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INSTRUCTOR MANUAL
INDUSTRIAL HYGIENE CHEMISTRY COURSE

LESSON NUMBER 18

April 1975

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Prepared by:

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Instructor manual for a one week "Industrial Hygiene Chemistry" course, designed to give program graduates expertise in environmental sampling and analysis. Lesson 18 encompasses principles, equipment, and applications for anodic stripping voltametry, sample concentration methods, and micro analysis.

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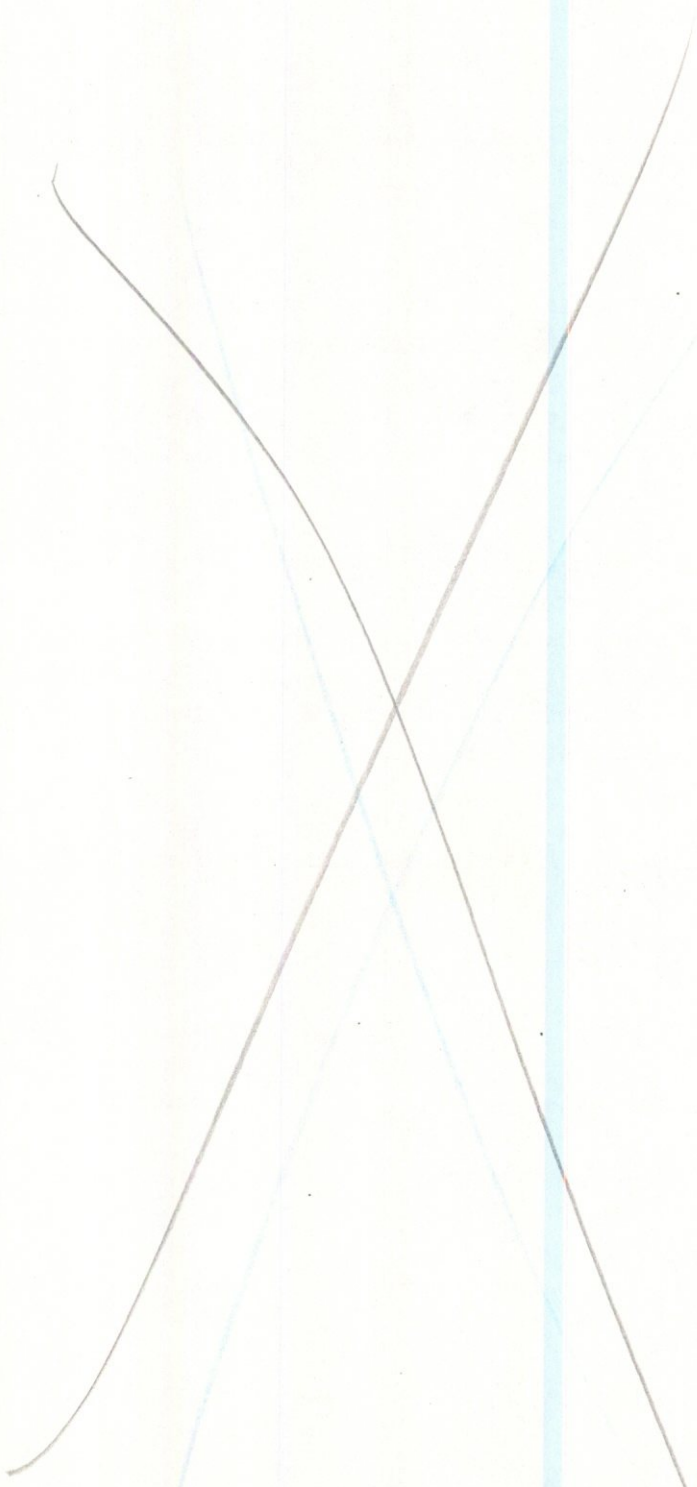

INTRODUCTION

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
Related Topics	18	1:35

BEHAVIORAL OBJECTIVE

The student will be able to list the principles, equipment and applications for anodic stripping voltametry, sample concentration methods and micro analysis.

SCOPE

Anodic stripping voltametry
Concentration Techniques
Micro analysis

VISUALS	EXHIBITS
18-1 through 18-17	None

EQUIPMENT

Overhead projector
35 mm. projector
Screen
Blackboard
Chalk

REFERENCES

LESSON TITLE

Related Topics

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ADDITIONAL READINGS

LESSON TITLE

Related Topics

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A. Anodic Stripping Voltametry

1. Anodic stripping voltametry (ASV) is a two step trace analytical method which has been applied particularly to the detection and determination of heavy metals. For the industrial hygiene chemist, it is a method which complements determinations made by atomic absorption. It is often more sensitive than flame atomic absorption and is sometimes as sensitive as non flame techniques. (1)

2. The two step process involves the electrolytic reduction of one or more analytes, which are deposited within, or plated on, a working electrode from a solution. This is a concentration step whereby 10^{-5} to 10^{-9} grams of an analyte may be deposited from sample volumes of 2 to 50 milliliters. During the deposition step, the working electrode is maintained at a potential negative to the reduction potential of all of the analytes to be determined. In the second step, the potential is reversed and progressively changed toward the anodic direction. During this gradual change of the potential in the positive direction, each of the analytes is sequentially oxidized and stripped from the electrode. Each analyte is identified as its oxidation potential is reached. The amount of analyte present is proportional to the faradic current produced. Visual 18-1 is a typical anodic stripping voltametric recording depicting the sequential response for zinc, cadmium, lead and copper. (1)

3. Anodic stripping voltametry has developed from the technique of polarography. Polarography is based upon the current-voltage curves which are derived at a microelectrode when the electrochemical reaction is controlled by the rate of diffusion. Such a microelectrode is said to be polarized when it accepts a potential impressed upon it with little or no change in current. As seen in Visual 18-2, when no reducible species is present, there is some appreciable current flow necessary to charge the double layer capacitance at the electrode surface. That is, the solution-electrode interface behaves as a capacitor in the measurement circuit. When metallic components 1 and 2 are present, a diffusion or faradic current flows as the half wave potential of component 1 is approached. As in anodic stripping voltametry, this potential is characteristic of the element being oxidized (ASV) or reduced (polarography). The net change in current, as indicated in Visual 18-2, is a function of the amount of component 1 present in the solution. When the voltage is

NOTES	Times (elapsed) projected	LESSON OUTLINE
	(---) 0:30	A. Anodic Stripping Voltametry 1. Use and sensitivity
Visual 18-1		2. 2 step process -- electrolytic reduction, reversed potential
Visual 18-2		3. Polarography -- description, basis, example, comparison with ASV, dropping mercury electrode

made more negative, component 2 is reduced at its half wave potential. This polarographic curve depicts the action of a dropping mercury electrode which is most commonly used in classical polarography. In a dropping mercury electrode (DME), a stream of high purity mercury is passed through a small bore glass capillary tube of about 0.06 mm. diameter to produce a steady flow of droplets at the electrode. Thus a constantly renewed electrode is provided for the repeated sampling of the solution. (2)

4. Stripping voltametry and polarography are both current measuring techniques as voltage is varied. Potentiometric techniques, including ion selective electrodes, measure the voltage in a system; conductometric techniques are concerned with the resistance of a system. Stripping voltametry is also known as linear-potential sweep stripping chromoamperometry. It can be considered as polarography in reverse. Total reduction and oxidation of a species which occurs in coulometry is not practiced in anodic stripping voltametry. The several species are reduced and deposited at a fixed voltage for a fixed period of time, and then the stripping curve is obtained. Comparative standards are seen in the same pure electrolyte solution; or more often, calibration is made by the method of standard additions. (2)

5. For deposition of a single metallic species, the current flow (i) at time t follows the Levich equation fairly closely. That is:

$$i(t) = 0.62\, n\, FAD^{2/3}\, \omega^{1/2}\, \mu^{-1/6}\, C(t)$$

where:

n = cation charge

F = Faraday constant

A = the electrode surface area

D = diffusion coefficient

ω = the rate of electrode rotation or the rate of solution stirring

NOTES	Times (elapsed) projected	LESSON OUTLINE
		4. Potentiometric and conductometric techniques definitions
Write equation on the blackboard. It is not necessary for the student to memorize this formula.		5. $i(t) = 0.62\ n\ F A D^{2/3}\ \omega^{1/2}\ \mu^{-1/6}\ C(t)$

μ = the kinematic viscosity of the solution

C(t) = the ion concentration at time t

In practical applications, the factors μ, ω, A and t can be controlled to increase the rate of deposition. The viscosity (μ) for aqueous solutions varies only over a narrow range; and since it is raised only to the -1/6 power, its effect is small. Increasing the stirring rate, increasing the area of the working electrode and increasing the deposition time contributes to an increase in the amount of analyte deposited. ( )

6. As anodic stripping voltametry developed from polarography, the first microelectrode to be used was the dropping mercury electrode. In this electrode, the flow of mercury was stopped with a single hanging drop of mercury used to collect the analytes, and then the analytes were released by stripping. In one early study, copper, lead, cadmium and thallium were determined in the range of 2×10^{-4} to 2×10^{-8} moles. In this case, the surface of the mercury working electrode was limited to the inner diameter of the capillary mercury delivery tube. The area of this electrode was about 0.05 square centimeters. This reduced the diffusion of the analytes within the mercury and allowed more of the analyte to be stripped. However, due to the limited area of the working electrode, less than 0.5 percent of these elements were deposited from a 25 milliliter volume in 5 minutes and about one half of this was recovered in the anodic cycle. (3)

7. The hanging drop mercury electrode (HDME) is used in many cases, despite the diffusion of the deposited analyte. The electrode is easily renewed, and the area of the drop surface can be reproduced within about 4 percent. Visual 18-3 depicts a hanging drop mercury electrode cell. The nitrogen gas purge is necessary to eliminate dissolved oxygen. The salt bridge connects to a reference electrode, which may be a silver-chloride electrode or a saturated calomel electrode (SCE). This reference electrode of constant potential can be considered a probe that senses the current in the vicinity of the HDME. The counter electrode is usually platinum or another inert conductive material with a large surface area. The cell material is generally quartz, Teflon, or some pure insulating material which is resistant to surface adsorption. In some cells samples as small as 50 to 100 microliters are buffered and diluted to 2 ml. for analysis. The analysis volume may range from 2 to 50 milliliters. Special precautions must be taken to ensure a pure supporting electrolyte in the solution. (2)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		6. Early study -- dropping Hg electrode to determine Cu, Pb, Cd, Tl
Visual 18-3		7. HDME -- description

