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PB82-147695

INSTRUCTOR MANUAL
INDUSTRIAL HYGIENE CHEMISTRY COURSE

LESSON NUMBER 15

April 1975

Prepared for:

National Institute for Occupational Safety and Health
Rockville, Maryland

Contract Number CDC-99-74-72

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ACKNOWLEDGEMENTS

Dunlap and Associates, Inc., of Darien, Connecticut wishes to acknowledge with sincere appreciation the support received from the National Institute for Occupational Safety and Health in the administration and conduct of this project. In particular, we would like to express our gratitude to Dr. Thomas Purcell, the Project Officer.

We wish also to thank our consultants who contributed directly to the preparation of course materials: Mr. J.D. Johnson of Spectrogram Corporation, Dr. C.L. Grant of the Center for Industrial and Institutional Development - University of New Hampshire, Dr. Melvin W. First of the Harvard School of Public Health, and Mr. Adrian L. Linch, private consultant.

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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
Titrametric Determination of SO_2	15	2:00

BEHAVIORAL OBJECTIVE

The student will be able to perform the titrametric determination of SO_2.

SCOPE

Introduction
Demonstration of a gas dilution system for standard concentrations of SO_2 using a permeation tube
Demonstration of a sampling train with midget impinger
Standardization of barium perchlorate titrant
Analysis of samples and blanks
Calculation and data analysis

EQUIPMENT, APPARATUS, AND FORMS

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

B & C.
- 5-cm. sulfur dioxide permeation tube (NBS)
- Water cooled condenser
- Constant-temperature water bath at 20°C with pump
- Cylinder of pure dry air
- Cylinder of pure dry nitrogen
- Pressure regulators and flow control valves
- Dry test meters
- 2-meter copper coil (in the water bath)
- Thermometers
- Mixing bulb
- Cassette with 0.8 - μm. cellulose membrane filter
- Midget impingers
- Trap containing glass wool
- Manometer
- Vacuum pump

EQUIPMENT, APPARATUS, AND FORMS (continued)

D. 50-ml. glass stoppered Erlenmeyer flasks (or equivalent)
100-ml. beakers and watch glasses
Buret funnel
10-ml. capacity buret
250-ml. wide mouth Erlenmeyer flasks
5-ml. pipets
50-ml. graduated cylinders
Glass stirring rods
pH test paper for the range 0-7
Standardized .005M H_2SO_4
Barium perchlorate (approximately 0.005M) to be standardized
ACS reagent grade isopropanol
1.8% perchloric acid
Thorin indicator solution

E. Midget impingers containing known concentrations of SO_2 and blanks
25-ml. volumetric flasks
Glass stirring rods
10-ml. pipets
50-ml. graduated cylinders
10-ml. capacity buret graduated in 0.05 ml. subdivisions
Buret funnels
250-ml. wide mouth Erlenmeyer flasks
pH test paper for the range 0-7
Standardized barium perchlorate
ACS reagent grade isopropanol
1.8% perchloric acid
Thorin indicator solution

Forms:

Gas Dilution System Calculation
Standardization of Barium Perchlorate Titrant
Calculation of SO_2 in Reference Samples

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:

