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INSTRUCTOR MANUAL
INDUSTRIAL HYGIENE CHEMISTRY COURSE

LESSON NUMBER 8

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Prepared by:

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INTRODUCTION

This Instructor Manual has been prepared for industrial hygienists and analytical chemists participating in the National Institute for Occupational Safety and Health's Regional Training Program. The purpose of this Manual is to assist these professionally qualified, but possibly inexperienced, instructors in the preparation and conduct of a one-week "Industrial Hygiene Chemistry" course. This Manual will guide instructors through both lecture and laboratory lessons. It is complemented by a matching Student Manual. The course is recommended for students having, as a minimum, an undergraduate degree in chemistry (or its equivalent) along with at least one year's experience in instrumental analysis.

It is not necessary for instructors to have had prior teaching experience although such experience would be desirable. All instructors should be thoroughly familiar with industrial hygiene chemistry procedures, instruments and equipment relevant to the subject areas they will teach. In addition, each instructor should attend the course director's orientation seminar presented before the start of each one-week "Industrial Hygiene Chemistry" course.

The remainder of this introduction describes the course objectives, lessons, and the organization and format of the documentation in each lesson, including lecture and laboratory lesson plans.

Course Objectives

The following course objectives will be attained by graduates of this program:

- Given a particular chemical health hazard commonly found in the occupational environment, the trainee will be able to select an appropriate sampling strategy using available sampling techniques and to select a corresponding appropriate analytical method for quantitative characterization of the sample by using his knowledge gained from the course and technical information referenced in the course.

- Trainee will be able to apply his knowledge of wet chemical and/or instrumental analysis in employment of current methodologies for evaluating the typical work environment.

- Trainee will be able to perform and evaluate quantitative analytical determinations for four classes (types) of hazardous substances using a correspondingly different method for each class or type.

- Given the analytical results obtained through proper measurement procedures, the trainee will be able to define the data in terms of actual environmental concentration levels and to interpret the results in light of existing exposure standards.

Lessons

18 lessons are presented in this course:

- Introduction to Course
- Introductory Topics
- Direct Reading Instruments
- Air Flow Calibration and Sampling
- Ion Selective Electrode Laboratory
- Introduction to Spectrophotometry
- Instrumentation and Application of Spectrophotometry
- Colorimetric Determination of Free Silica (Quartz) Laboratory
- Introduction to Spectroscopy
- Atomic Absorption Spectrometry
- Atomic Absorption Spectrometry Laboratory
- Introduction to Chromatography
- Insturmentation and Application of Chromatography
- Gas Chromatography of Organic Solvents Laboratory
- Titrametric Determination of SO_2 Laboratory
- Colorimetric Determination of SO_2 Laboratory
- Biological Monitoring
- Related Topics

Lectures

Each lesson that is to be presented as a lecture is documented in a standardized format.

A. Lecture Cover Sheet

A cover sheet for each lecture presents the following information:

- Lesson title
- Lesson number and length
- Behavioral objective
- Scope of the lesson
- List of visuals
- List of exhibits
- List of equipment needed for the lesson

B. References

After the cover sheet, there is a list of references. These references are keyed to the paragraphs within each lesson. The number in parenthesis following each paragraph is the reference number. These references are included so that the instructor, if he wishes, may further research specific instructional subject matter.

C. Additional Readings

Following the reference list, in most lessons, is another listing called "Additional Reading." This bibliography contains books and articles which are generally pertinent to the subject area covered in this lesson. These are considered as important secondary reference sources.

D. Expanded Outline (left-hand page)

On the left-hand page, beginning after the Additional Readings section, is an expanded outline. This outline indicates the information that should be emphasized and covered during the lecture. The sequence of the outline should be followed during

teaching. The expanded outline gives sufficient information to explain the brief outline which is on the right-hand page. All test questions (both self tests and course evaluator) come from the expanded outline. Additionally, there are descriptions of the visuals within the outline.

E. Brief Outline (right-hand page)

This page consists of a notes column and the outline.

1. Notes Column - times (both elapsed and projected) are indicated in this column. The elapsed time designates the time it should take the instructor to reach this point in the lecture starting from 0 at the beginning of each lecture. The elapsed time is in parentheses. The projected time designates the time it should take the instructor to reach the next major portion of the outline. A major portion of an outline is designated by a capital letter in the outline. In addition, transitional phrases connecting the major outline portions are included in the notes column. These phrases are to assist the instructor in bridging from one section of the outline to the next. Notations of what visual, exercise, table, etc., should be introduced at a given point in a lesson and miscellaneous notes to the instructor are contained also in this column.