8. The diffusion within the hanging drop mercury electrode causes stripping peaks to be broadened. The HDME may be dislodged by a high rate of stirring. These factors have led to the development and application of mercury thin film electrodes (MTFE). Typically, a 100 to 500 nanometer mercury film of about 1/4 inch diameter is deposited on an inert conductive surface. Wax impregnated graphite has been used for such a substrate. Dense forms of graphite may be used without impregnation, and the vitreous or glassy carbon structure is the most suitable. Plastic (styrene) impregnated graphite electrodes have also been used. These thin film electrodes are rotated in the cell at speeds as high as 3600 rpm. Care must be taken to prepare a surface which is reproducible and free of contamination. Although the MTFE yields a more sensitive detection than the HDME, the MTFE can be saturated with an analyte due to its limited volume. In some cases the deposition time must be decreased to avoid electrode film saturation while maintaining sharp, well resolved stripping peaks. (4)

9. Several different modes of stripping may be used to oxidize the analytes and obtain quantitative data. The most common mode has been a linear ramp increase in the voltage. It has been shown that the stripping peak current is directly proportional to the ramp rate of the potential scan. When scan rates of 50 millivolts per second or more are used, the capacitive current is increased so that the faradic current due to the analyte is less discernible above the background of the capacitive current. Therefore, as illustrated in Visual 18-4, other potential-time wave forms are used to strip the analytes. For AC stripping voltametry a small sine wave amplitude is impressed on the linear ramp. This places the faradic current out of phase with the capacitive current and a phase sensitive amplifier. However, changes in the resistance of the solution or electrode will vary the phase difference; therefore, AC stripping is useful with HDME (low resistance) and not with the MTFE (high resistance). (1)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		8. Disadvantage of HDME; MTFE -- types and advantages
Visual 18-4		9. Different modes of stripping

10. In differential pulse stripping voltametry, a square wave pulse of 50 to 100 m.V is periodically imposed on a linear potential ramp of about 5 m.V/sec. As seen in Visual 18-5, the capacitive current decays faster than the faradic current during the life of a single pulse. When the current is sampled immediately before the start of the pulse (Gate A) and immediately before the end of the pulse (Gate B), the difference is mostly due to the faradic current. This mode is suitable for the mercury thin film electrode. There is an additional bonus in this mode of operation. As the linear ramp passes through the potential region when the analyte is stripped, the oxidized analyte does not leave the vicinity of the electrode after each short pulse period. When the pulse is removed, a significant portion of the analyte is reduced and replated on the electrode. This amount of analyte then further contributes to the difference current measured. Differential pulse stripping is more sensitive than other operational modes by one to five orders of magnitude, with some increase in the complexity of the instrumentation. (1)

11. Anodic stripping voltametry can be applied to the determination of the following elements: Ag, As, Au, Ba, Bi, Cd, Cu, Ga, Ge, Hg, In, K, Mn, Ni, Pb, Pt, Rh, Sb, Sn, Tl, Zn. However, the majority of the practical analyses has been limited to: Ag, Au, Cd, Cu, Hg Rh, Sn, Tl, Pb, Zn. The detection limits by differential pulse stripping voltametry for these elements typically range from 0.005 to 0.4 nanograms per milliliter. Stripping analysis requires a plating time or reduction period of 1 to 10 minutes and a stripping time of 1 to 3 minutes for concentrations in the range of 10^{-8} molar. This is a longer analysis time than for flame atomic absorption, but the sensitivity is 10 to 50 fold greater for an equivalent amount of solution. Furthermore more than one element (4-6) per analysis may be determined by ASV. (1)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 18-5		**10.** Differential pulse stripping -- operation, benefits
		11. Applications of ASV -- elements, sensitivity, time, compared to AA

12. The determination of zinc in sea water is an example of the determination of a trace constituent (~2 ng./ml.) in a complex mixture. In this case, a tubular mercury-graphite electrode was placed in series with a silver-silver chloride reference counter electrode. A 50 to 80 milliliter nitrogen purged sample was contained in a 100 milliliter cylinder and pumped at a constant rate of 160 ml./min. through the tubular electrode system. After the deposition of the mercury film on the graphite electrode which was wax impregnated, the sample was plated for 2 to 5 minutes, and then anodically stripped as the solution continued to flow. The mercury film was removed at the end of each stripping and replated from a fresh solution for each subsequent analysis. (5)

13. Lead, cadmium and copper have been measured in two hour air samples collected with a spot tape sampler. A 3/4 inch circle was cut out of the tape sample area, ashed in a low temperature asher, dissolved in 0.1 ml. of 1:1 perchloric-nitric acid and diluted to 10 ml. with water. A 1.0 ml. aliquot of the sample was used for each analysis in the presence of 5 ml. of a buffer solution. Calibration was made by the method of standard additions. The reduction potential was - 1.4 volts and the linear positive sweep rate for stripping was 60 m.V/sec. The metals present in the samples ranged from 7 to 350 ng. of cadmium, 80 to 2400 ng. of lead and 6 to 1,000 ng. of copper. Though this work was for the analysis of ambient urban air, it shows a capability for short term sampling for industrial hygiene air analysis of a workplace. (6)

14. Zinc, cadmium, lead and copper have been determined in sea water and fresh water with differential stripping voltametry using a unique control of the pH. A pH electrode was included in the cell, and the usual nitrogen purge gas was replaced with a mixture of CO_2 and N_2. The pH was controlled by varying the ratio of the gases. In fresh water samples, the dissolved carbonic acid supplied sufficient electrolyte for the analysis. In this way, the addition of any contaminating reagent was avoided. This work was conducted with the hanging drop mercury electrode. The sensitivity was 0.005 micromoles for zinc and 0.001 micromoles for lead, cadmium and copper. (7)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		12. Zinc determination with Hg - graphite electrode 13. Lead, cadmium, and copper in air determination 14. Zn, Cd, Pb, Cu determined in water with pH control and HDME

15. Stripping voltametry can also be done with anion analytes. The simultaneous determination of bromide and chloride ions was made by cathodic stripping voltametry. The peak potentials of the bromide and chloride are difficult to resolve. A controlled deposition and equilibration of the deposited film at the surface of the mercury electrode allows each to be determined when the ratio of their concentrations is between 0.2 and 9.0. Concentrations as low as 1×10^{-5} molar have been determined with a precision of 7 percent. (8)

16. The co-deposition of more than one cathodic analyte can lead to the formation of intermetallic species in the mercury film. These inhibit the subsequent anodic stripping process. For instance, in the determination of Cd, Pb, Zn and Cu in water, urine and blood samples, it was found that low results for Zn were obtained as the concentration of Cu increased. When gallium was added to the sample, a Cu-Ga compound was formed on plating which prevented the formation of the Cu-Zn intermetallic compound. Furthermore, by adding a second increment of gallium to the sample and repeating the plating-stripping cycle, the recovery of Zn was verified and the Ga peak current could be used, within experimental limits, as an internal standard. Thallium was also investigated an an internal standard. The gallium peak appears between those of zinc and cadmium. (9)

17. Presently anodic stripping voltametry is best used by the industrial hygiene chemist for the determination of heavy metals in air, water and biological samples. Lead can be determined in blood and urine samples using a small sample of about 100 microliters with little sample preparation. (10)

B. Concentration Techniques

1. The concentration and enrichment of one or more analytes prior to the determination step is fundamental in trace analysis. The industrial hygiene chemist uses concentration techniques mainly for sampled air. He is concerned with the efficiency of the collection of the analyte, with contamination from apparatus and reagents, with the loss of the analyte in the sample treatment and with the form of the concentrate as prepared for the determination. The previous lessons have cited numerous examples of concentration methods for particular analytes. These include:

NOTES	Times (elapsed) projected	LESSON OUTLINE
		15. Bromide and chloride ions determined by cathodic stripping voltametry
		16. Co-deposition leads to formation of intermetallic species in Hg film
		17. IH -- determine heavy metals in air and biological samples
(Transition A.-B.) From ASV to concentration techniques.	(0:35) 0:25	B. Concentration Techniques
		1. Use of concentration techniques in IH, examples:

- The dithizone extraction of mercury prior to its spectrophotometric determination

- The reduction of mercury with stannous chloride and the evolution of mercury as a vapor for atomic absorption

- The collection of hydrogen sulfide in a cadmium impregnated filter and the formation of cadmium sulfide

- The evolution of arsine from urine and its collection in silver chloride for x-ray fluorescence analysis

- The collection of oil from air prior to measurement by molecular fluorescence

- The collection of organic solvents in charcoal and the preparation of a carbon disulfide solution concentrate

2. Many of these methods are limited by their specific application to a single analyte. The ability of instrumental techniques to determine many elements and many components in the same sample indicates the requirement for group separations and concentration techniques. Although the industrial hygiene chemist is often concerned with one contaminant or toxic hazard at a given workplace, the application of group separations and multi-determinations is useful. In many cases a single multi-procedure can be used for separate analytical problems which arise from different processes or work conditions. In addition, group separation and enrichment procedures often allow standards to be stabilized and used in analysis largely independent of the original matrix of the sample. Therefore, even though an analyte may be determined directly in a sample as collected, there is often an advantage in using a technique which, for instance, incorporates an internal standard and removes the analytes from the bulk of the original sample. In addition, the separated analyte may be presented in the most suitable form for the determination. (11)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		. Dithizone -- Hg . Hg -- stannous chloride . Hydrogen sulfide to cadmium sulfide . Arsine in urine collected in silver chloride . Oil in air . Organic solvents 2. Use of concentration techniques, single vs. group determination

