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INSTRUCTOR MANUAL
INDUSTRIAL HYGIENE CHEMISTRY COURSE

LESSON NUMBER 9

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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
Introduction to Spectroscopy	9	2:15

BEHAVIORAL OBJECTIVE

The student will be able to list the uses, conditions, sampling constraints and applications for x-ray diffraction, x-ray fluorescence, optical emission, and flame emission analysis.

SCOPE

Definition and description
Origins of atomic spectra
Spectral dispersion and resolution
X-ray diffraction
X-ray fluorescence
Optical emission

VISUALS	EXHIBITS
9-1 through 9-14	Exhibit 9-1 Exercise 9-1

EQUIPMENT

Overhead projector
35 mm projector
Screen
Blackboard
Chalk

REFERENCES

LESSON TITLE

Introduction to Spectroscopy

1. White, H. E. Introduction to Atomic Spectra, 2-22 and 304, McGraw-Hill, New York (1934).

2. Hochstrasser, R. M. Behavior of Electrons in Atoms, Ch. I and II, W. A. Benjamin, Inc., New York (1965).

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LESSON TITLE

Introduction to Spectroscopy

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16. Grant, C. L. Emission Spectroscopy, Ch. 20, The Industrial Environment--Its Evaluation and Control, USHEW-NIOSH (1973).

17. Lander, D. W., et al. Spectrographic Determination of Elements in Airborne Dirt, Applied Spectroscopy, 25, 270, (1971).

18. Seeley, J. L., and Skogerboe, R. K. Combined Sampling Analysis Method for the Determination of Trace Elements in Atmospheric Particulates, Analytical Chemistry, 46, 415, (1974).

19. Scott, R. H., Fassel, V. A., Kniseley, R. N., and Nixon, D. E. Inductively Coupled Plasma--Optical Emission Analytical Spectrometry, Analytical Chemistry, 46, 75, (1974).

20. American Society for Testing and Materials. Committee E-2 on Emission Spectroscopy, Methods for Emission Spectrochemical Analysis, 6th ed., E115-71, E116-70a, E305-70, ASTM, Philadelphia, Penn. (1971).

21. Sugimae, A. Emission Spectrographic Determination of Trace Elements in Airborne Particulate Matter Collected on Silver Membrane Filter, Applied Spectroscopy, 28, 458, (1974).

22. Webb, J., Niedermeir, W., and Griggs, J. H. Emission Spectrometric Determination of Trace Metals in Biological Tissues, Applied Spectroscopy, 27, 342, (1973).

23. Braman, R. S., Justen, L. L., and Foreback, C. C. Direct Volatilization--Spectral Emission Type Detection System for Nanogram Amounts of Arsenic and Antimony, Analytical Chemistry, 44, 2195, (1972).

ADDITIONAL READINGS

LESSON TITLE

Introduction to Spectroscopy

1. Abrens, L. H., and Taylor, S. R. Spectrochemical Analysis, Addison-Wesley, Reading, Mass. (1961).
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8. Sawyer, R. A. Experimental Spectroscopy, 3rd ed., Dover, New York (1963).

TITLE Introduction to Spectroscopy	LESSON NUMBER 9

A. Definition and Description

1. All spectroscopy is concerned with the interaction of electromagnetic radiation and matter. Atomic spectroscopy usually means the measurement of the interaction between atoms and electromagnetic radiation. Early experimental atomic spectroscopy contributed fundamentally to the development of the quantum theory of atomic structure. (1)

2. The application of spectroscopy to the quantitative chemical analysis of matter is dependent upon the physical aspects of the discrete absorption of energy by electrons and the subsequent emission of energy in discrete quanta. The wavelength of these quanta are the difference in the energy levels of the electrons. X-ray absorption, emission and fluorescence results from energy level changes in the first, second and third shells (K, L & M) around the nucleus of the atom. Optical atomic absorption, emission and fluorescence results from energy level changes in the outer or valence electron shells. Though the techniques differ in the physical equipment and method of operation, they are complementary in their analytical application. In many cases, samples of the same form may be used. (1)

3. The beginning of spectroscopy started with Newton who refracted sunlight and created bands of colors, a spectrum. However, not until Wollaston in 1802 and Fraunhofer in 1814 added a defining slit could the dark lines in the solar spectrum be observed. Fraunhofer mapped several hundred of these lines. The eight most prominent still carry his designation, the letters A through H. Kirchoff in 1859 defined these dark lines as those of atomic absorption. With the Rowland grating engine in 1882 and Balmer's discovery of the first hydrogen series in 1885, the modern study of spectra began. (1)

NOTES Times (elapsed) projected	LESSON OUTLINE
(---) 0:10	A. Definition and Description
	1. Atomic spectroscopy--measurement between atoms and radiation
	2. Spectroscopy creates wavelengths--x-ray absorption, emission and fluorescence
	3. History--Newton, Wollaston, Fraunhofer, Kirchoff, Rowland, Balmer

4. The following energy relationships are fundamental in spectroscopy. The energy of a photon is related to the frequency of wave motion by Planck's equation:

$$E = h\nu$$

where:

E = energy in ergs (centimeter-gram-second)

h = Planck's constant = 6.624×10^{-27} (erg-second)

ν = frequency of the wave motion

also:

$$E = \frac{hc}{\lambda_o}$$

where:

c = velocity of light in centimeters per second

λ_o = wavelength in vacuum in centimeters

The number of waves per centimeter or wavenumber is the reciprocal of the wavelength in vacuum (λ_o)

$$\bar{\nu} = \frac{1}{\lambda_o}$$

The wavenumber, $\bar{\nu}$, in cm^{-1} is related to the energy by:

$$E = (hc)\,\bar{\nu} \qquad (2)$$

NOTES Times (elapsed) projected	LESSON OUTLINE
Write equations on the blackboard as you are discussing them.	4. Planck's equation: $E = h\nu$ $\bar{\nu} = \frac{1}{\lambda_o}$ $E = (hc)\bar{\nu}$

5. The product of Planck's constant and the velocity of light (hc) is a universal constant. Thus the wavenumber is directly proportional to energy. Furthermore, since each quantum of electromagnetic energy, a photon, is capable of producing one electron, the energy of the electron may be expressed in electron volts (eV) thus:

$$1 \text{ eV} = 8067 \text{ cm}^{-1} = 1.24\,\mu\text{m}$$

The energy range of x-ray spectroscopy is about 1 to 100 kilo eV, emission spectroscopy, 1 to 20 eV and infrared spectroscopy, less than 1 eV. (2)

B. Origins of Atomic Spectra

1. The empirical equation which Balmer proposed to describe the wavelengths of hydrogen in the visible region is:

$$\lambda = 3645.6 \frac{n^2}{n^2 - 4}$$

where:

λ = wavelength in Angstroms

n = a series of integers, 3, 4, 5, 6....