2. Outline - this is a brief outline corresponding to the expanded outline on the facing page. Words and phrases in the brief outline key the instructor to the lesson's subject content and to the expanded outline on the left-hand page. There is sufficient space between the key words in the brief outline for the instructor to write his own additional notes when he is preparing his lecture.

F. Exercises and Problems

In some lessons, exercises and problems are included. These are given during class time. The answers to the problems are worked out with students after they have had an initial try at completing them on their own. Answers are provided in the Instructor Manual.

G. Self Tests

Self tests are included after most lessons. The Instructor Manual contains the correct answers, whereas the Student Manual does not. The students should first answer the questions, and then the instructor should review the answers, explaining fully the reasons for the correct answers. The self tests are not scored by the instructor and no records are kept of the individual student's performance. The instructor should use the information from the discussion of self tests to remove student misunderstandings or lack of understanding.

H. Copies of Visuals

Copies of visuals that are to be shown in a lecture are included at the end of that lesson documentation. These can be useful in preparing for the lecture presentation.

I. Homework

No specific homework assignments are included within the lesson documentation. However, there is a great quantity of information for the students to absorb during this one-week course. Therefore, students should be urged to review nightly all lessons covered during the day and all lessons to be presented on the following day. In particular, they should become familiar with the laboratory procedures for the following day. There is much to be accomplished in every laboratory and little time to do it. If the students are familiar with the procedure, the laboratory experiments will progress much more smoothly.

Laboratories

Each lesson that is to be presented as a laboratory is documented in standardized format consisting of four elements.

A. Laboratory Cover Sheet

A cover sheet for each laboratory presents the following information:

- Lesson title
- Lesson number and length
- Behavioral objective
- Scope of the lesson
- List of equipment, apparatus and forms

B. Special Preparation Section

This section will follow the laboratory cover sheet, and includes specific directions that must be followed prior to actual class time. These instructions are concerned with the preparation of apparatus, facilities, chemicals and materials that are necessary for the laboratory session.

C. Laboratory Procedures

The procedures for performing each laboratory are fully documented on the left-hand page. The elapsed and projected times are indicated for some lessons with the elapsed times appearing in parentheses. The right-hand page is a blank page for notes on specifics of the laboratory to aid the individual instructor in giving an efficient lesson.

D. Figures and Forms

Equipment figures and student forms are included after the procedures. The figures are presented to aid the instructor in setting up the experimental equipment. The forms are to be used by the students during the laboratory to assist them in recording, calculating and analyzing data.

LESSON TITLE	LESSON NUMBER	LESSON LENGTH
Colorimetric Determination of Free Silica (Quartz)	8	4:00

BEHAVIORAL OBJECTIVE

The student will be able to operate and calibrate a spectrophotometer and perform the necessary sample preparation to determine the amount of free silica (quartz) in mineral samples.

SCOPE

Introduction and review
Preparation of samples for analysis
Preparation of standards
Examining the absorption spectrum from 400 to 440 nm.
Color development in standards and samples and absorbance readings
Calculations and data analysis

EQUIPMENT, APPARATUS, AND FORMS

Equipment and chemicals for each section of the lab is as follows:

B. Silica-free water and polyethylene or polypropylene carboys (5 or 6.5 gallon capacity)
Reference samples labeled M, N and O (see "Special Preparation" section)
Redistilled nitric acid
85% ACS reagent grade phosphoric acid
1:10 (v/v) ACS reagent grade hydrochloric acid
48% ACS reagent grade hydrofluoric acid
47-mm. diameter 0.45-μm. cellulose membrane filters
Analytical balances
Spatulas
250-ml. Phillips borosilicate glass beakers
10-ml. and 25-ml. glass or polyethylene graduates
Hot plates
Bent-stem funnels
Precision Heaters with rheostats (see "Special Preparation" section)
Serological Rotators

EQUIPMENT, APPARATUS, AND FORMS (continued)

Crucible tongs padded with rubber or Tygon tubing
One-liter glass beakers
250-ml. glass or polypropylene graduates
Thermometers
Filter holder assembly for 47-mm. diameter filters and associated vacuum flask and tubing
150-ml. polyethylene or polypropylene beakers
50-mm. thin polyethylene discs
Polyethylene or polypropylene watch glasses for 150-ml. beakers

C. Silica standard solution
Silica-free water
150-ml. polyethylene beakers and polyethylene watch glasses
25-ml. and 50-ml. Nalgene (acrylic) burets with Teflon stopcocks

D. Spectrophotometer suitable for use between 380 and 450 nm.
25-ml. and 50-ml. pipets
Polyethylene stirring rods
Water bath (40°C)
50-ml. Nalgene buret
Cells for the spectrophotometer
Kimwipes
20-ml. pipet with rubber suction bulb
Silica-free water
5% Boric Acid Solution
Molybdate Reagent
10 N Sulfuric Acid

E. Same as D.

Forms:

The Absorption Spectrum from 400 to 440 nm.
The Absorbance Measurements on Standards and Samples
The Calibration Curve for Silica

SPECIAL PREPARATION

Special preparation for each section of the laboratory should be noted by the instructor before the lab begins, and concurrently as the experiments progress.