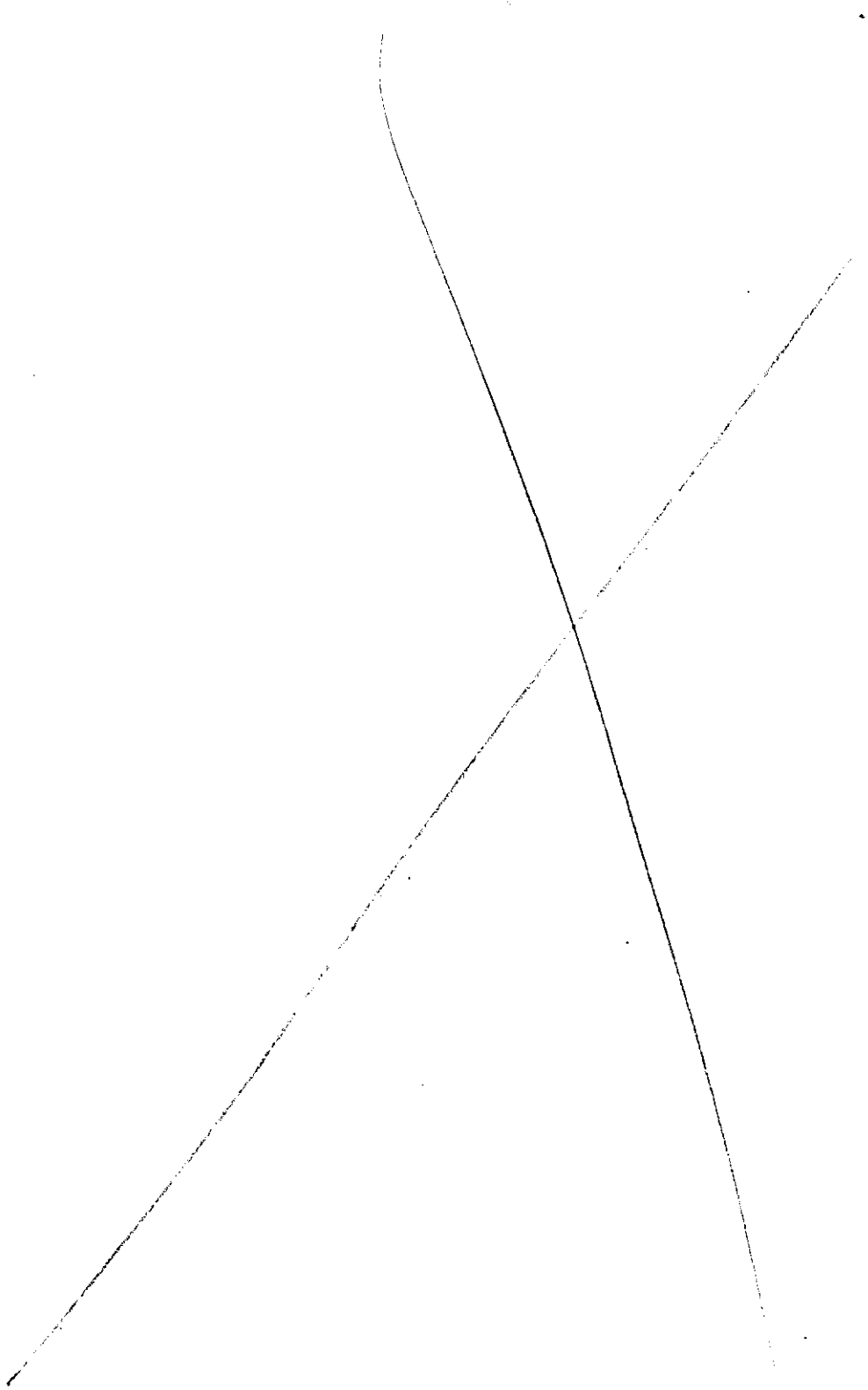
Cumulative time notations will not appear in the documentation of this laboratory. In fact, the sum of the several sections of the laboratory is greater than the two hours allocated. However, the laboratory can be completed within the alloted time by efficiently coordinating the working time of every student. This laboratory will be held concurrently with Lesson #16. This will require careful planning in order to ensure each student is spending his time profitably. The exact scheduling of students needs to be determined for each individual classroom situation. This will be dependent upon the number of students, quantities of equipment and amount of work space.

Section:

B & C. The 5-cm. SO_2 permeation tube can be obtained from the Office of Standard Reference Materials, Room B311, Chemistry Bldg., National Bureau of Standards, Washington, D.C. 20234. It is their Standard Reference Material 1626. The permeation rate is 1.4 μg./min. giving SO_2 concentrations of 0.535, 0.107 and 0.0535 ppm corresponding to gas flow rates of 1, 5 and 10 lpm, respectively. If the instructor is not familiar with the operation of the gas dilution apparatus in Figure 15-1, a concise discussion is given in ASTM: D2914-70T, pages 827-830. The same apparatus is suitable for calibration in Lesson #16, so all students should participate in the demonstration before starting either Lesson #15 or #16. Since it takes 30 minutes or more to collect each sample, it is impractical for each student to collect samples for calibration. However, the discussion should emphasize the advantage of this method over the use of aqueous calibration standards; i.e., this method includes the correction for collection efficiency. The sampling train is the same as the one used for fluorides (Lesson #5). The gas dilution apparatus can conveniently be operated at a nitrogen flow of about 0.05 lpm and an air flow of 2 lpm.