3. A wide variety of separation methods are available. The four most commonly used are: electrodeposition, ion exchange, liquid-liquid extraction and precipitation. The important considerations in the selection and evaluation of a group separation method for trace analysis include:

   - The method of determination following the separation
   - The number of analytes to be determined
   - The lower limits of concentration of the analytes
   - The recoveries of each analyte
   - The degree of contamination
   - The separation factor obtained
   - The required sample size
   - The complexity of the method
   - The time required for the separation (11)

4. The efficiency of the recovery and the contamination from other sources are the most difficult problems in trace analysis. Contamination from the reagents used is most common. Special precautions must be taken to purify water, acids and other chemicals used. The loss and the contamination due to the apparatus are difficult to estimate. The loss of one analyte and the contamination of another may occur simultaneously. Plastic ware is generally more suitable, for instance, than glassware in trace analysis. The effect of air contamination is often the least controlled and seldom realized. A well designed air conditioning system can spread mercury contamination throughout several physically separated laboratories. Special precautions must be taken during periods of ashing, dissolution and evaporation. (11)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		3. 4 methods for separation; considerations in choosing method: . Determination technique . Number of analytes . Lower concentration limit . Recoveries of analytes . Contamination . Separation factor . Sample size . Complexity of method . Time for separation 4. Precautions to avoid contamination -- analyte, equipment, air

5. Electrodeposition methods for separation are commonly used in the analysis of ferrous alloys. In this case, the major elements are reduced and deposited in a mercury cathode pool, leaving the alkalis, alkaline earths, B, Al, P and the refractory elements to be determined in the aqueous phase. The previous discussion on anodic stripping voltametry illustrates the desirable method of concentrating an analyte in a small volume of mercury from a large volume of solution. Elements that are not suited to stripping analysis can be determined by other means. For instance, the mercury can be evaporated and such elements as Co, Fe, Ag, Au, Pd, Rh, and Pt can be determined directly on the graphite substrate by optical emission with spark excitation. Since the mercury evaporation temperature of 360°C causes loss of volatile elements (i.e., Cd), the mercury amalgam can be dissolved and analyzed spectrophotometrically. When a large amount of mercury is used, such as 0.1 to 1 gram, the following elements can be quantitatively deposited from a dilute sulfuric acid solution: Cr, Ce, Co, Ni, Cu, Zn, Ga, Ge, Mo, Tc, Rh, Pd, Ag, Cd, In, Sn, Re, Ir, Pt, Au, Hg, Tl, Bi and Po. The elements As, Se, Te, Os and Pb are separated from the electrolyte but, in this instance, are not quantitatively deposited in the mercury. At higher concentrations, many of these elements can be determined directly in a mercury film by x-ray fluorescence analysis. Due to the high mass of mercury, a thin film is desirable ($\sim$ 0.1 to 0.2 nanometers). The elements that remain in the electrolyte can be concentrated by the following methods for further analysis. (12)

6. Ion exchange methods are suitable for trace analysis, particularly when the analytes are retained on a column while the major elements pass through without being retained. The analytes may then be separated as they are gradually eluted from the column. On the other hand, the analytes may be removed for an instrumental determination from a short column in a minimal volume without separation from each other. When the distribution coefficient of the analytes is large, a batch separation may be made. That is, the ion exchange beads are added directly to the solution, stirred until equilibrium is reached, filtered and analyzed separately. (11)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		5. Electrodeposition methods for separation
		6. Ion exchange methods -- allowed to separate in column or removed before separation

7. Ion exchange resin loaded papers are excellent media for collecting and concentrating microgram and nanogram amounts of analytes by a simple filtering process. The paper is suitable for direct analysis by x-ray fluorescence. Papers are available for both cation and anion exchange. The drawing in Visual 18-6 shows some selected analytes with their detection limits in micrograms. Typically, 40 milliliters is the volume of the sample. This sample is passed through the paper three to five times.

8. Liquid-liquid extraction is the separation method most widely used in industrial hygiene chemistry. Often a single element is determined after the extraction by atomic absorption. However, the extraction of a large number of analytes can be made for spectrographic analysis. For instance, 30 trace elements have been separated by extraction with oxine and dithizone into chloroform and determined by emission spectrography. The analysis was performed directly on the evaporated residue of the extracted analytes. (11)

9. Coprecipitation is a separation process wherein trace analytes are precipitated from solution in the presence of a host element. Often this element is added to the sample, and in many cases it can perform as the internal standard in the subsequent determination. The precipitate may be inorganic as in the case of trace elements collected in a host of lanthanum or yttrium hydroxide. This host can include the analytes As, Bi, In, Pb, Sb, Se, Te and Tl. The precipitate may be a metallo-organic compound similar to those involved in liquid-liquid extraction. In a well established procedure, 14 to 20 elements found in plants and biological materials were precipitated with aluminum as the matrix. The precipitation was performed at a pH of 5.2 with a mixture of oxine, tannic acid and thionalide. The precipitate was ashed and analyzed spectrographically with a direct current arc. (15)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 18-6		7. Ion exchange resin loaded paper 8. Liquid-liquid extraction to determine many elements spectrographically 9. Coprecipitation -- host element

10. The filtration efficiency for small amounts of precipitate from an aqueous solution is improved by the use of membrane filters when compared with filter papers. The precipitates can be easily washed and are more completely retained. The 0.4 micrometer pore size filter is often used for aqueous samples, whereas 0.8 micrometers is commonly used for the collection of air samples. When prepared on the flat surface of the membrane filters, the precipitate may be analyzed directly by x-ray fluorescence, redissolved for solution analysis, or ashed for emission spectrography. In addition, optical and scanning electron microscopic examinations may be made directly. Visuals 18-7 and 18-8 illustrate membrane filter holders which can be adapted to solution filtration. Chloride ion has been determined as a silver chloride precipitate by x-ray fluorescence when filtered on a membrane filter and suspended in a sandwich of mylar film. Precipitates may be weighed on a microbalance (as illustrated in Visual 18-9), and the data used in the analytical procedure. (16, 17)

C. Micro Analysis

1. Trace analysis is the determination of microgram, nanogram and subnanogram quantities of constituents in a bulk homogeneous sample. Micro analysis is the determination of the major and minor constituents in samples weighing from a milligram to a nanogram or less. This micro sample often exists within a heterogeneous sample. Optical and electron microscopy techniques reveal that solid homogeneous appearing materials are actually heterogeneous. The industrial hygiene chemist is concerned with the size and chemical composition of particulate matter in air and biological samples. The particle size range of 0.1 to 10 micrometers is directly related to material that is retained during the breathing process and deposited on lung tissue. Visual 18-10 shows a scanning electron micrograph of a particle on the surface of a membrane filter. The four pore holes in the filter are each about one micrometer in diameter. The optical microscope is limited in its resolving power to particle sizes of 0.4 to 1 micrometer. (19, 21)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 18-7, Visual 18-8, Visual 18-9		10. Use of membrane filter to improve filtration efficiency
(Transition B.-C.) From sample concentration methods to micro analysis. Visual 18-10	(1:00) 0:25	C. Micro Analysis 1. Micro analysis definition and description

2. During the past 20 years, a drastic change has occurred in micro analysis. Physical analytical techniques have been developed which have supplemented chemical techniques with the optical microscope. These physical methods include:

   - Transmission electron microscopy
   - Electron microprobe analysis
   - Scanning electron microscopy
   - Ion microprobe analysis (22)

3. Each of these physical analytical techniques gives additional characterization data beyond that which is derived from chemical microscopy with the light microscope. Optical microscopy is the starting point for micro analysis, regardless of the degree of sophisticated instrumentation which is ultimately applied to the micro sample. A first examination of particulates may be made with a stereo microscope as shown in Visual 18-11. A magnification of 10 to 400 x is used with a good field depth. This examination will show the major components of the material and it may indicate micro particles which require further identification. (22)

4. The second stage in micro analysis is to use a more powerful optical microscope such as shown in Visual 18-10 which will resolve micro samples of one micrometer or less in diameter. Many materials can be instantly identified by their shape - their morphological characteristics. Natural and synthetic fibers, pollen grains, crystalline materials, bacterial cells, metallic chips, plant tissue, fly ash and hair may be recognized. The degree of identification depends upon the experience of the chemist-microscopist and the correlation with materials known to exist in the workplace. Photomicrographs obtained with an added camera (Visual 18-13) aid in this identification. At this point a needle like probe and micromanipulators may be used to physically isolate individual particles for further analysis. (19, 21)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		2. Physical analytical techniques:
		. Transmission electron microscopy
		. Electron microprobe
		. Scanning electron microscopy
		. Ion microprobe analysis
Visual 18-11		3. Optical microscopy as starting point
Visual 18-12, Visual 18-13, Visual 18-14		4. More powerful optical microscope

5. The optical microscope may be supplemented with polarized or interference optics to increase the contrast of some materials and reveal details that might otherwise be invisible. The polarizing microscope is used to differentiate, in particular, between isotropic and anisotropic components. It shows the orientation of crystals in a microsample. The most stable and reliable interference microscope is the Nomarski differential interference system. Here a polarized light beam is split into two wave fronts which pass through or are reflected from the specimen. The two wave fronts are separated by about one micrometer. This approximates the resolving power of the microscope. On recombination of these wave fronts, the specimen is seen in geometric relief with extremely high contrast within the depth of the field. Ion transmitted light phase contrast may also be used to enhance the contrast of materials which differ in their index of refraction. (23)

6. The light microscope may be combined with many spectroscopic techniques, including infrared, ultraviolet and visible absorption, for micro analysis. For instance, molecular fluorescence microscopy is used in many branches of biology and medicine of concern to the industrial hygienist. With ultraviolet excitation of the specimen, the fluorescing species emit in the visible region and show a high contrast against a dark-field background. Tissue cells, organic fluorescing compounds and inorganic phosphors are rapidly identified. (24)

