set a bottle of phenol crystals in a bath of hot water. When melted, pour 180 gm into a weighed beaker and add 20 ml water. Stir well and store in a dark bottle.

Phenolphthalein indicator: 1 gm in 100 ml alcohol. Keep in dropping bottles.

Phloroglucinol: Dissolve 2 gm in 100 ml alcohol and mix with 100 ml concentrated HCl.

Picric acid: 5 gm in 1 liter

Potassium iodide: Dissolve 100 gm in 500 ml water.

Salt brine, saturated

Schweitzer's reagent: Put about 120 gm fine copper turnings in a 4-liter wide-mouthed bottle. Add 3 liters of a mixture of 2250 ml concentrated HN_4OH, 750 ml water, and 3 gm cane sugar. Arrange any method for bubbling air through this mixture while it is being stirred. The air should first be passed through a bottle containing reagent NH_4OH.

Silver nitrate: Make a 2% solution.

Soap (5/1): Dissolve 40 gm good quality commercial soap in 8 liters water. Warm part of the water, add soap, stir until dissolved, and then add the rest of the water.

Soap, alcoholic solution: See page 53.

Soda ash: 10 gm Na_2CO_3 per liter

Sodium hydroxide (23%): Dissolve 300 gm NaOH in enough water to make 1 liter.

Sodium nitrite: Dissolve 15 gm in 500 ml water. This solution must not be kept more than 1 week.

Sodium silicate: Make up to a specific gravity of 1.03.

Sodium thiosulfate (1.0 N solution): Dissolve 248.2 gm $Na_2S_2O_3$-$5H_2O$ in 200 ml water. Transfer quantitatively to a 1 liter volumetric flask and fill up to the mark with water.

Sodium thiosulfate (0.1 N solution): Dissolve 24.82 gm $Na_2S_2O_3$-$5H_2O$ in 200 ml water, transfer to a 1 liter volumetric flask, and make up to the mark with water.

Standard hard water: See page 48.

Standard soap solution: See page 48.

Stannic chloride (sp gr = 1.275): This solution contains about 300 gm anhydrous $SnCl_4$ per liter.

Starch solution (make up fresh each time): Put 0.5 gm soluble starch in 50 ml water and boil gently for 2 minutes.

Sulfuric acid (66% by volume): Add 660 ml concentrated H_2SO_4 in small amounts, stirring and cooling, to 340 ml water. This will require 30 minutes.

Tartaric acid (0.5%), 5 gm/l

Texchrome dye: May be purchased from Fisher Scientific Co., Pittsburgh.

$ZnCl_2$-I_2 reagent: Dissolve 12.5 gm KI in 30 ml water, add 0.5 gm I_2, and stir until the iodine dissolves. Dissolve 120 gm $ZnCl_2$ in 60 ml water. Add first solution to the second. Stir. Store in small glass-stoppered dark bottles so that it can be used with a dropper.

Miscellaneous Solid Materials

- Absorbent cotton
- Cotton muslin
- Cotton knitting yarn
- Electric iron
- Fabrics for analysis
- Ironing board
- Litmus paper (red and blue)
- Rayons
  (viscose, acetate, and Bemberg)
- Silk, in the gum
- Silk, pure dye crepe
- Soap, pure castile
- Soap, commercial brands
- Sodium bisulfite
- Sodium chloride
- Stopcock grease
- Wool, in the grease, fine and coarse
- Wool, yarn, 3- or 4-fold knitting

APPARATUS REQUIRED

This list is divided into two groups, (1) apparatus that may be kept in individual lockers and (2) items that may be used by groups of students or the entire class and should be kept outside the lockers. In some cases, for obvious reasons, it may be necessary for students to work together even with individual apparatus.

In the Locker

- Beakers, 1 50-ml
  2 150-ml
  2 250-ml
  1 450-ml
  1 600-ml
- Bottles, glass-stoppered 250-ml,
  wide-mouthed, 4-oz
- Burette, 50-ml
- Burners, 2 Bunsen, with tubing
- Casseroles, 1 500-ml
  2 250-ml

orating dish, 7-in
er paper
sks, Erlenmeyer, 1 50-ml
2 200-ml
volumetric, 250-ml,
100-ml
Forceps
Funnel, 2-in., short-stem
Glass plate, 4-in
Glass rods, 3
Graduates, 10-ml
100-ml
Iron rings, 2 4- to 6-in.
Pipettes, 20-ml
50-ml
Test tubes, 6 0.5 x 6-in.
1 1 x 8-in.
Test tube brush
Test tube holder
Thermometer
Towel
Watch glasses, 1 3-in.
2 6-in.
Wire gauze, 2-4 in.

Outside the Locker

Büchner funnel and filter flask
Balances, open-pan scales, semiquantitative
Desiccator, large
Funnel rack
Iron wire squares (page 31)
Oven for drying
Tensile strength machine
Test tube rack
Weights for balances