D. Standard 0.005 M H_2SO_4 is prepared by adding 0.57 ml. of concentrated H_2SO_4 to 2 liters of distilled water. Triplicate 50-ml. aliquots should be pipetted into 250-ml. wide mouth Erlenmeyer flasks and titrated with 0.02 M standard NaOH solution using 2-3 drops of phenolphthalein as indicator. If no standard sodium hydroxide is available, it can be prepared by adding 0.8 g. of NaOH (as a saturated solution freed of precipitated Na_2CO_3) to a liter of CO_2-free distilled water. This solution can then be standardized by titrating exactly weighed portions (about 0.15 g.) of primary standard potassium acid phthalate dissolved in CO_2-free water. The molarity of the 0.005 M H_2SO_4 should be calculated to three significant figures, and the average deviation of the three results should not exceed 5 parts per thousand. The .005 M $Ba(ClO_4)_2$ is prepared by dissolving 5.0 g. of barium perchlorate trihydrate in 500 ml. of water. Add 2 liters of reagent grade isopropanol. With the aid of a pH meter, adjust the apparent pH to about 3.5 with 1.8% perchloric acid. The 1.8% perchloric acid is prepared by diluting 25 ml. of reagent grade (72%) to 1 liter with distilled water. The Thorin indicator is prepared by dissolving 0.15 g. in 100 ml. of distilled water.

E. Prepare the 0.3 N H_2O_2 absorbing solution by adding 85 ml. of 30% H_2O_2 to 5 liters of distilled water. Prepare a reference sample for analysis by mixing 500 ml. of 0.05 M H_2SO_4 (this will have to be accurately standardized using 0.1 M NaOH as described earlier) with 2000 ml. of the H_2O_2 absorbing solution. [Note: If desired, this standard H_2SO_4 could be prepared and then carefully diluted 1-10 for use as the 0.005 reference standard in part D.] When this solution is mixed with the H_2O_2, the concentration is approximately 0.01 M. Later when a 10 ml. aliquot is taken from a 25 ml. total volume, the equivalent concentration will be approximately 0.004 M (known exactly after standardization). Pipet exactly 15.00 ml. of this solution into each of two midget impingers for each student. Into a third impinger pipet 15.00 ml. of the absorbing solution for use as a blank. If an insufficient number of impingers is available, the solutions could be placed in vials but this abandons the opportunity to manipulate the solutions in impingers.



TITLE	LESSON NUMBER
Titrametric Determination of SO_2	15

A. Introduction 0:15

1. Discussion of Chemical Reactions:

   - Collection of SO_2 in H_2O_2 based on

     $SO_2 + H_2O_2 \longrightarrow H_2SO_4$

   - Titration with barium perchlorate:

     $H_2SO_4 + Ba(ClO_4)_2 \longrightarrow BaSO_4\downarrow + 2\,HClO_4$

2. Describe the five parts of the laboratory

   - Demonstration of a gas dilution system for standard concentrations of SO_2 using a permeation tube

   - Demonstration of a sampling train with midget impinger

   - Standardization of barium perchlorate titrant

   - Analysis of samples and blanks

   - Calculation and data analysis

B. Demonstration of a Gas Dilution System for Preparation of Standard Concentrations of SO_2 Using a Permeation Tube 0:20

1. An experimental arrangement suitable for generating standard concentrations of SO_2 is shown in Figure 15-1. Concentrations of a preselected value can be produced for either the titrametric or the colorimetric procedure by varying the gas flow rates, the collection time and the permeation tube. The instructor will demonstrate its operation.

INSTRUCTOR'S NOTES

2. To calculate the concentration of SO_2 in the air sample produced, the following relationship is used:

$$C = \frac{(P \times M)}{R + r}$$

where:

C = concentration of SO_2 in ppm

P = permeation rate, μ g./min.

M = reciprocal of vapor density = 0.382 l./μ g.
(The value of M is calculated for each gas due to molecular weight differences. For SO_2, the value is obtained by dividing the μg.-mole volume [24.5] by the molecular weight of SO_2 [64.0].)