7. The most versatile electron microscopic tool (which goes below the limits of the light microscope) is the scanning electron microscope (SEM). The specimen is placed in an evacuated chamber and a beam of electrons is directed to the surface of the specimen, as in the case of a transmission electron microscope. In the case of the SEM, the electron beam is scanned over the specimen surface in a raster pattern. The secondary electrons reflected in the sample are detected and displayed by means of a closed loop TV system. Visual 18-15 shows a system which incorporates both light and scanning electron microscopy. The SEM has a high resolving power since the electron beam diameter is 50 nanometers or less. The contrast is due to the fact that low energy electrons from the valence bands of the elements in the sample are detected. The depth of field is 100 times greater than the light microscope, and this is due to the small electron beam aperture. (20, 25)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		5. Polarizing microscope -- use, Nomarski differential interference system, ion-transmitted light phase contrast
		6. Light microscopy with spectroscopic techniques
Visual 18-15		7. SEM -- description, use, contrasted with light microscopy

8. Visual 18-16 illustrates the effects of an electron beam at and below the sample surface. As the beam enters the solid surface Auger electrons from the K, L & M shells of the elements are released in the A region. Secondary or valence electrons are released from regions A and B. The depth of region A and B is about 5 nanometers, and almost 90 percent of the electrons detected are within the beam diameter. This accounts for the high resolution of the SEM. The SEM images are photographed directly from the cathode ray tube. The magnification may be varied in the range of 100 to 15,000 x. A 50 nanometer resolution can be obtained at 100 x with a depth of field of 300 micrometers. SEM images appear to be almost 3-dimensional. (25)

9. The x-rays that originate in regions A, B and C of Visual 18-16 are detected in some SEM instruments with an energy dispersive detector and displayed on the same cathode ray tube. This produces a topographical map of the elements over the scanned area. A series of images are recorded with different energy levels within the x-ray detector. The resolution of the x-ray images has degraded to 500 to 1000 nanometers due to the electron scatter within the sample. Samples with high average atomic number will have the best resolution. (26)

10. A more quantitative micro analysis of samples, in the range of . to 5 micrometers in diameter, is obtained with the electron microprobe analyzer. These instruments were developed before the SEM from the transmission electron microscope. A light microscope is incorporated to view the area where the electron beam strikes the sample. As the beam remains in a fixed position on the sample, both wavelength dispersed spectrometers and non-dispersive detectors measure the intensity of selected wavelengths. Empirical and mathematical computational methods are used to convert the intensity data to compositional data. With suitable corrections, a 2 cubic micrometer sample may be analyzed for elements which are present at 0.1 to 1 percent or greater with accuracies of 2 to 20 percent of the amount present. (27)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 18-16		8. Effects of electron beam and sample 9. X-rays detected in some SEM's and displayed 10. Electron microprobe analyzer -- description and use

11. A more recent development for micro analysis is the ion microprobe. A selected beam of ions is focused on a solid surface. The beam diameter may be varied from 1 to 50 or more micrometers. The action of the ions is to sputter ions of the sample from the surface. The sample ions are accelerated and pass through a double focusing mass spectrometer. The instrument differs from electron beam analysis in that the sample is removed from the surface and a depth profile analysis may be performed. In addition, isotopic analysis can be made. The initial ion beam may be inert argon, or it may be a chemically reactive element such as oxygen. The ion microprobe analyzer is one of the most sophisticated and expensive instruments for analysis. It illustrates the great progress that has been made in micro analysis during the past 20 years. The instrument has been applied to the analysis of single micrometer-size airborne particles. (28, 29)

12. Rapid semiquantitative analysis of micro samples with diameters of 20 to 250 micrometers can be achieved with a laser microprobe. This technique combines a laser, a light microscope and a fast optical emission spectrograph or spectrometer. In practice, a sample is placed on a stage with the surface in optical alignment with the spectrograph. A particle or inclusion is then located and centered with the light microscope. A beam of laser pulses is then directed through the object lens of the microscope and concentrated within a 20 to 50 micrometer spot diameter. Typically, 0.1 to 1 joule of energy is directed to this spot over a period of 1 to 2 microseconds. This causes 30 to 500 nanograms of material to be removed from a conical crater in the surface in the form of an expanding plume of atoms and ions. As this plume rises between two horizontally placed electrodes charged with 1500 to 2000 volts, a single spark discharges which causes additional optical emission spectra to be emitted from the sampled material. The analysis of this spectra requires a system with high optical speed and high detector response. The intensity of spectral lines has been related to the weight of sample vaporized by optical measurement of the volume of the conical crater produced by the laser action. The weight of sample is then calculated from knowledge of its density. Because the spark discharge produces a background which is largely independent of the sampled weight, sometimes the detection of the spectra is delayed for several microseconds after initiation of the pulse. On the other hand, some people have eliminated the crossed spark excitation and have relied upon the latter pulses in the energy band from the laser to excite the atoms in the plume. Although the reasonance lines are heavily self absorbed in this case, a rapid qualitative analysis of the selected sample is obtained, particularly when the spectra is recorded on Polaroid film. (30)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		11. Ion microprobe analyzer -- description and use 12. Laser microprobe--procedure and use

13. A further advantage of the laser microprobe lies in its ability to sample nonconducting as well as conducting material. The sampling is dependent upon the capability of the material to absorb the laser energy which is typically in the near infrared region (1.06 μm. for a neodymium coated glass rod). Therefore, ceramics, fibers, paper, membrane filters and tissues may be sampled directly in the open atmosphere. Extensive applications have been made on biological materials including live tissue, such as the skin of a laboratory animal. A comparison of the capabilities of these microanalytical techniques is summarized in Visual 18-17. (31)

D. Self Test

1. Test instructions and review of questions are presented.

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 18-17		13. Advantages and use of laser microprobe
	(1:25)	
Self Test		D. Self Test
	0:10	
		1. Instructions and review
	1:35	