General:

Cumulative time notations will not appear in the documentation of this laboratory. In fact, the sum of the several sections of the laboratory is greater than the four hours allocated. However, there are several waiting periods required. During these times, other sections of the laboratory can be started. By efficiently coordinating the working time of every student, the laboratory can be completed within the alloted time. The extent to which starting points will have to be staggered will depend on (a) how many students are performing the experiment, (b) how many serological rotators and precision heaters are available, (c) how much hood space is available and (d) how many spectrophotometers there are. The instructors may decide that it is imperative for students to work in pairs.

While some of the students start on sample preparation (Section B) which is the most time consuming, others can begin directly with the standards preparation (Section C). By the time a group has completed the standards preparation, the balances should be free and some of this group can start on sample preparation. Others of the group which started on standards preparation should continue with obtaining the absorption spectrum (Section D). Meanwhile, those students who started with sample preparation (Section B) may find time to begin standards preparation (Section C) during waiting periods.

Explanation of the chemistry involved in sample preparation can be found in Talvitie, N.A., Anal. Chem. 23 (4), 623-26 (1951). Explanation of the reactions involved in the color formation can be found in numerous texts on Colorimetric Analysis.

Section:

B. Preparation of Samples For Analysis

Silica-free water can be prepared by passage through cartridge demineralizers. It is estimated that approximately 1 gallon per

student will be required if they do their own apparatus washing. Otherwise, 0.5 gallon per student will be enough since reagents will be prepared in advance of the laboratory.

The reference samples should be prepared from 48W0516 Dickite No. 16 available from Wards Natural Science Establishment, P.O. Box 1712, Rochester, New York 14603. This mineral is economical, available in kilogram amounts from stock, and nearly 100% soluble in orthophosphoric acid. It is very low in natural free silica. (Alternatively, 48W1240 Montmorillonite No. 24 containing about 1% quartz can be used. This material is also available from Wards). The Dickite is spiked with known amounts of pure quartz which can also be purchased from Wards. The quartz crystal should be ground to pass a 200 mesh U.S. Standard screen.

Sample M is the pure Dickite

Sample N is Dickite plus 17.0 mg. of quartz/gram of Dickite, i.e., 1.70% added free silica as quartz

Sample O is Dickite plus 11.0 mg. of quartz/gram of Dickite, i.e., 1.10% added free silica as quartz

Mixtures N and O must be very thoroughly blended to obtain a homogeneous distribution of quartz. A rotating V mixer is useful for this purpose. After blending, approximately 0.3 grams of each blend should be placed in individual vials for distribution to the students.

As an alternative to this preparation procedure, mixtures can be obtained from Chemplex Industries, Inc., 34 Bradley Road, Scarsdale, N.Y. The standard mixtures may be less well suited than the ones described above which were specifically developed for this procedure as presented.

Redistilled nitric acid can be prepared from reagent grade acid using an all-glass still or it may be purchased from J.T. Baker Chemical Company.

The bent stem funnels are prepared from straight stem funnels to allow contact with the side of the beaker (Figure 8-1).

The Precision heater, type RD, 550-watt, 115-volt (Precision Scientific Company) coupled with a 750-watt variable transformer with voltmeter is suitable to achieve the 240°C required temperature when it is operated at about 70 volts. The heater should be turned on at least 45 minutes before use. It is mounted on a Serological Rotator to achieve swirling action. Several suitable rotators are available from a number of laboratory supply houses. Ideally, several set-ups should be available because each student has four samples to process (8 minutes each).