This is now expressed in terms of wavenumber,

$$\bar{\nu} = 109,737 \left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad (2)$$

NOTES Times (elapsed) projected	LESSON OUTLINE
	5. Planck's constant is universal, electron volts
(0: 10) (Transition A. -B.) From a general discussion of spectroscopy to the details of atomic spectra. 0:20 Write equations on blackboard. Cover all equations quickly. It is not important for students to memorize them. It is important for them to understand the basic concepts.	B. Origins of Atomic Spectra 1. Balmer equation: $\lambda = 3645.6 \quad \frac{n^2}{n^2 -4}$ $\overline{\nu} = 109,737 (\frac{1}{2^2}, - \frac{1}{n^2})$

2. Rydberg extended the Balmer equation and Bohr gave the general equation:

$$\bar{\nu} = RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R = Rydberg's constant of 109,700 cm^{-1}

n_1 = an integer, fixed for a given series

n_2 = a sequence of integers, corresponding to successive lines in a given series. n_2 starts with an integer greater than n_1

Z = the atomic number of the element.

The limit of each nth series is then

$$\bar{\nu} = \frac{RZ^2}{n_1^2}$$

This is the potential energy required to release an electron from the atom, called the ionization potential. (2)

3. The first three series of the hydrogen atom are illustrated in Exhibit 9-1. The limit for the Balmer series is $\frac{109,700}{2^2}$ or 27,425 $cm.^{-1}$, which is equivalent to 365 nm. Any ejected electron which has kinetic energy above this 27,425 $cm.^{-1}$ or 3.4 electron volts will cause a non-discrete emission or a continuum below 365 nm. Thus hydrogen and deuterium discharge lamps are used as continuum sources in ultraviolet spectrophotometry. When the electron has lost its kinetic energy and becomes bound to the hydrogen ion, discrete photon energies are emitted at the wavelengths indicated in Exhibit 9-1 until the ground state at $n_1 = 1$ is reached. (2)

NOTES Times (elapsed) projected	LESSON OUTLINE
	2. $\bar{\nu}\ RZ^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ $\bar{\nu} = \frac{RZ^2}{n_1^2}$
Exhibit 9-1	3. First three series of hydrogen

4. After Roentgen discovered x-rays with a Crookes vacuum tube in 1895, Moseley studied the K radiation of the elements calcium through zinc in 1913 and announced that the frequency of the K line for each element was approximately proportional to the sequence of its atomic number, A. Thus:

$$\nu = R(Z-\sigma)^2 K$$

where ν = frequency in cm^{-1}

R = Rydberg constant of 109737cm^{-1}

Z = atomic number of element

σ = a constant

K = a constant (1)

5. Analogous with the hydrogen-like atoms, Moseley wrote:

$$\nu = R(Z-\sigma)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

For the K_2 series of spectra for the elements,

$$n_1 = 1,\ n_2 = 2 \text{ and } \sigma = 1$$

$$\therefore \nu = \frac{3}{4} R(Z-1)^2$$

and for the L series, Moseley's Law also holds. For example, for the $L_{\beta 1}$ line, $n_1 = 2$, $n_2 = 3$ and $\sigma = 7.4$

$$\therefore \nu = \frac{5}{36} R(Z-7.4)^2$$

NOTES Times (elapsed) projected	LESSON OUTLINE
	4. $\nu = R(Z - \sigma)^2 K$ 5. $\nu = R(Z - \sigma)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

For chromium of atomic number 24, the K_α line is at 0.229 nm and the excitation potential is approximately 6K eV. This work clearly indicated for the first time that the elements in the periodic table are constructed with extreme regularity. This spectroscopic data formed part of the background for the laws of quantum mechnics as related to the origin of spectra. (1)

6. As is well known, the energy of any electron is defined by four separate variables: n, l, m and s, known as the quantum numbers.

   - n is the principal quantum number and has the integral values 1, 2, 3... for the K, L, M... shells.
   - l is the angular quantum number for the shape of the electron orbit and has values O and up to (n-1).
   - m is the magnetic quantum number and takes values of +l, -l or 0.
   - s is the spin quantum number and has values of ± 1/2. (3)

7. Pauli's exclusion principle states that no two electrons in the same atom can have the same energy, or combination of quantum numbers, and, therefore, the maximum number of electrons in each shell is $2n^2$. Then, the atom can be constructed with a maximum of 2 electrons in the first K shell, 8 in the second L shell and 18 in the third M shell. As a result of quantum mechanics, the atom's total energy is limited to a relatively small number of special values, which can be represented by an energy level diagram.

NOTES Times (elapsed) projected	LESSON OUTLINE
	6. Quantum numbers . n . l . m . s 7. Pauli's exclusion principle

8. Another variable in the quantum numbers is the vector sum of l and s, known as the J value for total angular momentum. This is due to the large effect of the spin quantum number on the energy level. The energy level for atoms with one electron in the outer shell becomes two levels, the higher one with s equal to + 1/2 for parallel directions and the lower one with s equal to - 1/2 for multiparallel direction. With two or more electrons in the outer shell, this multiplicity in atomic spectra becomes more complex. (3)

9. The resonance lines arising from the ground states of the alkali elements are, therefore, doublets at the wavelengths shown in Visual 9-1. Actually lithium is a doublet with a separation of 0.015 nanometers. The heavier alkali atoms have a lower ionization potential, because the single electron in the valance shell has a lower energy level. Because of the single electron in the outer shell, the alkali metals yield high analytical sensitivity in low temperature flames. (3)

10. The ion of an atom will yield a spectral series similar to the spectra of the neutral atom next lower in atomic numbers. Thus, at first, the visible spectra of the helium ion (He^+), observed in a star, was assumed to be a form of hydrogen. (1)

11. The effective production of atomic spectra in emission (or absorption and fluorescence) depends upon the release of the analyte atom from other atoms in the gaseous state and the subsequent raising of the energy level from the ground state for emission of photon energy. Most often, these two processes occur simultaneously or in rapid succession. A single power source, such as an arc, a high frequency spark or a chemical flame is usually used. There are laser micro sampling, ion beam sputtering, thermionic evaporation and chemical vaporization techniques, where at least some of the sampling to the ground state is independent of the excitation process. In all cases, atomic spectra are emitted from an analyte with relatively little interference from the matrix elements of the sample. The greatest deterent to the emission of an intensity, which is proportional to increasing concentration of the analyte, is the presence of an expanding cloud of ground state atoms of the analyte around the central core of the excitation. These cause atomic absorption. In severe cases the effect can be a complete self reversal of the resonance lines of an element. (3)

NOTES Times (elapsed) projected	LESSON OUTLINE
	8. Total angular momentum--effect of spin quantum energy level
Visual 9-1	9. Resonance lines--alkali elements
	10. Ion spectra = spectra of next lower atom
	11. Production of atomic spectra, release analyte to ground then to photon energy