SELF TEST	Page 1 of 1
LESSON TITLE Related Topics	LESSON NUMBER 18

1. What is anodic stripping voltametry? (briefly)

See A. 1 - A. 2

2. What types of contamination will hinder accurate trace analysis?

reagent contamination

apparatus contamination

analyte contamination

air contamination

3. Briefly define coprecipitation?

See B. 9

4. List four physical analytical techniques used in micro analysis:

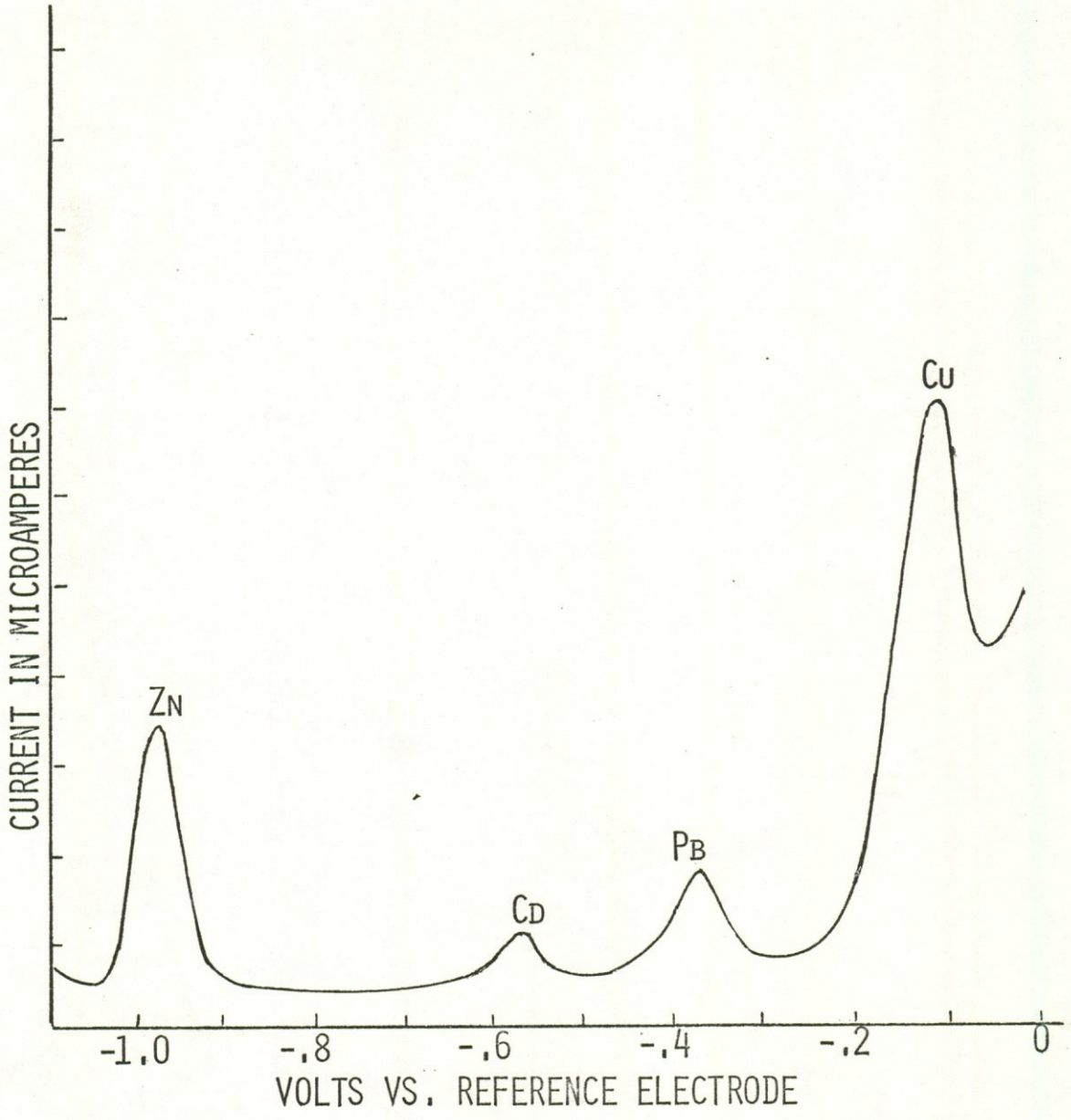
transmission electron microscopy

electron microprobe analysis

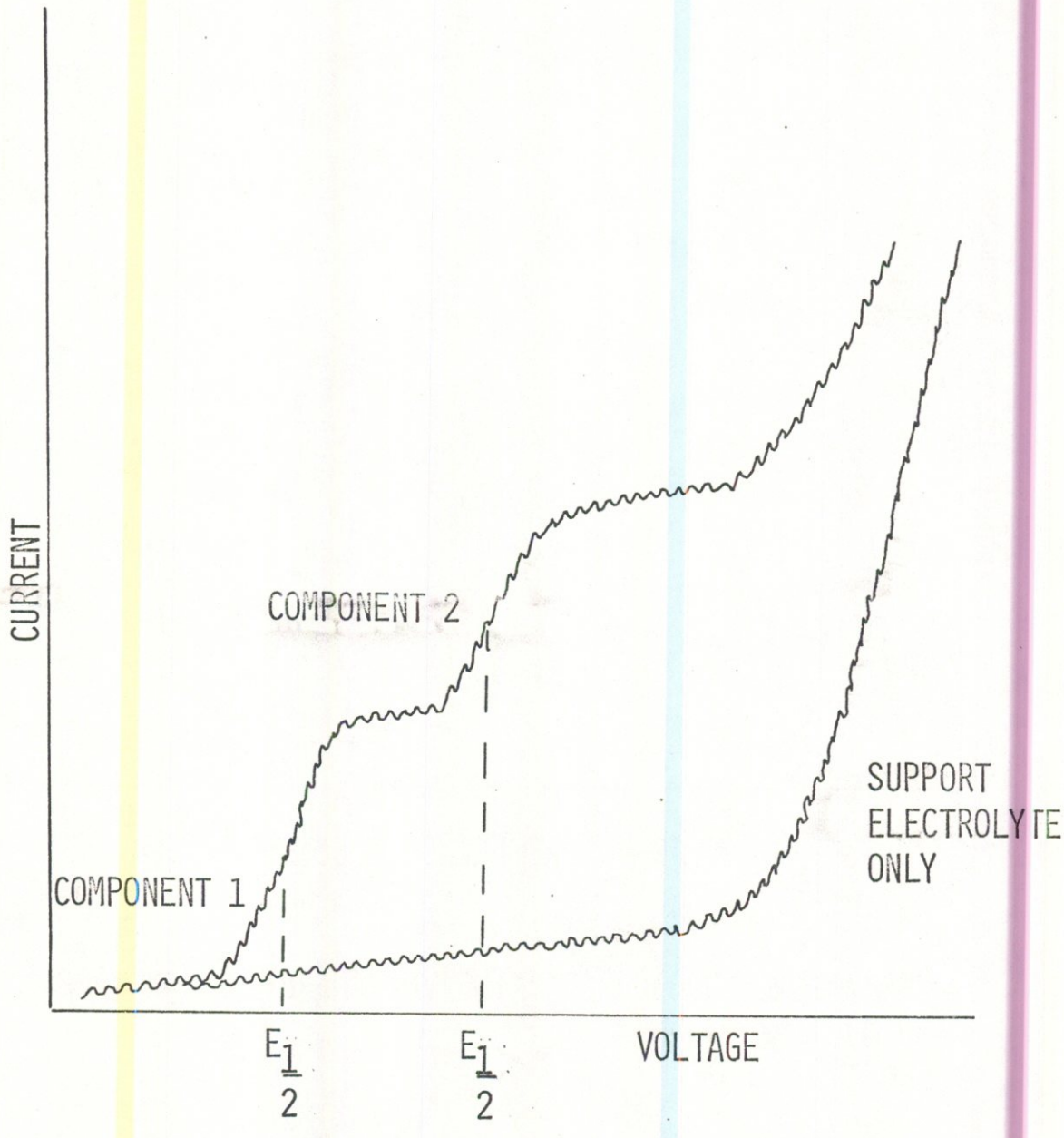
scanning electron microscopy

ion microprobe analysis

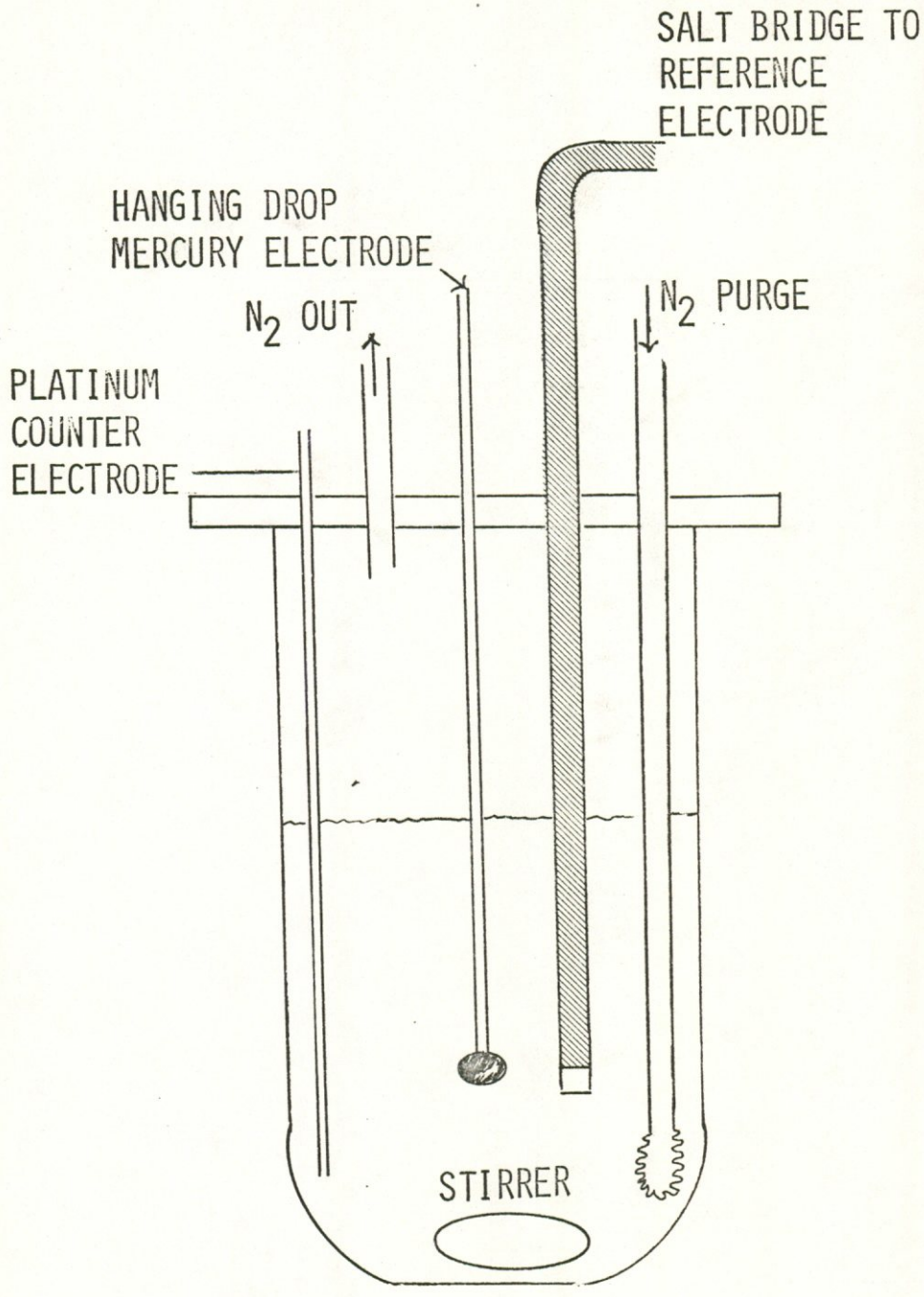
VISUALS, TABLES, FIGURES AND EXHIBITS



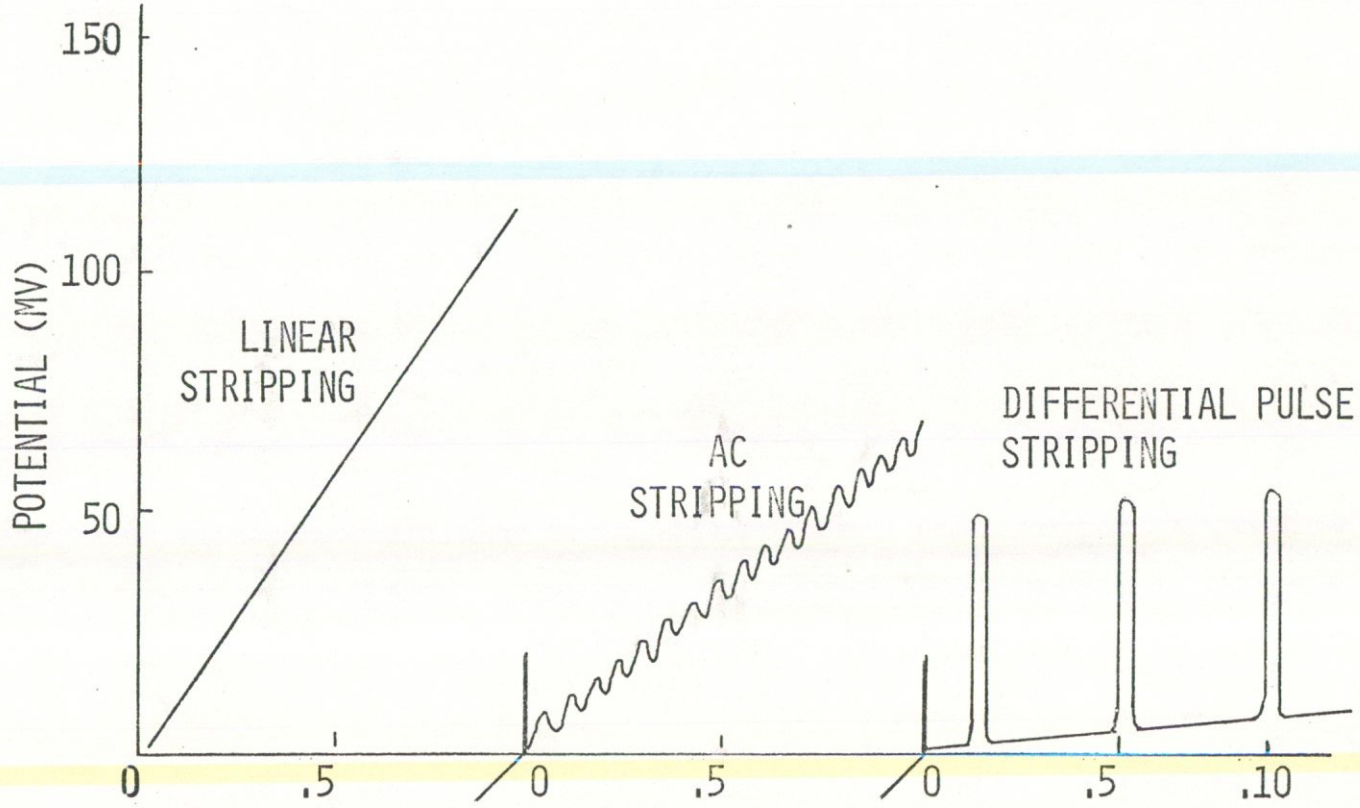
TYPICAL ANODIC STRIPPING VOLTAMETRIC CURVE