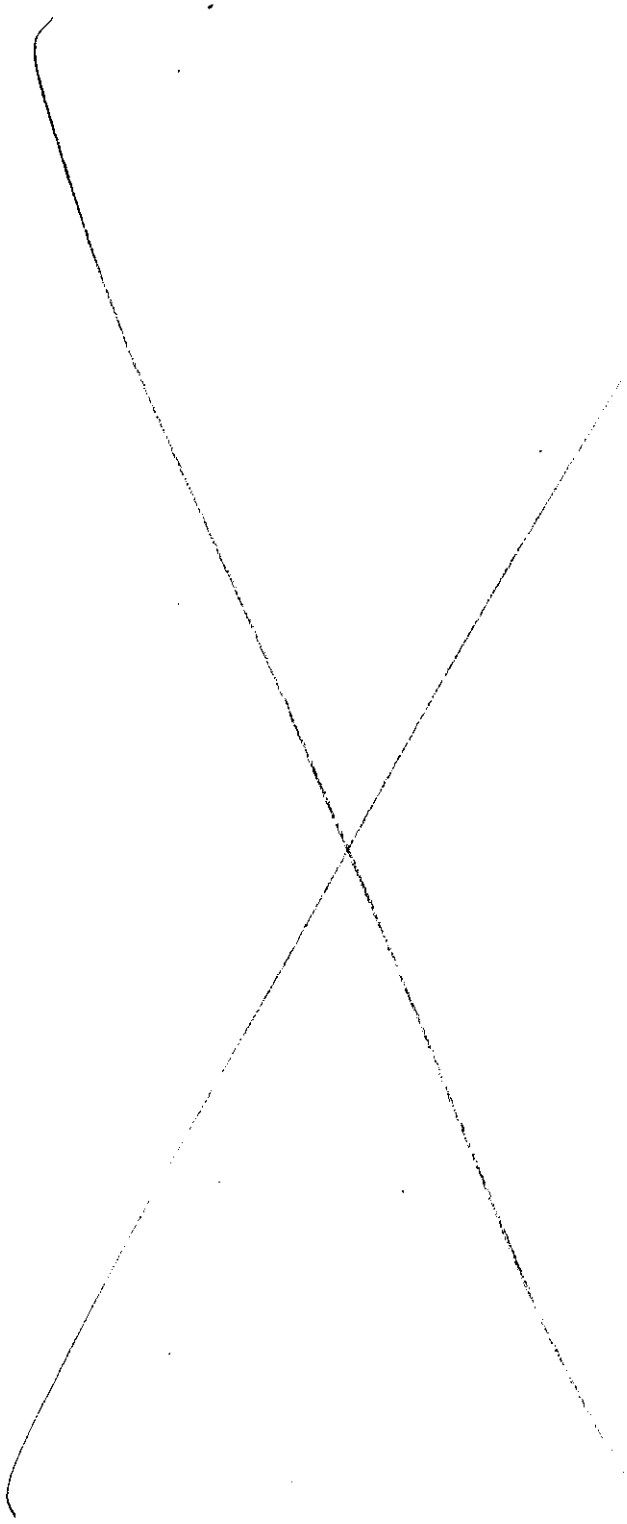
C. The 0.500 mg./ml. silica stock standard is prepared in advance by dissolving 1.000 grams of finely ground, acid-washed quartz in 40 ml. of 48% ACS reagent grade hydrofluoric acid in a polyethylene beaker. Solution rate is slow and will probably require standing overnight. Dilute to a final volume of exactly 2 liters and store in a polyethylene bottle. Each student will require a minimum of 26 ml. of standard. One-oz. polyethylene bottles will hold a little over 30 ml. and can be used. Alternatively, two-oz. bottles can be filled a little over half full.

D. Boric Acid Solution, 5%. With some allowance for losses, an average of 600 ml. will be needed per student. The solution can be prepared by dissolving 50 grams of ACS reagent grade boric acid crystals per liter of warm, silica-free water. After cooling, filter with vacuum through a 0.45-μm. membrane filter and store in a polyethylene carboy.

Molybdate Reagent. At <u>least</u> 50 ml. per student should be prepared. Dissolve 100 g. of ACS reagent grade ammonium molybdate tetrahydrate in about 800 ml. of silica-free water. Acidify with 80 ml. of concentrated sulfuric acid. Cool, dilute to one liter and store in the dark.

10 <u>N</u> Sulfuric Acid. At least 250-ml. per student will be needed. Cautiously add 555 ml. of ACS reagent grade concentrated sulfuric acid to about 1.3 liters of silica-free water. Cool and dilute to 2 liters.

E. Students may need some assistance in the spectrophometric absorbance measurements in order to maintain the 2 minute measurement interval, until they have completed 2 or 3 measurements.



TITLE	LESSON NUMBER
Colorimetric Determination of Free Silica (Quartz)	8

A. Introduction and Review 0:30

1. Describe the five parts of the laboratory emphasizing the need for students to start at different points in the exercise due to equipment and facilities limitations and unavoidable waiting periods.

   - Preparation of samples for analysis
   - Preparation of standards
   - The absorption spectrum from 400 to 440 nm.
   - Color development in standards and samples and absorbance readings
   - Calculations and data analysis

2. Briefly outline the chemical reactions involved in sample preparation and color development.

3. Explain that a lower concentration range can be covered by using 1-amino-2-naphthol-4 sulfonic acid and reading absorbance at 820 nm. This procedure is omitted from the experiment due to time limitations but it requires no new knowledge or skills which are not covered in this exercise.