12. The effective production of characteristic x-ray fluorescence spectra is due to the irradiation of a sample with photons of sufficient energy to eject one or more electrons from the K, L or M shells. The most intense lines for the K and L spectra are shown in Visual 9-2. They are emitted as the electrons return to the lower energy levels. Due to the limits imposed by x-ray sources and crystal dispersion of x-rays, the K spectra is observed for the elements Na ($Z=11$) through Cs ($Z=55$); the L spectra is observed for the elements Sn ($Z=50$) through Pu ($Z=94$). This corresponds to a wavelength range of 1.19 nm. to 0.040 nm. and and 0.36 nm. to 0.087 nm. respectively. (4)

13. X-ray fluorescence excitation is essentially non-destructive, although there may be radiation damage to organic materials. Samples are analyzed as solids, liquids and solutions with gases having limited applications. The depth of excitation within a sample depends upon the source intensity, the wavelength, the density, the average atomic number of the components in the sample and the absorption coefficients of all elements in the samples. In contrast to optical emission, the intensity of an x-ray line is highly dependent upon the matrix of the sample. This dependency is greatly reduced when the sample is diluted by solutioning in mineral acids, by fusion of the sample in a salt or by thin film presentation. (4)

C. Spectral Dispersion of Resolution

1. These methods of x-ray fluorescence and optical emission analysis are dependent upon dispersing spectrometers or spectrographs. These will deliver the resolutions necessary for the unambiguous separation of the analyte energy and yet not sacrifice an unnecessary part of the net signal. Although resolution and dispersion are related through the optics of the system, they are independent functions and need to be optimized separately for trace analysis. For instance, two spectral lines which are not resolved may be excessively dispersed without increasing the resolution. On the other hand, two lines which are completely resolved to the background level may not be separated by the defining slit or the detector system until the dispersion is increased.

NOTES Times (elapsed) projected	LESSON OUTLINE
Visual 9-2	12. Production of x-ray fluroescence
	13. X-ray fluorescence and samples used
(---) (Transition B. -C.) From a general theoretical discussion of atomic spectra to the basis for spectral dispersion and resolution used in spectroscopy. 0:30	C. Spectral Dispersion and Resolution 1. Dispersion and resolution--related through optics but independent functions

2. Diffraction is the most common method of resolving and displaying spectral energies in x-ray and optical emission analysis. Since x-rays have wavelengths in the order of 0.05 to 1 nm., single crystals, having approximately the same lattice spacing, are used to diffract x-rays. In optical emission, mechanically ruled gratings are used. These are generally plane or curved surfaces of aluminum metal evaporated on a glass or quartz base in which typically 300, 600, 1200 or 2400 grooves per millimeter have been ruled. (3, 4)

3. In either case, when a parallel polychromatic beam is incident upon such an orderly array, there is coherent scattering in certain directions by multiple interferences. In other words, at a particular exit angle, there will be a reinforcement of a certain wavelength or a wavelength times the order of diffraction. This product of a whole number of wavelengths ($n\lambda$) is then equal to the increased pathlength of each ray of the beam when there is such reinforcement. In the Bragg reflection, from a single crystal, the incident angle and the exit angle are equal. (4)

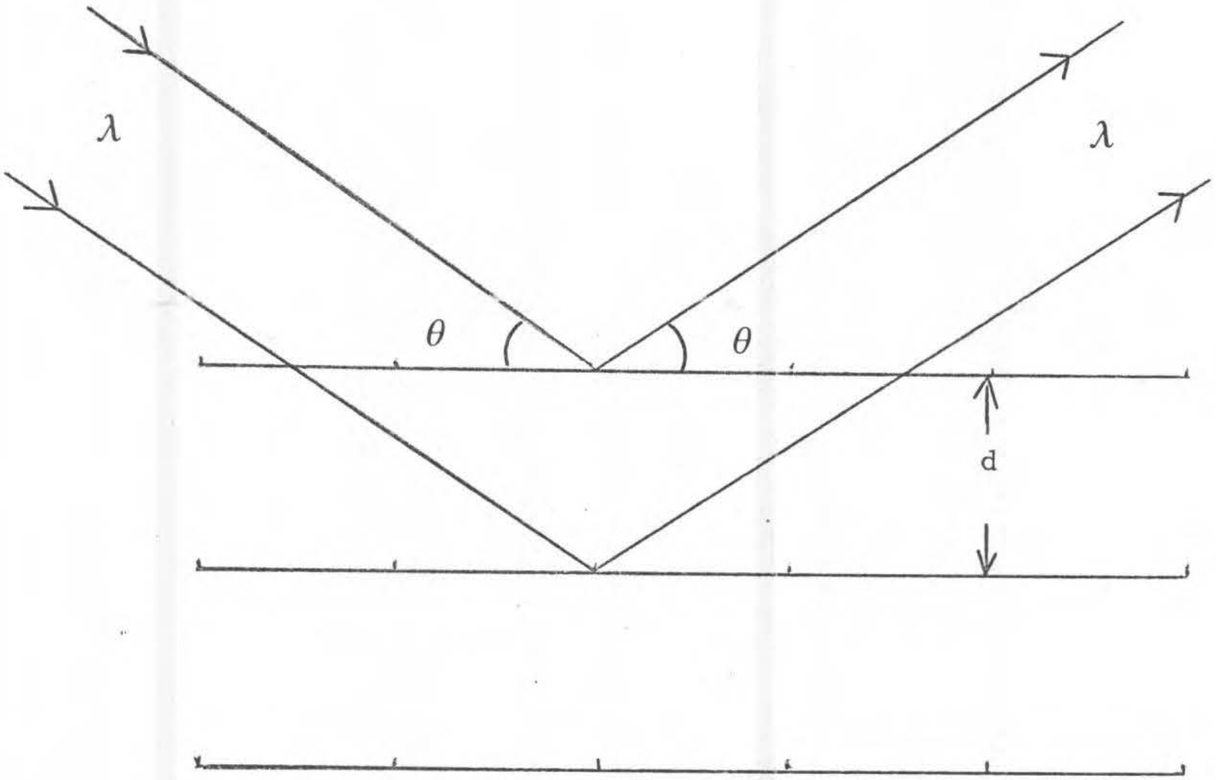
4. Geometric derivation of the Bragg Law. (4)

5. The significance of the product ($n\lambda$) is exampled by the case when the Cu K_2 line is resolved by a crystal at a fixed angle. Other wavelengths from other elements may appear coincident or nearly so, as indicated in Visual 9-3. These interferences due to overlapping orders are reduced or nullified by the fact that crystals have different efficiencies at each order and by the use of an energy discriminating detector, such as a proportional counter. (4)

NOTES Times (elapsed) projected	LESSON OUTLINE
	2. Diffraction by crystals and gratings
	3. Bragg reflection
Exercise 9-1 Spend about 15 minutes total on this exercise.	4. Derive equation
Visual 9-3	5. Interferences due to overlapping orders of n λ

EXERCISE 9 - 1	Page 1 of 2
LESSON TITLE Introduction to Spectroscopy	LESSON NUMBER 9

A parallel beam of wavelength λ is incident upon a crystal of d spacing in the lattice. The reflected beam angle equals the incident beam angle and the reflected beam is a maximum because it is reinforced. Derive Bragg's Law for diffraction.