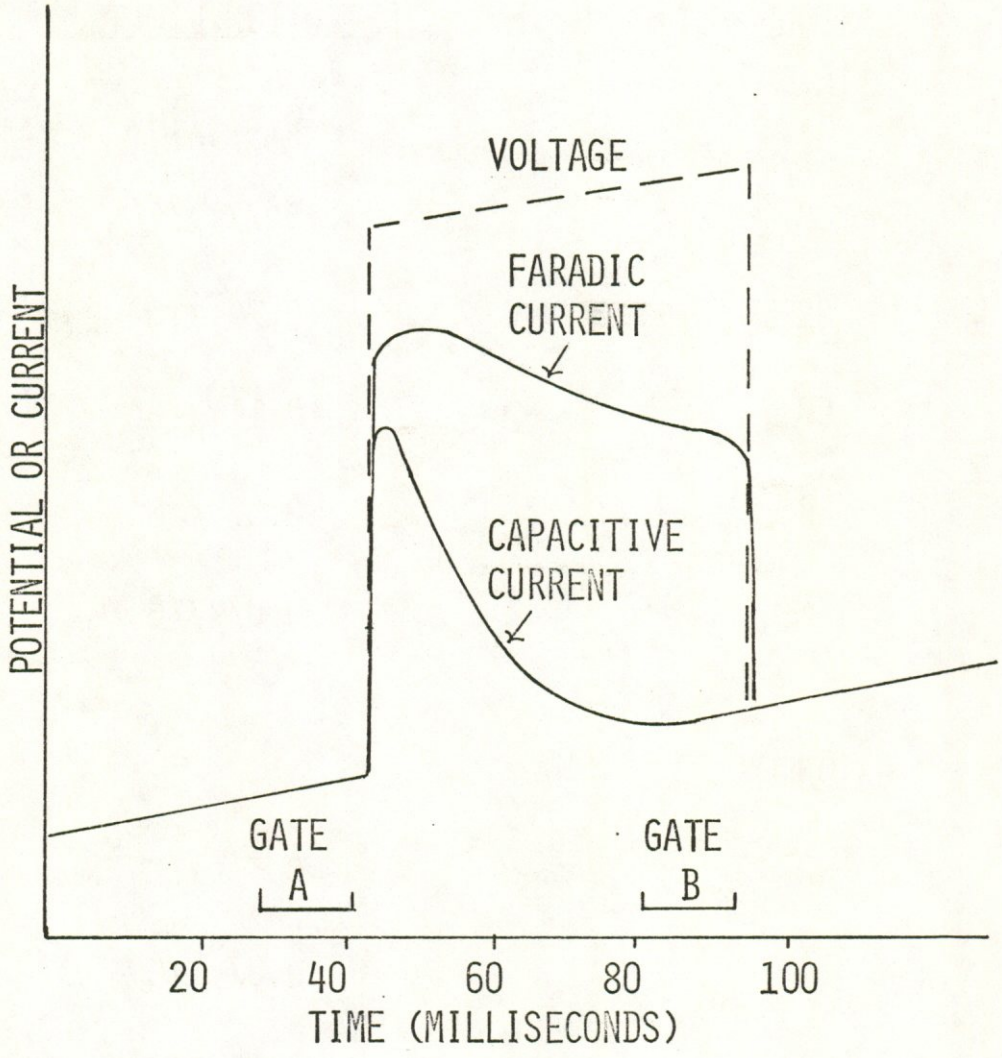
TYPICAL POLAROGRAPHIC CURVE



HANGING DROP ASV CELL



ANODIC STRIPPING POTENTIAL-TIME WAVEFORMS



SINGLE PULSE IN
DIFFERENTIAL PULSE STRIPPING

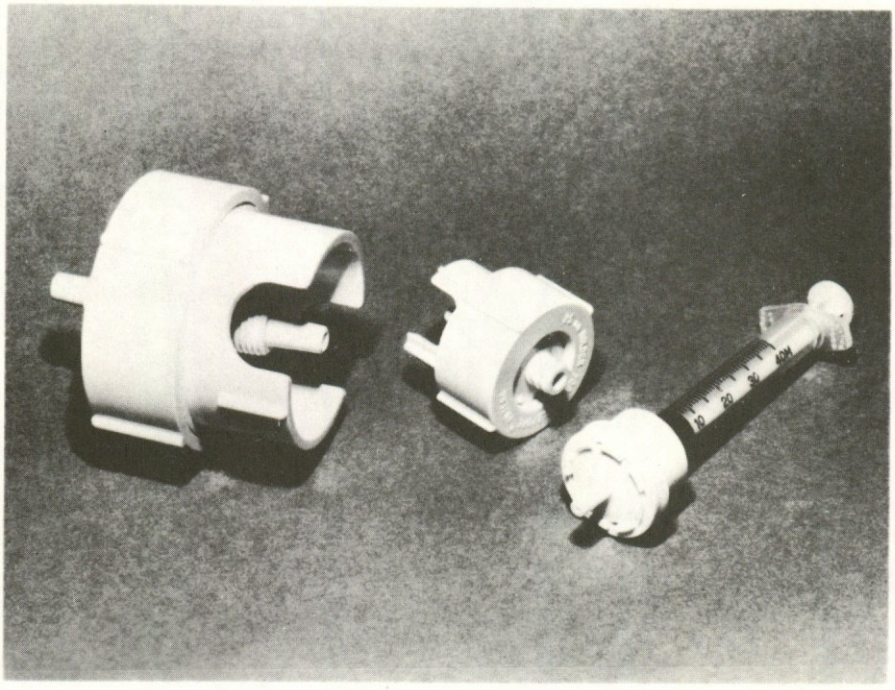
DETECTION LIMITS WHEN USING LOADED PAPER

CATIONS	DETECTION LIMITS
BI	0.61 μG
CD	0.77 μG
CR	0.22 μG
CU	0.11 μG
PB	0.55 μG
ZN	0.07 μG

ANIONS	
BR^-	0.33 μG
I^-	0.07 μG
$CR_2O_4^=$	0.19 μG
$MoO_4^=$	0.41 μG
$FE(CN)_6^{-4}$	0.088 μG