4. A sampling train is omitted. Sampling is done in the same manner as for lead which will be covered in Lesson 11.

B. Preparation of Samples For Analysis 2:30

All glassware and plastic ware must be detergent washed and given a final rinse in silica-free water from a polyethylene or polypropylene carboy.

1. Obtain from the instructor three reference samples labeled M, N and O.

INSTRUCTOR'S NOTES

2. Place a 47 mm. diameter 0.45 - μm. cellulose membrane filter on an analytical balance and record the weight to the nearest mg.

3. Transfer to the paper a portion of reference sample M amounting to 100±10 mg. and weight to the nearest mg. Use a spatula for this transfer and be sure to obtain as representative a sample as possible.

4. Transfer the filter plus sample to a clean labeled 250-ml. Phillips borosilicate glass beaker.

5. Repeat this process for reference samples N and O.

6. Into a fourth 250-ml. Phillips beaker, place a 47-mm. diameter 0.45-μm. cellulose membrane filter as a blank.

7. In a hood, use a 10-ml. graduate to add 3-4 ml. of redistilled nitric acid to each beaker. Heat to dryness. A single treatment may consume the filter leaving only a white residue. If there is evidence of residual organic matter, add a second portion of redistilled nitric to each beaker, including the blank.

8. With a graduate, add 25 ml. of 85% ACS reagent grade orthophosphoric acid to each of the four beakers. Cover each with a bent stem funnel.

9. In a hood, place the beakers on a preheated Precision Heater at 240°C and heat for exactly 8 minutes, swirling by the action of a Serological rotator.

10. Remove the beakers with padded crucible tongs and swirl each for one minute.

11. While the samples are cooling, heat 750 ml. of silica-free water in a one-liter beaker to a temperature of 60-70°C. When the acid solutions are cool, add approximately 125 ml. of the 60°C water to each, washing down the sides of the beaker in the process. Swirl to mix the acid and the water.

INSTRUCTOR'S NOTES

12. Filter each solution with suction through a 47-mm. diameter 0.45-μm Millipore membrane filter in a standard filter assembly. Be sure to effect a complete transfer of the particles from the beaker to the filter. Wash thoroughly with 1:10 (v/v) hydrochloric acid.

13. Place each membrane flat in the bottom of a 150-ml. polyethylene beaker. Add dropwise 0.5 ml. (10 drops) of 48% ACS reagent grade hydrofluoric acid to the particles on each membrane surface. Float a 50-mm. polyethylene disc over each membrane, cover the beakers with polyethylene watch glasses and allow to stand for at least 30 minutes.

14. Further processing will be done simultaneously with the standards.

C. Preparation of Standards 0:30

1. Obtain from the instructor a 1-oz. polyethylene bottle filled with 0.500 mg./ml. silica stock standard.

2. Label seven 150-ml. beakers and add the amounts of stock standard and silica-free water shown below. Additions of the stock standard and the water can be made from 25-ml. and 50-ml. Nalgene (acrylic) burets with Teflon stopcocks, respectively.

Label	ml. 0.500 mg./ml. silica	ml. silica-free water	mg. silica in standard
A	1.00	24.00	0.50
B	2.00	23.00	1.00
C	3.00	22.00	1.50
D	4.00	21.00	2.00
E (Two)	5.00	20.00	2.50
F	6.00	19.00	3.00

3. The extra E standard will be used to examine the spectral absorption between 400 and 440 nm.

INSTRUCTOR'S NOTES

4. Cover each of the beakers with polyethylene watch glasses until ready to develop the color simultaneously with the samples.

D. Examining the Absorption Spectrum from 400 to 440 nm. 1:00

1. Turn on the spectrophotometer to allow time for warm-up.

2. To one of the two E standards, add by pipet 25.0 ml. of silica-free water and 50.0 ml. of 5% boric acid solution. Stir with a polyethylene stirring rod and replace the watch glass. Reserve the pipets for use with the same reagents in Section E.

3. Heat the solution in a 40°C water bath for 10 minutes.

4. From a 50-ml. Nalgene buret, add 4.00 ml. of molybdate reagent while stirring. Record the time of the addition. This buret and reagent will also be used in Section E.

5. With the aid of the instructor, set the wavelength of the spectrophotometer at 400 nm. Rinse a reference cell with distilled water, fill and gently wipe the exterior with a Kimwipe. Carefully place the reference cell in the holder of the spectrophotometer. Adjust the absorbance scale as specified in the operating directions.

6. Exactly 20 minutes after the addition of the molybdate reagent, add 20.0 ml. of 10 N sulfuric acid using a pipet and rubber bulb. Mix thoroughly.