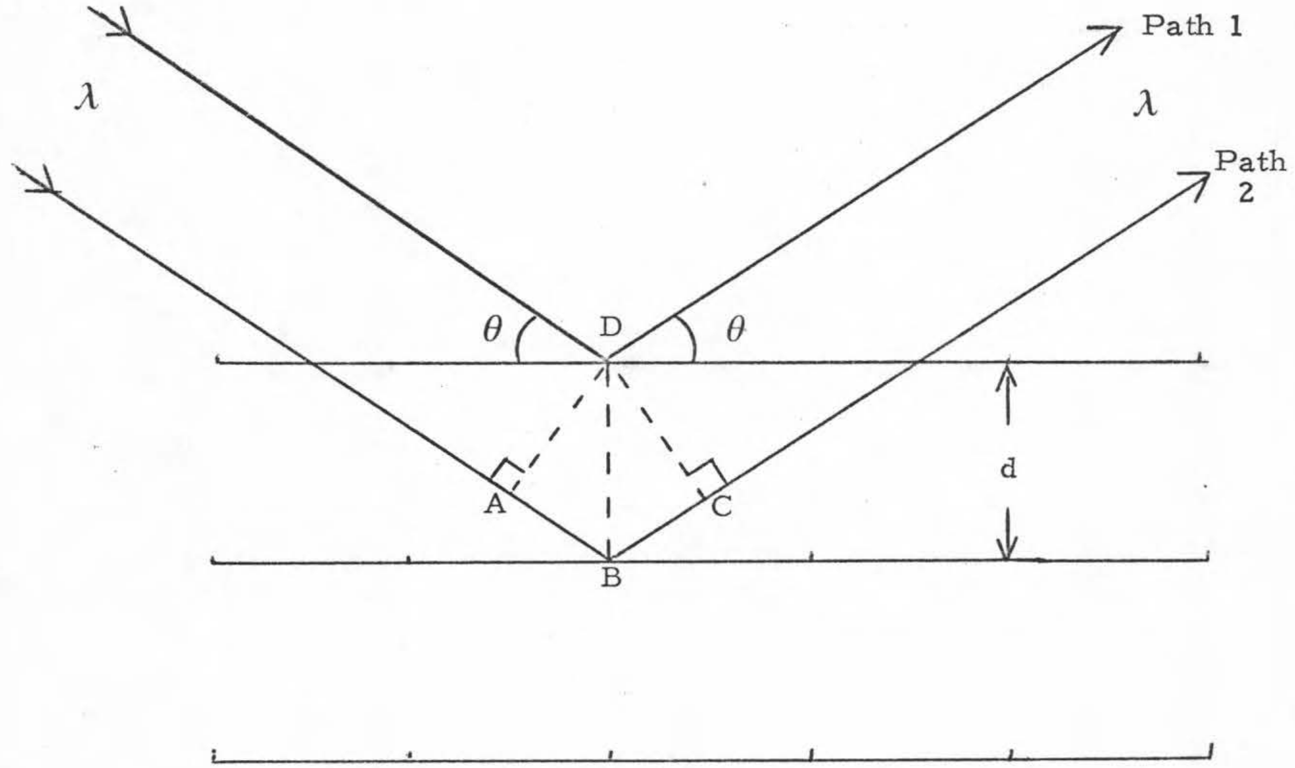
EXERCISE 9-1

LESSON TITLE
Introduction to Spectroscopy

LESSON NUMBER
9

Solution:

1. Construct the right triangles DAB and DBC
2. DB = d
3. AB = BC = d $(\sin \theta)$
4. AB + BC = difference in the pathlengths of Path 1 and Path 2 = $n \lambda$
5. Therefore: $n \lambda = 2 \, (d) \, (\sin \theta)$



when: n = diffraction order

λ = wavelength in nm.

d = lattice spacing in nm.

θ = incident and reflection angle

6. Optical gratings are typically plane reflecting, or concave reflecting surfaces of an aluminum coating. On these surfaces are 300, 600, 1200, or 2400 grooves per millimeter evenly spaced and exactly parallel. The angle of the surface of each groove is chosen to direct most of the diffracted energy toward a particular wavelength region where the greatest efficiency is needed. This is the blaze angle of the grating. In typical applications, the incident angle and the reflected angle are not the same. Very often both beams lie on the same side of the plane normal to the grating. Although reflection and diffraction are surface effects in this case, the analogy with the Bragg law holds such that:

$$n \lambda = d (\sin i + \sin \theta)$$

i = incident angle; θ = reflected angle

This is the general expression for the grating. If the beams lie on opposite sides of the normal, the smallest angle takes a negative sign. (3)

7. The angular dispersion is obtained by differentiating the grating equation to yield:

$$\frac{\Delta \theta}{\Delta \lambda} = \frac{n}{d \cos \theta}$$

In an optical instrument, where the focal plane is normal to the grating, the linear dispersion is obtained by multiplying by the focal length of the instrument. A nomograph has been constructed to conveniently relate the focal length, the grating rulings per millimeter, the dispersion and the resolution. (5)

8. Theoretical resolution is a product of the order of observation and the total number of diffracting elements used across the grating surfaces.

$$\frac{\lambda}{\Delta \lambda} = (n)\,(\text{number of total grooves})$$

Practical resolution depends upon the quality of the grating and the slit width of the optical system. It is important that the full width of a grating be used in optical applications, so that the maximum resolution is retained. (3)

NOTES Times (elapsed) projected	LESSON OUTLINE
	6. General expression for grating: $n\lambda = d\,(\sin i + \sin\theta)$ 7. $\frac{\Delta\theta}{\Delta\lambda} = \frac{n}{d\cos\theta}$ 8. $\frac{\lambda}{\Delta\lambda} = (n)$ (number of total grooves)

9. The first dispersion of spectra was accomplished with a prism. When a beam of light passes from air into a transparent medium, at an angle greater than the normal, the beam is bent in the medium toward the normal. The angular deviation is a measure of the index of refraction, and this index of refraction varies with wavelength. The dispersion of a prism instrument is a function of the refraction index, the shape of the prism and the angles of the beam entering the prism and leaving the prism. The dispersion rapidly increases toward shorter wavelengths. The resolution of a prism is directly proportional to the size of the prism and the rate of change of the refractive index with wavelength. Gratings have replaced prisms in optical emission applications for the most part excepting in special applications, such as the separation of overlapping orders from a diffraction grating. (6)