R = flow rate of diluent air, lpm

and r = flow rate of diluent nitrogen, lpm

Record the values used in this demonstration and calculate the concentration of SO_2.

C. Demonstration of A Sampling Train With Midget Impinger 0:15

1. The sampling train (Figure 15-2) is the same as the one used for fluorides (Lesson #5). The most important point to note is that the combination of a gas dilution system and a sampling train can produce standards with a built-in correction for collection efficiency. This factor is omitted when aqueous calibration standards are used. The disadvantage of the gas dilution - sampling train system is that it is time consuming and may not be justified if the quality of the samples is inadequate to maximize the accuracy of analysis.

2. The instructor will demonstrate the use of the sampling train in conjunction with the gas dilution system, using 15 ml. of 0.3 N H_2O_2 in the impinger and a sampling rate of about 1 lpm.

INSTRUCTOR'S NOTES

D. Standardize the Barium Perchlorate Titrant 0:50

1. Obtain a portion of standard H_2SO_4 (approximately 0.005 M - use the exact value given) in a 50-ml. glass stoppered Erlenmeyer flask or suitable equivalent container.

2. Obtain about 75 ml. of approximately 0.005 M $Ba(ClO_4)_2$ titrant in a 100-ml. beaker and cover with a watch glass.

3. With the aid of a buret funnel, pour $Ba(ClO_4)_2$ into the 10-ml. buret, being certain to completely wet the walls. Drain the buret nearly to the level of the stopcock into a waste beaker, taking care to exclude all bubbles from the stopcock and buret top. If the walls of the buret drain without retaining droplets, rinse once more and fill. Otherwise the buret is not adequately clean and it must be washed prior to use.

4. Into three 250-ml. wide mouth Erlenmeyer flasks, accurately pipet 5 ml. of standard H_2SO_4.

5. Add 40 ml. of isopropanol with a graduated cylinder. With a stirring rod and pH test paper, adjust the pH to between 2.5 and 4.0 with 1.8% perchloric acid, if required.

6. Add two drops of Thorin indicator.

7. Record the initial volume reading on the buret by estimating to the nearest 0.01 ml. Titrate with $Ba(ClO_4)_2$ taking the change from yellow or yellow-orange to pink as the end point. Record the final volume reading of the buret by again estimating to the nearest 0.01 ml.

8. Calculate the individual and average molarities of the $Ba(ClO_4)_2$ to insure that the agreement is satisfactory.

INSTRUCTOR'S NOTES

E. Analysis of Samples and Blanks 0:30

1. Obtain from the instructor two midget impingers containing a reference sample (duplicates) of SO_2 and one midget impinger containing only the absorbing solution to serve as a blank.

2. For each of the three, remove the impinger stem, tap gently against the inside wall of the impinger and rinse the stem with 1-2 ml. of unused 0.3 $\underline{N}$ H_2O_2.

3. Transfer each solution from the impinger to a 25-ml. volumetric flask with the aid of a stirring rod. Use 0.3 $\underline{N}$ H_2O_2 to rinse in order to obtain a quantitative transfer and then make to volume with 0.3 $\underline{N}$ H_2O_2.