7. Within a few seconds, rinse the sample cell with two portions of the standard, fill, wipe the exterior of the cell with a Kimwipe and place the cell in the holder. Record the absorbance. (If the instrument has only a % T scale, convert % T to absorbance, A, by the equation $A = 2 - \log \%T$).

INSTRUCTOR'S NOTES

8. Remove the cell containing standard E, replace the reference cell in the light beam, change the wavelength to 410 nm., readjust the scale settings, replace the reference cell with the cell containing standard E and record the new absorbance. This manipulation should be done quickly since the color is only stable for a short time.

9. Continue the process as rapidly as possible for wavelengths of 415, 420, 425, 430 and 440 nm.

10. Plot A vs. wavelength and draw a smooth curve. Determine if 420 nm. is the proper setting for quantitative measurements.

E. Color Development in Standards and Samples and Absorbance Readings 1:20

1. To each of the six standards, three samples and the blank, add by pipet 25.0 ml. of silica-free water and 50.0 ml. of 5% boric acid solution. Stir with a polyethylene rod.

2. Heat the ten solutions in a 40°C water bath for 10 minutes.

3. From a 50-ml. Nalgene buret, add 4.00 ml. of molybdate reagent to standard A while stirring. Start a stopwatch. At 2 minute intervals, make the same addition to the remaining nine beakers.

4. Twenty minutes after the first molybdate addition, add 20.0 ml. of 10 N sulfuric acid to standard A using a pipet and rubber bulb. Stir thoroughly. Immediately check the zero absorbance setting of the spectrophotometer with the distilled water reference cell at a wavelength of 420 nm. Rinse a sample cell with standard A, fill, wipe with a Kimwipe, place in the spectrophotometer and read the absorbance.

5. Continue with each standard, sample and blank in the same sequence as the molybdate addition. Two minute intervals should be maintained as close as possible. The zero setting of the spectrophotometer need not be checked each time unless drift is a serious problem. The sample cell should always be rinsed twice with the next solution to be measured and then wiped with a Kimwipe.

INSTRUCTOR'S NOTES

6. Subtract the blank absorbance from each of the standard and sample absorbances.

7. Plot corrected absorbance vs. mg. of silica in the standards and draw the best fitting straight line through the origin.