10. The refraction of x-rays is a very small effect, the index of refraction being of the order of 0.99999. The Bragg Law is corrected for this effect in only the most precise work in x-ray diffraction. (4)

D. X-Ray Diffraction

1. If a monochromatic beam of x-ray energy passes through or is reflected from a surface of a crystal, the angles of diffraction can be used to calculate the interatomic spacing within the crystal. This is based on Bragg's Law: $n\lambda = 2\,d\sin\theta$. (7)

2. A crystal can be defined as the regular polyhedral form of a chemical compound bounded by smooth surfaces. A crystal is formed by the action of interatomic forces when material passes under suitable conditions from a gaseous or liquid state to that of a solid. This infers that a crystal is the normal form of all solid elements and chemical compounds. Many substances which are amorphous can be considered metastable. With sufficient time and temperature a crystal develops from the amorphous material. Carbon, for example, can be observed as amorphous powder, as a vitreous isotropic fused solid, as a crystalline anisotropic graphite in platelet form, or as a diamond in the form of a tetrahedron. (7)

NOTES Times (elapsed) projected	LESSON OUTLINE
	9. Prism--refractive index, dispersion, resolution
	10. X-ray index of refraction = 0.99999
(1:00) (Transition C.-D.) From basis of spectroscopy to the specifics of x-ray diffraction. 0:15	D. X-Ray Diffraction
	1. Determination of crystal's interatomic spacing
	2. Crystal-- definition

3. X-ray diffraction has wide application in the identification and structural analysis of materials. It can be applied effectively to small amounts of material. It is not generally used in chemical analysis but is often used in a supplementary manner. (7)

4. The techniques of x-ray diffraction may be classified as:

   - Polychromatic Laue method on single crystals
   - Monochromatic Weissenberg method on single crystals
   - Vibrating or rotating crystal spectrometric method
   - Bulk or thin film powder method with spectrometer
   - Debye-Scherrer powder camera method
   - Para-focussing powder method
   - Monochromator pinhole method (7)

5. As an illustration, the instrumentation for the thin film powder diffractometer technique typically consists of the components shown in Visual 9-4:

   - The x-ray source is a water cooled Coolidge tube with typical mode targets of Mo, Cu, or Cr.

NOTES Times (elapsed) projected	LESSON OUTLINE
	3. X-ray diffraction--applications
Mention only briefly	4. Techniques of x-ray diffraction
	. Polychromatic Lane
	. Monochromatic Weissenberg
	. Vibrating crystal
	. Bulk
	. Debye-Scherrer
	. Para-focussing
	. Monochromator pinhole
Visual 9-4	5. X-ray diffraction spectrometer:
	. Source and mode target

- The K_α monochromatic line from the target of the x-ray tube is isolated by preferentially filtering out the K_β line. For instance, the critical absorption edge for zirconium lies between the wavelengths for Mo K_α and Mo K_β. Therefore, a 50 micrometer thick foil of zirconium reduces the Mo K_β line by almost a factor of 10 relative to the Mo K_α line.
- The beam passes through apertures and a Soller slit or collimator and is diffracted from the sample.
- The sample is placed at the center axis of a gonimeter. For one degree of sample surface rotation the detector rotates two degrees. This satisfies the Bragg reflection.
- The diffracted beam passes through a further Soller slit or aperture and is detected in an ionizing radiation detector. The Geiger tube detector has been largely replaced by scintillators and other detectors.
- The detected pulses are converted to an analog signal and displayed on a recorder as the gonimeter scans through the region of interest.
- Further intensity is gained by eliminating the K_β source filter and using a fixed crystal spectrometer on the detector arm to isolate the K_α component.
- The spectrometer may be oriented vertically or horizontally. (7)

NOTES Times (elapsed) projected	LESSON OUTLINE
	- K_α monochromatic line - Soller slit - Gonimeter - Ionizing radiation detector - Signal displayed on recorder - Further sensitivity by removal of K_β filter and fixed detector arm - Vertical or horizontal spectrometer

6. Since the sample is a powder and the crystals are randomly oriented, all possible interplanar "d" spacings (from Bragg's law) will be recorded as the gonimeter is scanned through an angular range. As the wavelength is known and the diffraction angle is measured, the several "d" spacings within the crystal lattice may be calculated. The relative intensities of the diffraction angles will vary according to the structure of the crystal. These data may be compared against a library of known crystal patterns for a rapid qualitative identification of the crystal. Furthermore, for mixtures of powdered samples, standard samples may be blended with the unknown sample for a quantitative analysis by measuring the ratio of diffraction intensities. Thus, x-ray diffraction serves to identify and quantify many substances significant in occupational health. (8)

7. The determination of free silica in atmospheric dust is of prime interest and is not confined to mining operations. Two to five milligrams of dust are collected on a plastic membrane filter. The sample and filter are ashed and the ash is slurried in water with an internal standard suspension of fluorite. After ultrasonic agitation, the product is filtered on a silver membrane filter. (0.45μm.) The dried filter is then inserted in an x-ray diffractometer and scanned to record the most intense lines for quartz at .334 nm., cristobalite at .405 nm., tridymite at .380 nm., and fluorite at .315 nm. The ratio of the intensities of the three components relative to that of fluorite is determined and compared with those for weighed and filtered standard mixtures. Free silica is reported as the sum of these three components. The method is sensitive to 5 micrograms of each component. This sensitivity is comparable to colorimetric and infrared methods. The inherent advantage of x-ray diffraction is its ability to distinguish the separate species of free silica and to detect other mineral species in the sample. (6, 9)

NOTES Times (elapsed) projected	LESSON OUTLINE
	6. Method of qualitative and quantitative analysis 7. Determination of free silica captured on filters by x-ray diffraction

8. Sample preparation of powders for x-ray diffraction usually consists of drying and blending to obtain a representative sample of uniform consistency. As indicated above, sample preparation for an x-ray diffraction spectrometer may be a thin film on a flat filter. For larger sample sizes the sample may be held loosely and level - full in an open tray or cup. Otherwise, it may be compressed into a pellet. (7)

9. In the Deboye-Scherrer powder camera technique, the sample is often held in thin walled (0.01 mm.) glass or plastic capillary tubing at the center of the camera. Careful preparation is required to obtain sharp images in the developed film. Although the powder camera method requires long exposure time, it has the advantages of giving useful structural data on samples of a few micrograms. When the inner diameter of the capillary is 0.1 to 0.3 mm. the sample must be carefully centered in the camera by using optical magnification. (7)

E. X-Ray Fluorescence

1. If a polcychromatic beam of x-ray energies is diffracted from a crystal of known 2 d spacing, the wavelengths in the beam may be calculated. This is based on Bragg's law. These wavelengths are unique to the elements in the sample from which the polychromatic beam originated. Also the wavelengths occur in order of the atomic number of the elements. (4)