4. Pipet 10.0 ml. into a 250-ml. wide mouth Erlenmeyer flask.

5. Add 40 ml. of isopropanol with a graduated cylinder and adjust the pH, if necessary, as in Section D.

6. Add 2 drops of Thorin indicator.

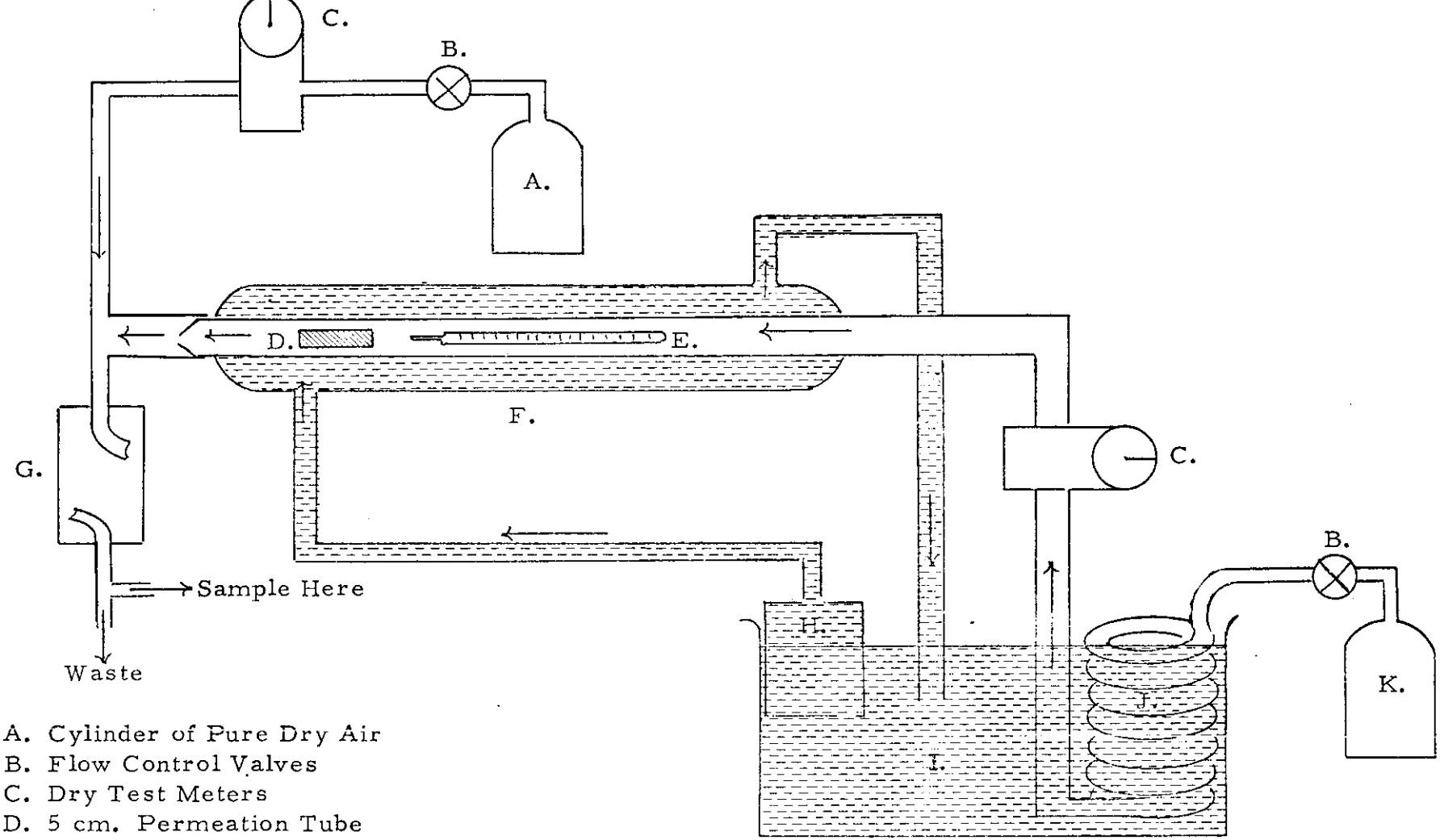
7. Record the initial buret reading, titrate as in Section D and record the final buret reading.