Filter Holder

Illustration Courtesy of Gelman Instrument Company
Ann Arbor, Michigan

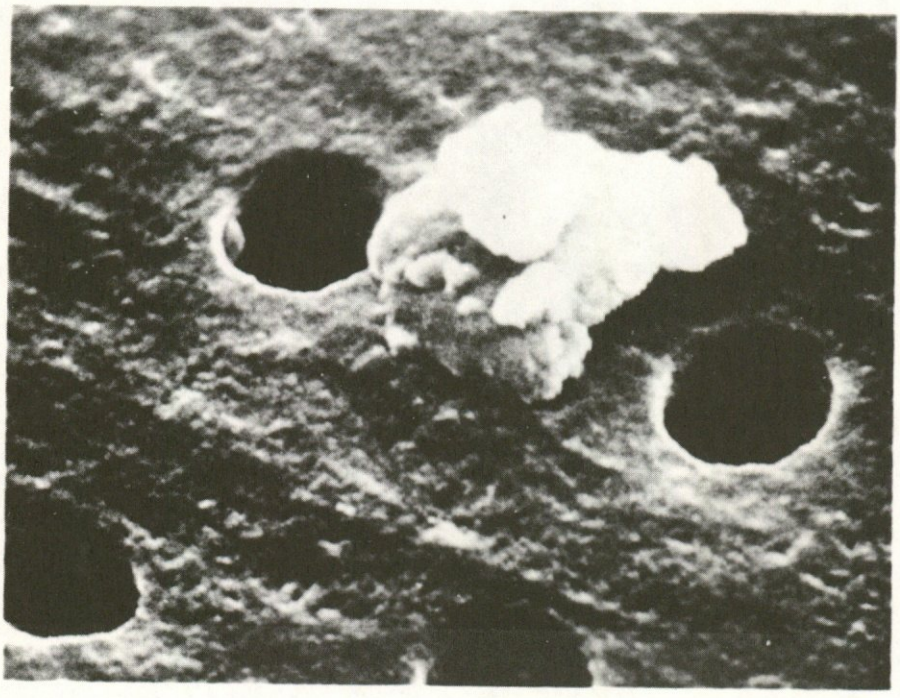


Membrane Filter Holder

Illustration Courtesy of Nuclepore Corporation
Pleasanton, California

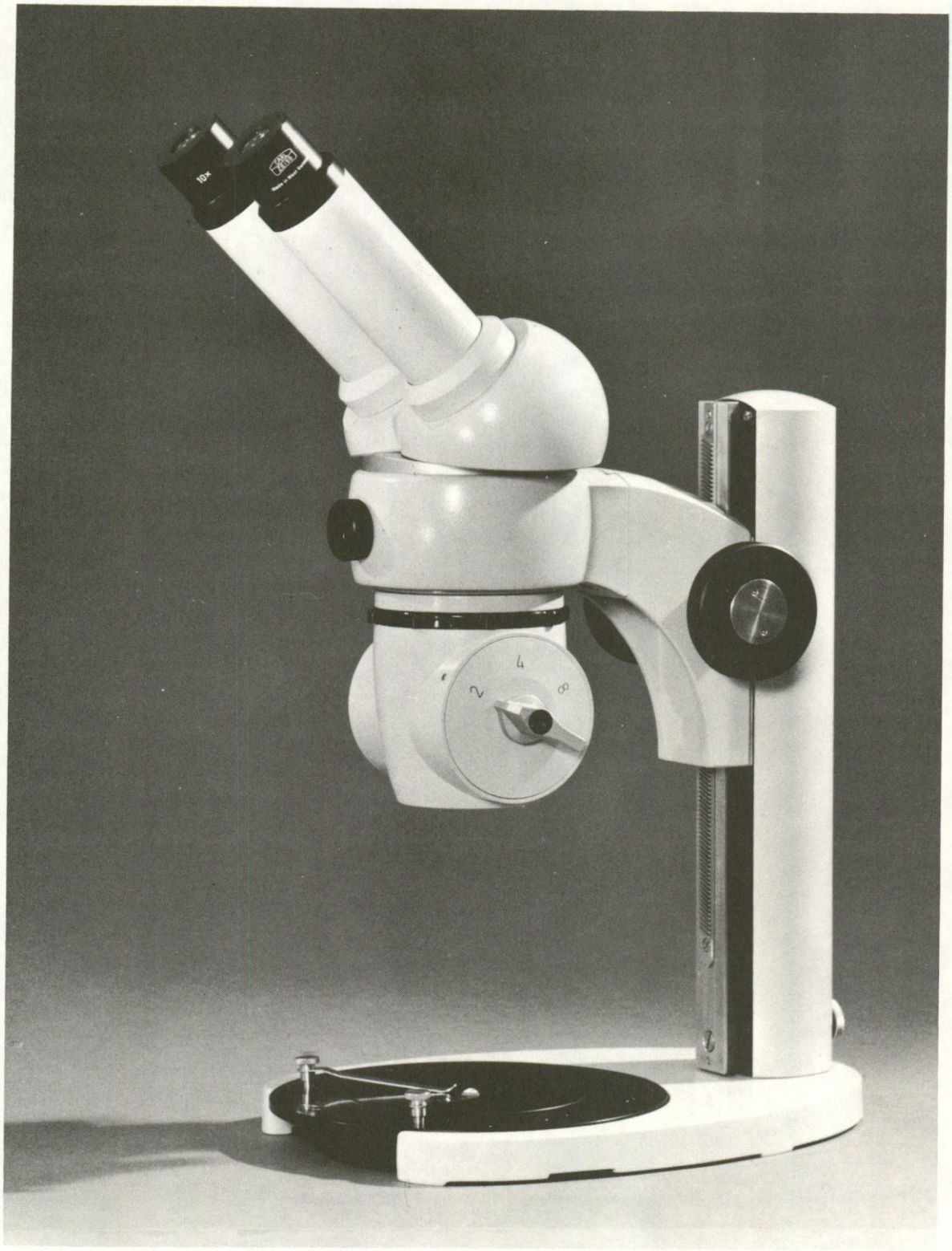
Microbalance

Illustration Courtesy of Cahn Instruments
Cerritos, California



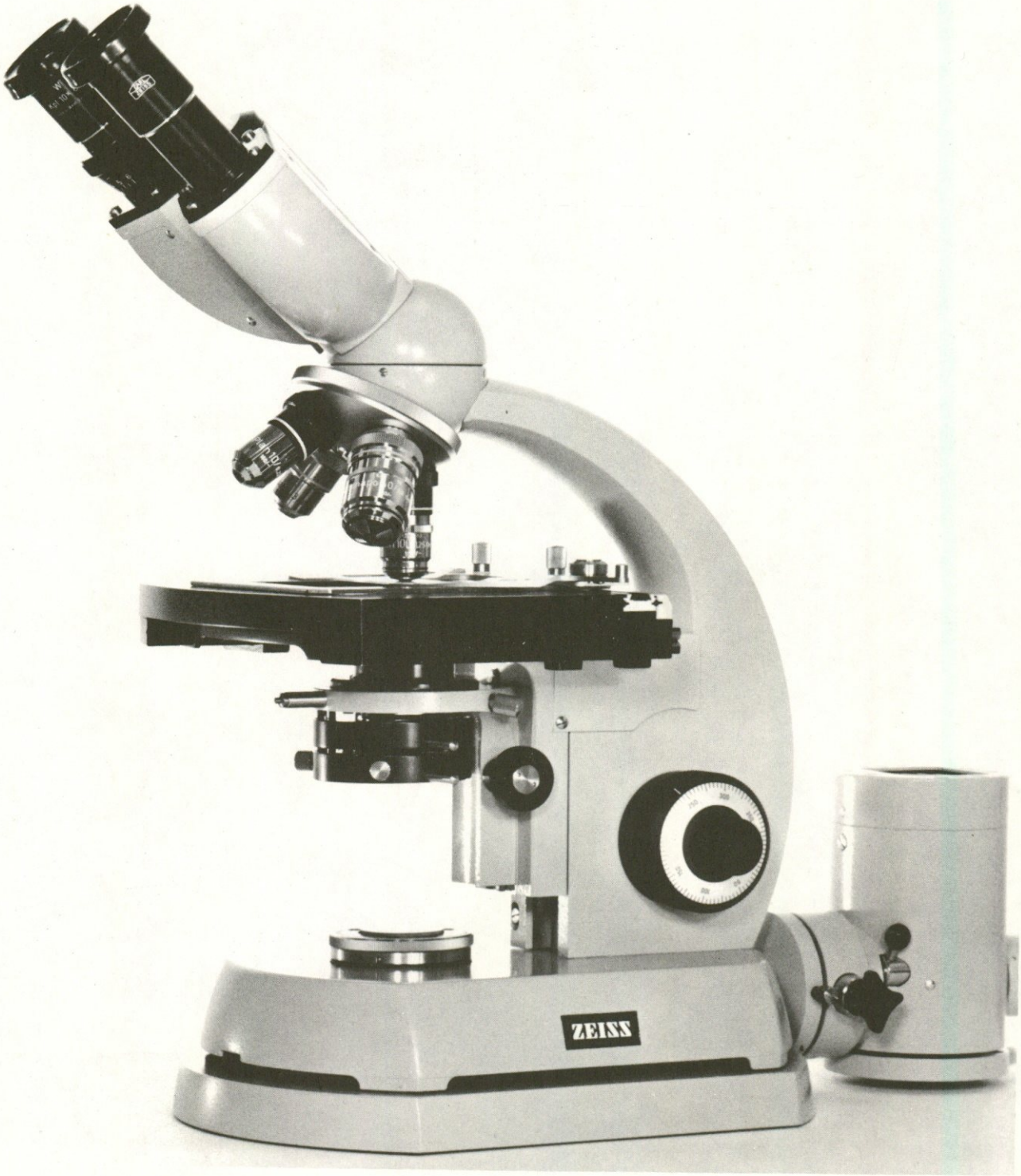
Particle on Membrane Filter with
One μm. Pore Size