2. X-ray analysis is widely applied to the analysis of:

   - Metals and alloys
   - Geochemical samples
   - Solutions for plating
   - Plating composition and thickness

NOTES Times (elapsed) projected	LESSON OUTLINE
	8. Sample preparation -- thin film or larger
	9. Deboye-Scherrer camera technique
(1:15) From one application of spectroscopy, x-ray diffraction, to another, x-ray fluorescence. 0:20	E. X-Ray Fluorescence
	1. X-ray diffracted from crystal of known 2 d spacing
Describe any personal experience with these types of analyses.	2. Applications: . Metals and alloys . Geochemical samples . Solutions for plating . Plating composition and thickness

- Catalysts
- Nuclear fuels and materials
- Petroleum products
- Plastics
- Industrial ceramics
- Glass and insulation material (4)

3. The advantages of x-ray fluorescence analysis are its direct application to the analysis of material surfaces and the highly precise determination of many elements, nondestructively, in the same sample. In the case of solutions and suspensions in process streams, x-ray fluorescence analysis can provide continuous analysis. Since x-ray fluorescence from a sample radiates in all directions, several fixed wavelength spectrometers may be arranged around a sample to provide simultaneous multi-element analysis. A disadvantage of x-ray fluorescence analysis is the dependency of the line intensity of an element in the total composition of the sample. (4)

4. The direct excitation of samples by electrons to produce characteristic x-rays is reserved for x-ray microprobe analysis, Auger analysis and electron spectroscopy techniques. The generation of fluorescent x-rays in a sample is most often accomplished by irradiation with an intense beam of "white" continuous radiation from an x-ray (Coolidge) tube. This is typically operated at 45 kilovolts with a filament current of 20 to 30 milliamperes. The sample is irradiated over an area of about 1.5 x 2.0 centimeters. The fluorescent radiation from this area is slit defined or collimated with Soller slits and diffracted by an analyzing crystal. The energies at separate wavelengths are detected by scintillation detectors, proportional counters or flow proportional counters. (4)

NOTES Times (elapsed) projected	LESSON OUTLINE
	• Catalysts • Nuclear fuels and materials • Petroleum products • Plastics • Industrial ceramics • Glass and insulation material 3. X-ray fluorescence--advantages and disadvantages 4. General method of analysis

TITLE	LESSON NUMBER

5. The x-ray fluorescence spectrometer is based on the same type of accurate angle measuring goniometer used in x-ray diffraction. Visual 9-5 shows the more common flat crystal spectrometer with collimators before and after the analyzing crystal. The resolution attained is a function of the crystal dispersion and the degree of collimation. As in all monochromators and polychromators, the gain in intensity derived from coarse collimation or wide slits must be balanced against the loss in resolution. Again, the spectrometer may be constructed in the vertical or horizontal plane. (4)

6. The intensity losses due to the flat crystal collimators are eliminated if the crystal is bent or bent and ground to produce the focussing properties shown in Visual 9-6. In this case, defining entrance and exit slits are used. Due to spherical aberrations, which are corrected by mechanical variations over a range of wavelengths, the curved crystal spectrometer is most often used in fixed spectrometer instruments where several elements are determined simultaneously. (4)

7. The two types of detectors used in x-ray analysis with crystal dispersion are proportional counters and scintallation counters. The proportional counter is a gas ionization device in which a photon causes an avalanche of ions to be discharged as a single pulse of current is detected at a wire anode. The anode is maintained at 700 to 1000 volts above ground. The energy of the photon is reflected in the intensity of the pulse. This pulse height can be isolated electronically so that the detector operates as either an energy or wavelength filter. When the proportional counter is used with thin windows and a purging flow of gas, it is suitable for "soft" x-rays and can be used over the range of 0.25 to 1 nanometers. (4)

8. The scintillation detector is a two-stage device. In this detector, a photon causes a phosphor to emit radiation which is detected in a closely coupled multiplying phototube. The scintillation detector can also be operated in the pulse height mode but is not as discriminating as the proportional counter. The scintillation detector has a generally uniform response for "hard" x-rays over the range of 0.03 to 0.25 nanometers. (4)

Times NOTES (elapsed) projected	LESSON OUTLINE
Visual 9-5	5. Flat crystal x-ray spectrometer
Visual 9-6	6. Curved crystal x-ray spectrometer
	7. Proportional counter as detector in x-ray analysis
	8. Scintillation detectors in x-ray analysis

9. Sample preparation techniques in x-ray fluorescence analysis are many and varied. Samples may be presented as flat ground surfaces, powders, briquets, solutions, fusions and thin layers. The thin film techniques are most suitable for trace analysis in occupational health. The mass absorption effect which is severe in x-ray analysis is diminished when a sample is highly diluted in a solution. A thin film can be considered as a spatial dilution. That is, as a film of sample becomes thinner the intensity of a line of an analyte is a direct linear proportion to the thickness of the analyte or to the area concentration, i.e., micrograms per square centimeter. (10)

10. Visual 9-7 illustrates the effect of two thicknesses, A and B, of an element and indicates an infinite or critical thickness for that element. If each element in a sample is presented at one half or less than its critical thickness, then interelement absorption and enhancement are negligible. (10)

11. Thin film samples are best supported on materials having low atomic number elements to reduce background reflections. These support materials include: filter paper, chromatographic paper, ion exchange resin impregnated paper, plastic films, graphite thin sheets, membrane filters. (10)

12. In one study using x-ray fluorescence, atmospheric aerosol samples were collected on a 0.2 μm cellulose membrane filters at a flow rate of 1.6 liters per minute per square centimeter. Ten elements were determined in the 0.6 to 2.2 milligrams collected on the filter, and the results were compared with neutron activation and atomic absorption analysis. The elements were Ca, Ti, Cr, Mn, Fe, Ni, Cu, Ln, Br, and Pb. The lowest value was Ni at 0.06 micrograms and the highest was Fe at 53 micrograms. (8)

13. This evaluation uses an x-ray fluorescence method in which crystals are not used to diffract and disperse x-rays. Semiconductor detectors have been developed which are much more energy selective than proportional counters. They are silicon or germanium devices which have a trace of lithium partially diffused or "drifted." These detectors operate as a selective filter as well as an intensity measurement detector. The resolution has improved in recent years so that the K_α and K_β lines of an element are clearly resolvable. A typical nondispersive x-ray fluorescence spectrometer is shown in Visual 9-8. (12)

NOTES Times (elapsed) projected	LESSON OUTLINE
	9. Sample preparation for x-ray fluorescence
Visual 9-7	10. Infinite thickness in thin film analysis
	11. Supports for thin film samples
	12. Study comparing x-ray fluorescence with AA
Visual 9-8	13. Evaluative uses of x-ray fluorescence

14. In a quantitative comparison of wavelength dispersion versus energy dispersion in the analysis of filtered air particulates, it was concluded that the resolution of energy dispersion was not adequate for the wide analytical range seen in air pollution samples. Thirteen elements were evaluated and the limits of detection with wavelength dispersion varied from 3 to 1000 nanograms per square centimeter. (13)

15. A sensitive determination of arsenic in urine is possible by a modification of the Gutzeit test. Arsenic is evolved as arsine (AsH_3) and trapped in a 13 mm. diameter paper disc impregnated with silver chloride. The analytical range is 0.1 to 25 micrograms arsenic using a standard x-ray spectrometer to measure the arsenic K_α line. The method is suitable for the determination of the normal levels of arsenic in human urine.