F. Calculations and Data Analysis 0:30

1. Read the mg. of silica in M, N and O from the graph.

2. Calculate the % silica in each of the three samples.

3. Subtract the % silica in M from N and O to find the % added to N and O.

4. Obtain the results from the other students for the % added to N and O.

5. Obtain the correct values from the instructor.

6. Analyze the results in terms of precision and accuracy.

INSTRUCTOR'S NOTES

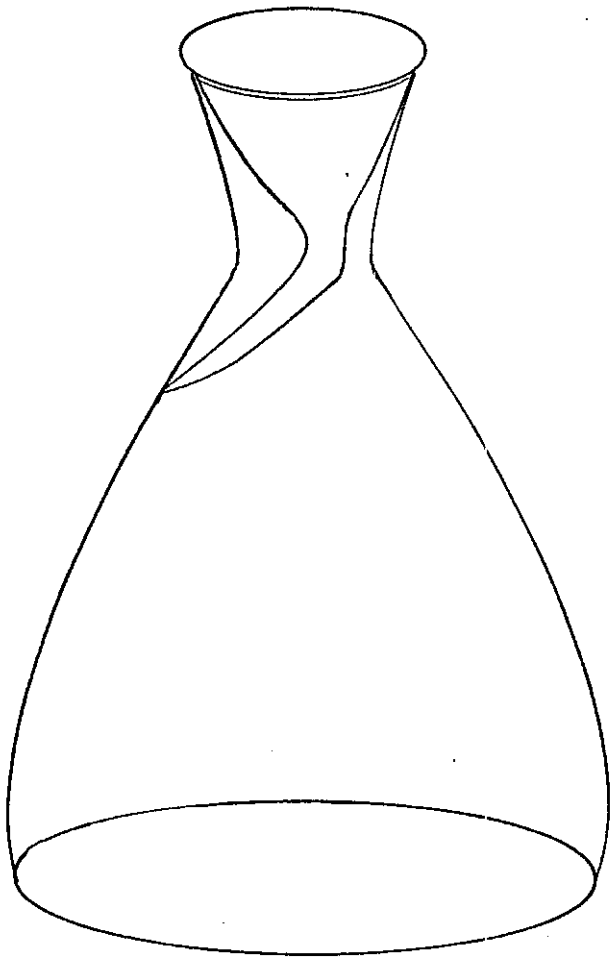
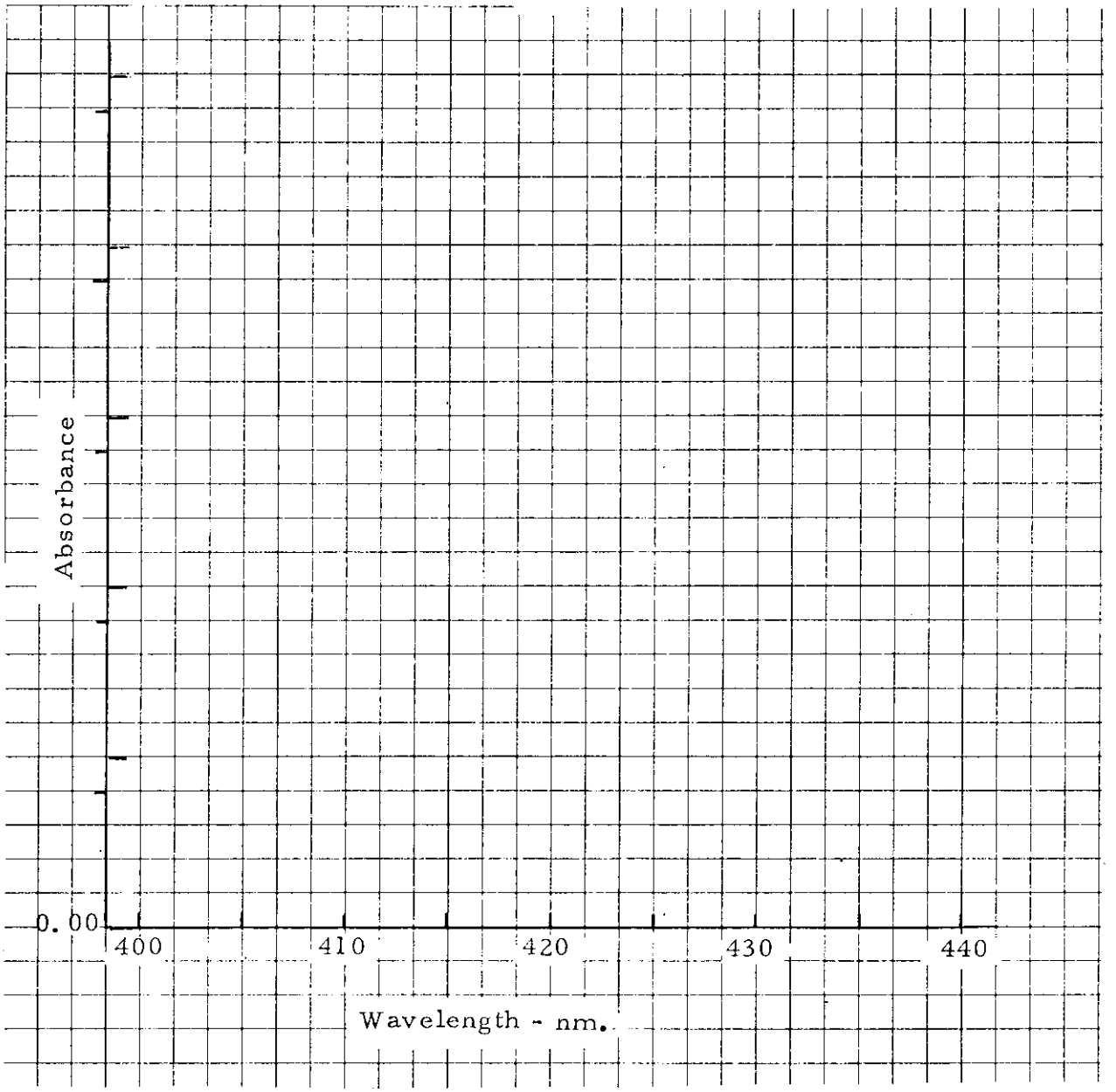


Figure 8 - 1. Apparatus for heating Sample

The stem of the small funnel is sharply bent to make contact with the side of the beaker. By drawing it out to a point or beveling, condensed liquid returns more easily to the sample.