Illustration Courtesy of Nuclepore Corporation
Pleasanton, California



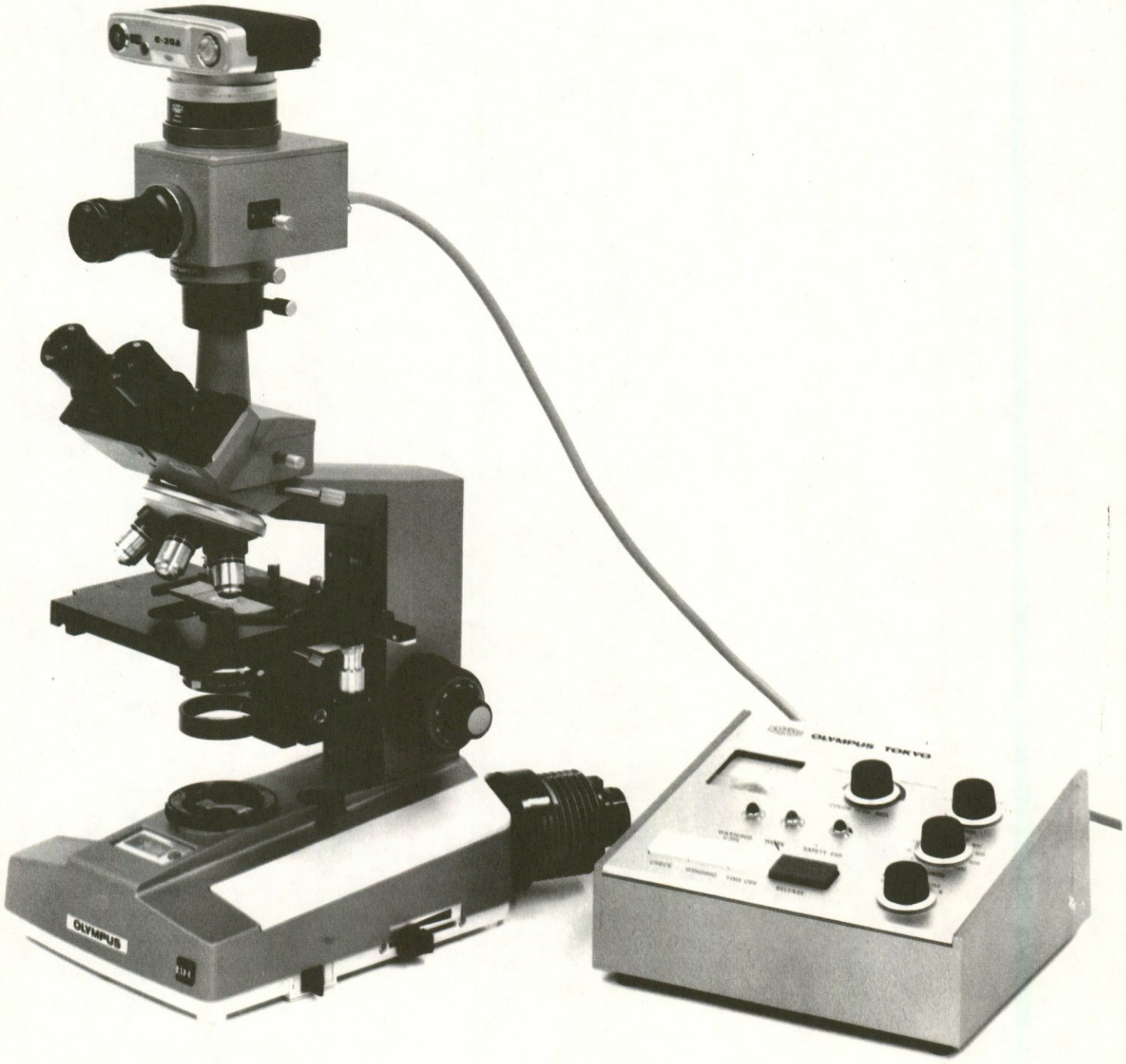
Stereomicroscope

Illustration Courtesy of Carl Zeiss, Inc.
New York, New York



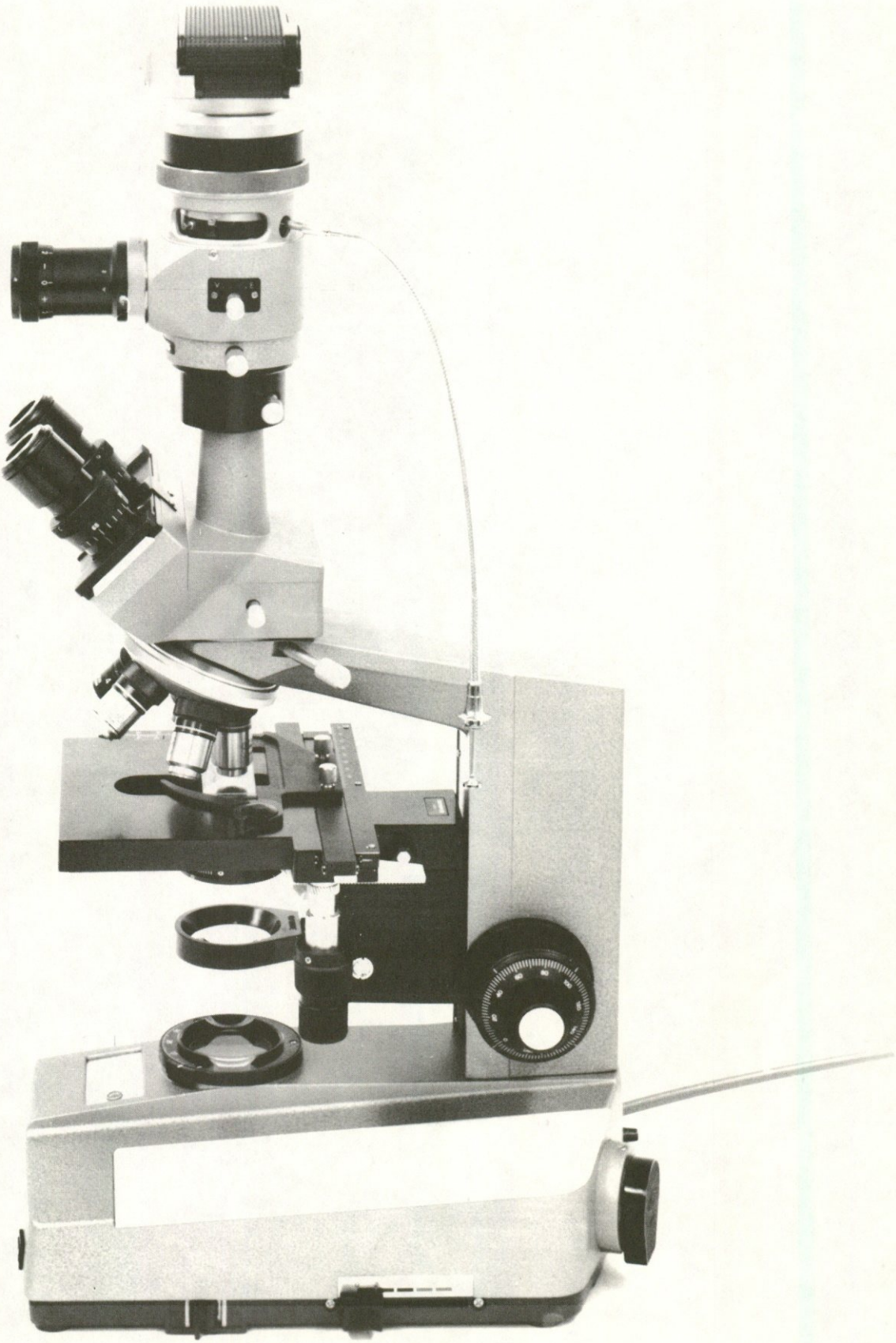
Standard Optical Microscope

Illustration Courtesy of Carl Zeiss, Inc.
New York, New York



Optical Microscope With Camera

Illustration Courtesy of Olympus Corporation of America
New Hyde Park, New York

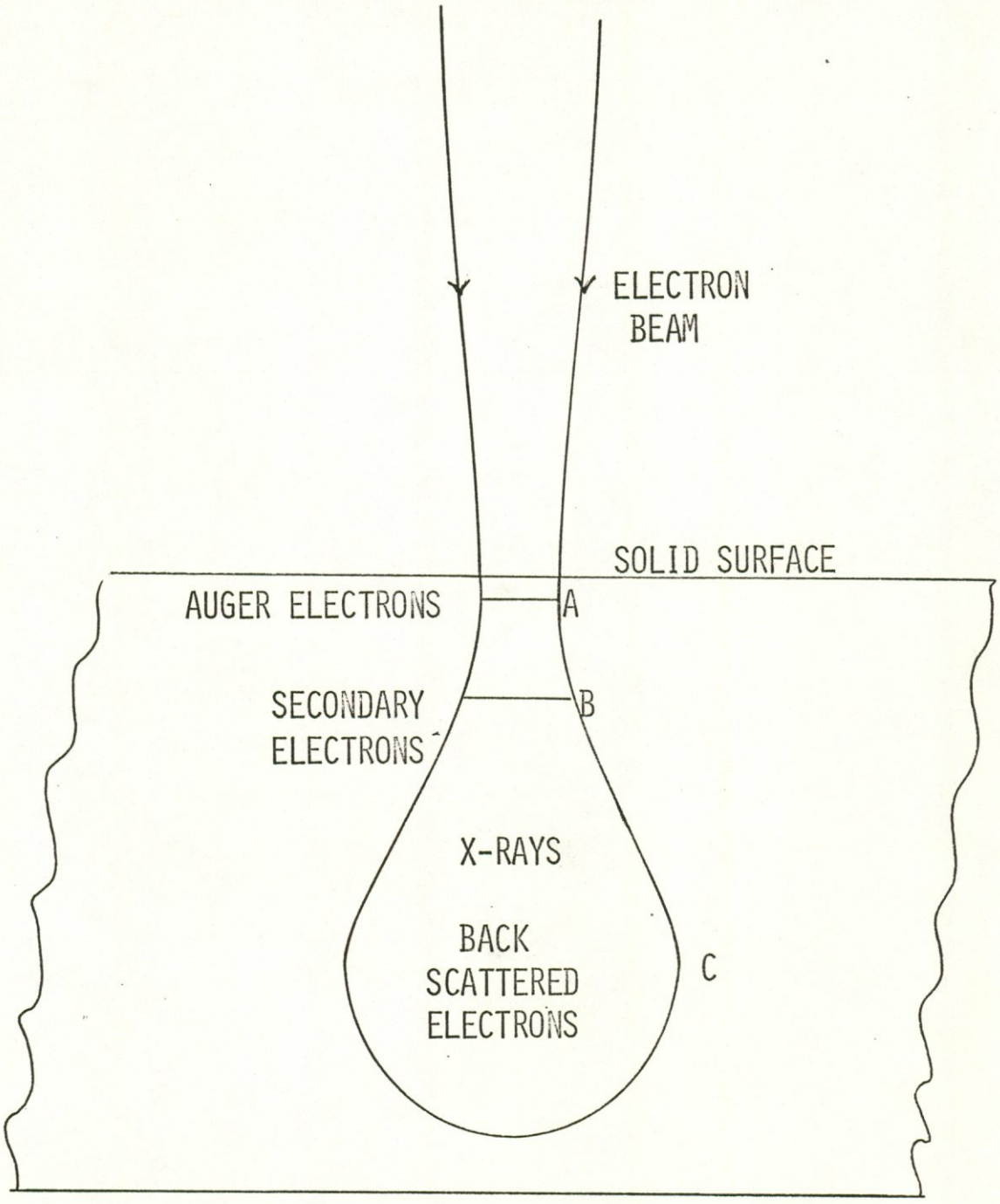


Optical Microscope With Camera

Illustration Courtesy of Olympus Corporation of America
New Hyde Park, New York

SEM System

Illustration Courtesy of Bausch and Lomb
Analytical Systems Division
Rochester, New York



SCHEMATIC OF ELECTRON BEAM
INTERRACTION WITH A SOLID

COMPARISON OF MICROANALYTICAL TECHNIQUES

FOR ELEMENTAL ANALYSIS

TECHNIQUE	SAMPLE SIZE	DETECTION LIMIT
LASER MICROPROBE	10^{-8} G. 20 TO 50 μM. DIA.	10^{-12} TO 10^{-15} G.
ELECTRON MICROPROBE	10^{-12} G. 0.2 TO 1 μM. DIA.	10^{-15} TO 10^{-17} G.
ION MICROPROBE	10^{-11} G. 1 TO 5 μM. DIA.	10^{-17} TO 10^{-19} G.