F. Calculations and Data Analysis 0:15

1. Calculate the mg. of SO_2 in the duplicate reference samples.

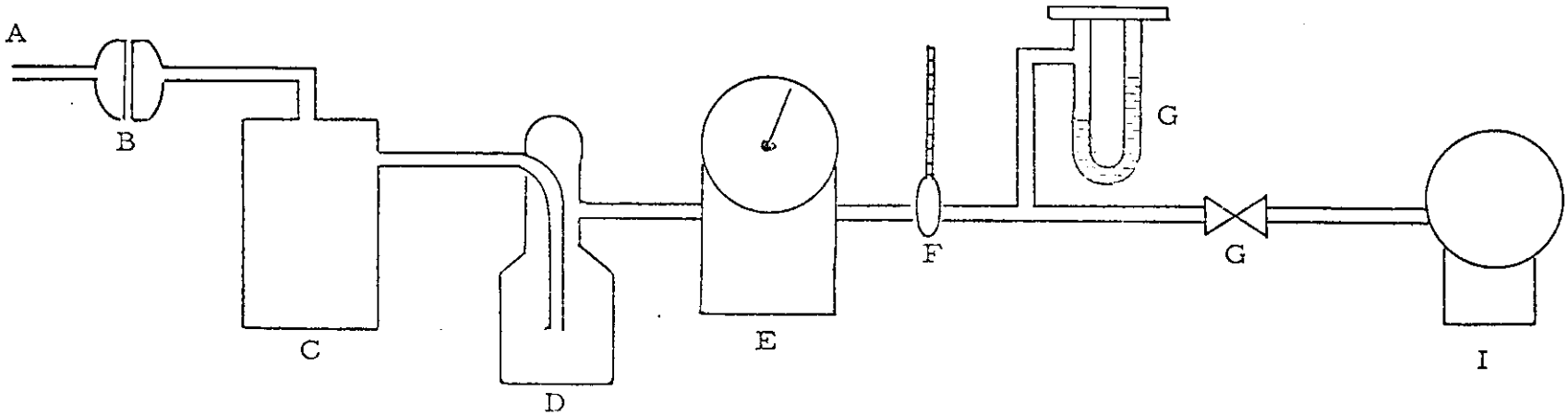
2. Compare the reproducibility of your duplicate determinations with the reproducibility of results between students.

INSTRUCTOR'S NOTES



A. Cylinder of Pure Dry Air
B. Flow Control Valves
C. Dry Test Meters
D. 5 cm. Permeation Tube
E. Thermometer
F. Condenser
G. Mixing Bulb
H. Water Pump
I. Water Bath (20°C)
J. 2 mm. Copper Coil
K. Cylinder Pure Dry N_2

Figure 15 - 1. Gas Dilution System for Preparation of Standard Concentrations of SO_2 Using a Permeation Tube.



A. Sample Inlet

B. Prefilter (0.8 m cellulose membrane) in cassette

C. Midget Impinger

D. Absorption Tube containing glass wool to collect splashover

E. Dry Test Meter

F. Thermometer

G. Manometer

H. Flow Control Valve

I. Vacuum Pump

Figure 15-2 Sampling Train for SO_2

Gas Diluation Rate for Preparation of Standard Concentrations SO_2
Using a Permeation Tube
(Section B)

P = Permeation Rate, μg./min.

M = 0.382 μl./μg.

R = Air Flow, lpm

r = N_2 Flow, lpm

$$C \text{ (ppm } SO_2) = \frac{P \times M}{(R + r)}$$

$$C = \frac{\_\_\_\_\_ \times 0.382}{(\_\_\_\_\_ + \_\_\_\_\_)} = \_\_\_\_\_ \text{ppm}$$

Standardize the Barnum Perchlorate Titrant (Section D)

$$M_{Ba(ClO_4)_2} = \frac{ml._{H_2SO_4} \times M_{H_2SO_4}}{ml._{Ba(ClO_4)_2}}$$

	Titration 1	Titration 2	Titration 3
Final Buret Reading			
Initial Buret Reading			
ml. $Ba(ClO_4)_2$ used			

$$\frac{5.00 \times \_\_\_\_\_}{\_\_\_\_\_} =$$

	$M_{Ba(ClO_4)_2}$	Deviation from Average	Deviation x 1000/Avg. M
1			ppT
2			ppT
3			ppT
Avg		Avg Dev*	ppT

* Should not exceed 5.

Calculation and Data Analysis
(Section F)

$$mg.\,SO_2 = \frac{ml._S \times M_{Ba(ClO_4)_2} \times MW_{SO_2} \times V}{Valiq}$$

mls. = ml $Ba(ClO_4)_2$ required for the sample minus ml. required for the blank.

$M_{Ba(ClO_4)_2}$ = molarity of the titrant (from Section D)

MW_{SO_2} = molecular wt. of SO_2 = 64

V = Volume of solution = 25 ml.

Valiq = ml. of sample titrated = 10 ml.

Replicate 1.

mg. SO_2 = _____ x _____ x 64 x 25 / 10 = _____mg.

Replicate 2.

mg. SO_2 = _____ x _____ x 64 x 25 / 10 = _____mg.

	Replicate 1	Replicate 2	Blank
Final Buret Reading, ml.			
Initial Buret Reading, ml.			
Volume used, ml.			