The Absorption Spectrum from 400 to 440 nm.
(Section D)

Wavelength, nm.	Absorbance
400	
410	
415	
420	
425	
430	



Absorbance Measurements on Standards and Samples

(Sections E and F)

Standard	mg. Silica	Absorbance	Corrected Absorbance (Subtract Blank)
A	0.50	_____	_____
B	1.00	_____	_____
C	1.50	_____	_____
D	2.00	_____	_____
E	2.50	_____	_____
F	3.00	_____	_____

Samples		
M	_____	_____
N	_____	_____
O	_____	_____

Blank		_____

$$\% \text{ Silica} = \frac{(\text{mg. } SiO_2)\ (100)}{\text{mg. of sample}}$$

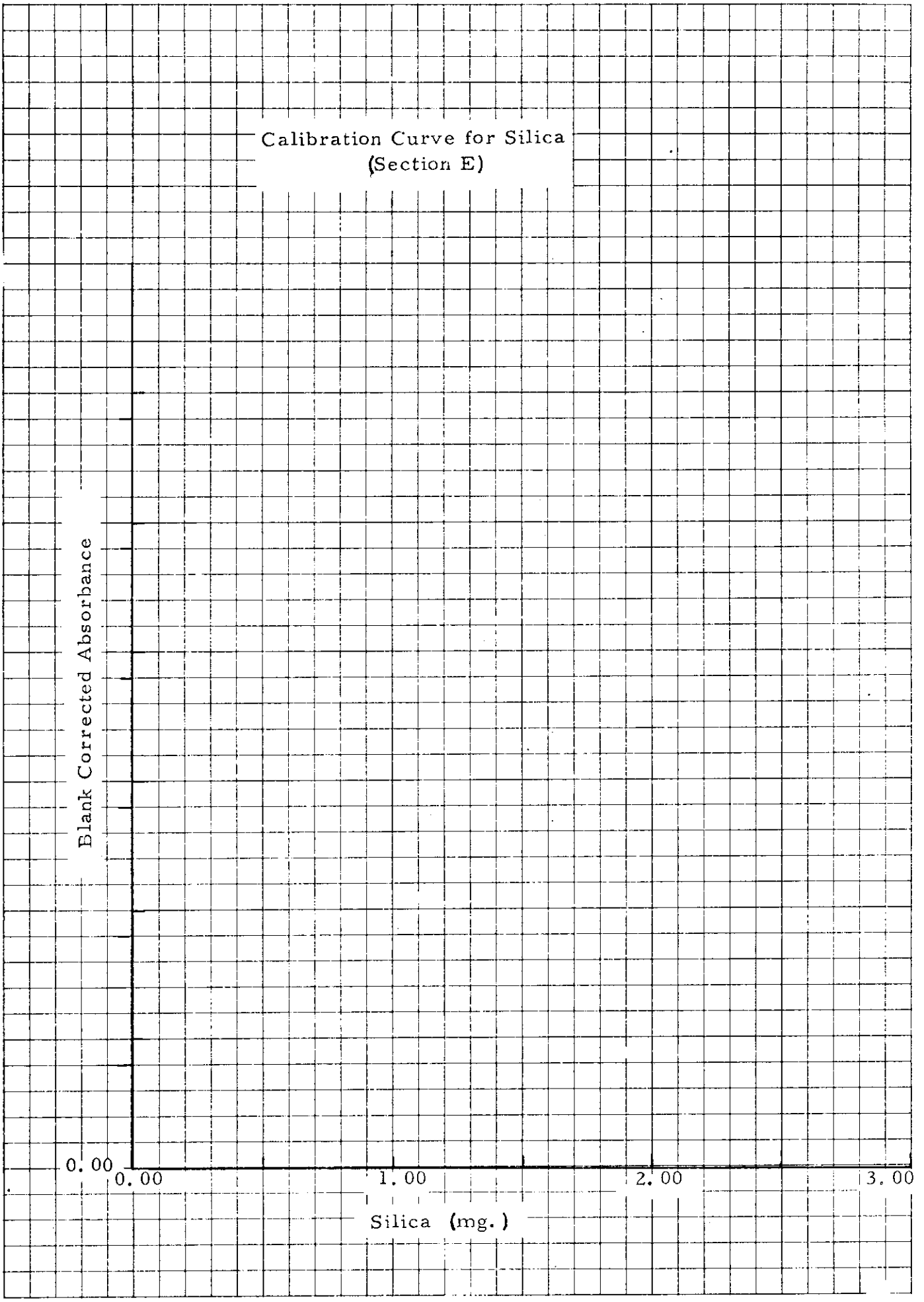
$$\% \text{ Silica in M} = \frac{(\quad)\ (100)}{(\quad)} = \_\_\_\_\_\ \%$$

$$\% \text{ Silica in N} = \frac{(\quad)\ (100)}{(\quad)} = \_\_\_\_\_\ \%$$

$$\% \text{ Silica in O} = \frac{(\quad)\ (100)}{(\quad)} = \_\_\_\_\_\ \%$$

% Added Silica in N = % in N - % in M = _____ %

% Added Silica in O = % in O - % in M = _____ %


Calibration Curve for Silica
(Section E)
Blank Corrected Absorbance
0.00
0.00
1.00
2.00
3.00
Silica (mg.)