16. Many types of concentration methods have been applied in x-ray fluorescence analysis. These include: evaporation, electrolysis, coprecipitation, extraction, ion exchange. The application of these techniques with thin film sample presentation make x-ray fluorescence applicable to trace analysis for the industrial hygiene chemist. (15)

17. Additional sample preparations, used with or without these concentration techniques consist of aqueous solutions and glassy fusions in borax or lithium tetraborate. These preparations have the advantage of presenting a representative homogeneous sample to the x-ray excitation beam. In trace analysis for industrial hygiene, special precautions must be taken to prevent the loss of the analyte during the sample preparation and to prevent the contamination of the analyte from reagents apparatus and laboratory air. (10)

NOTES Times (elapsed) projected	LESSON OUTLINE
	14. Energy dispersion not adequate **15.** Determination of arsenic in urine **16.** Concentration methods **17.** Additional sample preparation

F. Optical Emission

1. Optical emission spectrocopy is applied to samples as solids, liquids and gases. Most of the more than 80 elements which can be determined have their principal wavelengths in the 200 to 800 nanometer spectral range. This range is extended to 180 to 900 nanometers in special cases. Optical emission can probably survey the total composition of a material more completely than any other method of analysis. Furthermore, the method has high specificity and detection capability with adequate precision and accuracy at minor and trace levels of concentration. (16)

2. The selection of an instrument with adequate resolution and dispersion is not just dependent upon the elements to be determined. Rather, it depends upon the total complexity of the spectra of the major and minor elements of the sample, coupled with the type of source employed. For instance, high atomic number refractory elements such as tungsten, molybdenum, vanadium, zirconium and uranium require reciprocal linear dispersions of 0.1 to 0.3 nm. per mm. at the focal plane. Samples of the alkalis and alkaline earth elements might only require a dispersion of 1 to 2 nm. per mm. For samples of limited size, (less than 0.5 mg.) small spectrographs are more suitable due to their greater light yield. (6)

3. Visual 9-9 shows a schematic of a concave grating spectrograph or spectrometer based upon the Rowland circle. It is the Paschen-Runge mounting, normally built with a 1, 1.5 or 2 meter radius of curvature. As a spectrograph, 35 mm. film is used in the camera. A 1.5 meter instrument with a 1200 groove per mm. grating has a dispersion of approximately 0.55 nm. per mm. (6)

NOTES Times (elapsed) projected	LESSON OUTLINE
(1:35) (Transition E. -F.) From the method of x-ray fluorescence to optical emission. 0:30	F. Optical Emission
	1. Capabilities and uses in general
Relate experience relevant to this issue.	2. Instrument selection depends upon major elements in sample and source
Visual 9-9	3. Paschen-Runge mounting spectograph

4. As a spectrometer, the camera is replaced by a number of fixed exit slits to select the wavelengths of the elements of interest. Behind each exit slit is an integrating multiplying phototube which measures the intensity of each line over a selected time period. Such a dedicated direct reading spectrometer can analyze a large number of samples with high precision. Therefore, these instruments are used in the metals industries or anywhere that routine quality control is required. The industrial hygiene chemist more often would require the use of a spectrograph, due to the variety of sample types and the variety of elements to be determined. (6)

5. A large grating spectrograph is shown in Visual 9-10. This is the Ebert-Fastie mount in which a plane grating receives a collimated beam from a portion of a spherical mirror. Another portion of the same mirror serves to focus the diffracted wavelengths at the focal plane. With a focal length of 3.4 meters and a 1200 groove per mm. grating, the dispersion is about 0.24 nm. per mm. Wavelength change is made by a rotation of the grating in the horizontal plane. Spectra are recorded on 2 or 3 photographic plates of 4 by 10 inch size, giving a wide wavelength range per exposure. Forty or more exposures are recorded on each plate. (6)

6. When a grating is rotated to a high angle, ($\sim 63^{\circ}$) and the incident and reflected angles are almost equal, a large number of overlapping orders will occur at the focal plane. These orders may be separated vertically with a cross dispersing prism. Such a grating is called an echelle prism, and it has coarse rulings of a special blaze to yield high efficiency over a small angle. An echelle spectrometer gives high resolution and dispension. Visual 9-11 is an echelle spectrometer which operates usually from the 40th through the 100th order. (3)

NOTES Times (elapsed) projected	LESSON OUTLINE
	4. Direct reading spectrometer
Visual 9-10	5. Ebert-Fastic mounting spectrograph
	6. Echelle spectrometers

7. The dispersion of the boron doublet is separated by 0.1 nm. in Visual 9-12. This is an echellogram in which the orders increase from the bottom to the top. (3)

8. The vaporization and excitation process in optical emission spectroscopy is the most critical part of the operation. Historically, the high voltage, high frequency spark is the most precise source. As the analytical gap breaks down, the spark produces a bombardment of the conducting sample with positive ions and high energy electrons. The spark is commonly used for the direct analysis of metal surfaces, but it is also useful for the direct analysis of solutions with porous cup electrodes, vacuum cup electrodes and rotating disc electrodes. These are shown in Visual 9-13. The rotating disc system has been shown generally to be the most reliable. In other solution residue methods, microliter amounts of a solution are evaporated on the surface of graphite, silver or copper electrodes, and then the residue is sparked. (16)

9. In an unusual and rapid technique with the high voltage spark, elements in airborne dust are determined with a direct reading spectrometer. The sample is collected on one inch diameter filter paper. The filter is folded in half and then rolled into a cylindrical form and placed in a hollow graphite sample electrode with an 1/8 inch bore. The filter and sample electrode are sparked directly for a period of thirty seconds as a push rod drives the rolled filter paper up into the analytical gap at a rate of one inch per minute. Al, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Ni, Si, Sn and Zn are determined in the range of 0.1 to 100 micrograms per electrode. The type of filter paper, (S + S, 589-1H) is chosen for its low blank level. Membrane type filters may be combined with a paper filter to provide a suitable sample. The high voltage spark may be used directly on the surface of graphite filters as well. Powder samples may be blended with graphite and compressed into pellets for a direct analysis with the high voltage spark. (17)

NOTES Times (elapsed) projected	LESSON OUTLINE
Visual 9-12	7. Eschellogram
Visual 9-13	8. Graphite electrodes for direct solution analysis.
	9. Direct reading spectrometer using hollow graphite electrodes

10. The low voltage direct current arc has been considered the most sensitive source for trace analysis by optical emission spectroscopy, although precision suffers. Typically, powders, residues and ashed products are placed in the crater of a supporting carbon or graphite electrode. Powdered graphite or spectroscopically pure buffers (i.e., lithium carbonate) may be blended or added to improve the stability of the arc. In most work, the cratered electrode is the anode, and the crater behaves as a microfurnace from which elements of the sample distill and otherwise evolve at various times during the burning period. (16)

11. Visual 9-14 shows a variety of electrode systems for direct current excitation. Electrode A (Scribner) was originally designed for the distillation of impurity elements from uranium oxide with the aid of an added "carrier" (i.e., gallium oxide). Electrode B is a typical deep crated electrode with a large counter electrode surface. The arc wanders drastically around electrode B and the discharge does not remain on the optical axis of the instrument. Electrode C has a "boiler cap" added for the preferential distillation of only the most volatile elements. Electrode D (Stallwood) is designed so that the walls of the electrode are consumed at about the same rate as the sample it contains. Also it is designed to be used with an annular stream of gas directed up around the electrode. This electrode D reduces selective volatilization. (16)

12. Many processes and solid state reactions, largely unsuspected, occur in the electrode with direct current excitation. For instance, the U_3O_8 in electrode A is rapidly reduced to UO_2 at the start of the burn with 10 amperes current. The UO_2 then begins to diffuse into the graphite wall as a uranium carbide. Also with tungstic oxide and graphite powder in electrode D, there is a total formation of tungsten carbide. As the wall erodes and exposes the molten carbide surface, a gradual surface oxidation occurs with some evolution of tungsten. The addition of a little halogenated hydrocarbon (i.e., Freon 12) to the annular gas stream immediately increases the evolution of tungsten, presumably as the halide. The temperature of the free-burning 10 ampere direct current arc has been reported to range from 5,000 to 6,200 degrees Kelvin. (16)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		10. Low voltage direct current analysis
Visual 9-14		11. Four graphite electrodes for direct current analysis
		12. Examples of unexpected reaction in direct current electrodes--with U_3O_8 and tungsten oxide

13. The determination of trace elements in atmospheric particulates is accomplished by the addition of HCl gas to an argon flow through a tubular electrode. In this case, the tubular porous cup electrode is both the sampler for atmospheric particulates as well as the anode in the direct current arc excitation. Al, Be, Cr, Co, Hg, Mg, Mn, Mo, Ni, Pb, Ti, V, W and Zn are determined with detection limits in the range of 0.1 to 5 nanograms. Almost half of these elements could be expected to form carbides during a direct current arcing procedure. This would have remained in the graphite sampler-electrode were it not for the addition of the HCl gas to the axial stream of argon during the spectrographic exposure period. (18)

14. During the past ten years a sensitive source has been developed for the analysis of solutions. First, a high temperature plasma of argon is generated by induction coupling to a high frequency generator. The temperature is in the range of 9,000 to 10,000 degrees Kelvin. Second, a solution is nebulized. Three to five percent of the solution, as a fine aerosol, is injected into the center of the plasma. The plasma is penetrated by the aerosol. The plasma forms an annular ring around the aerosol which is rapidly converted to free atoms of the sample. Due to the high temperature and the confinement of the analyte the excitation efficiency is high. Detection limits for the inductively coupled plasma range from 0.1 to 50 nanograms per millileter for most of the elements of the periodic table. The majority fall in the range of 1 to 10 ng./ml. By contrast, the majority of detection limits for atomic absorption spectroscopy fall in the range of 50 to 1000 ng./ml. This source has been applied to the determination of As, Co, Cr, Cu, Mn, Mo, Mi, Se and Sn in blood with detection limits at or below their normal concentration levels. It is applicable to many analyses in occupational health. (19)

NOTES Times (elapsed) projected	LESSON OUTLINE
	13. Determination of trace elements in atmospheric particulates 14. Inductively coupled plasma--process, application, sensitivity and comparison with AA

15. In emission spectroscopy spectra are recorded on photographic plates and films or by direct reading photoelectric detectors. Practices in the development of the photographic image, the measurement of the line intensity with a microphotometer, the calibration of the photographic plate, and the computing of spectrochemical data are well established and documented. The precision of the measurement of photographic intensities is generally in the range of 1 to 3% relative, while the precision of measurement of photoelectric intensities with corresponding integration periods fall in the range of 0.1 to 0.8% relative. The greatest precision error of an analytical technique is more often due to source variations and sample preparation. (16)

16. The principle of internal standardization for quantitative analysis originated with emission spectroscopy because of the many variables affecting the absolute line intensity. It is used where a direct comparison with a known standard does not yield the required precision or accuracy. With the internal standard, the concentration of the analyte is measured against the ratio of the analyte line intensity to the intensity of a line of another element. This element is present at a fixed concentration in all samples and standards. It may be a major element of the sample or one that has been deliberately added. Ideal correction by internal standardization is not always possible, but the lines of both analyte and internal standard should be equally affected by all variations in source, detection and measurement techniques. (16)

17. Optical emission procedures have been used to survey the elements in air particulates in high volume samples for many years. These techniques have most often been semiquantitative. However, with special filters and selected internal standards, more reliable data can be obtained with the wide scope of the method still retained. Air particulate samples are collected on silver membrane filters. The filter with air particulates is dissolved in nitric acid and cobalt and indium are added as internal standards. Graphite powder is added, and the silver is precipitated as Ag Cl. Particulates which do not dissolve are included in the whole mixture as it is

NOTES Times (elapsed) projected	LESSON OUTLINE
	15. Precision of emission spectroscopy
	16. Internal standardization in emission spectroscopy
	17. With filters and internal standards air particulate samples can be analyzed with emission spectroscopy

evaporated to dryness. Standards are made in the same manner. The mixture of Ag Cl, graphite, and particulate salts is then blended. One hundred milligrams is taken for spectrographic analysis. The 100 mg. is loaded and compacted into a Scribner electrode (Type A, Visual 9-13) and exposed for 60 seconds with a 10 ampere direct current arc. Al, Bi, Cd, Cr, Fe, Pb, Mn, Mo, Ni, Sn, V and Zn are determined with a precision of 5 to 18 percent relative standard deviation. (21)

18. The advantages of the method are that no ashing is used to destroy organic matter; complete dissolution of air particulates is not required; and a homogeneous blend of the entire sample is analyzed. Although the concentrations determined are greater than the blank levels in the filter, these filters must be carefully checked for impurities. This method can be used in industrial hygiene by varying the amount of sample taken and by changing the excitation to a controlled atmosphere D. C. Stallwood electrode. (Type D, Visual 9-13). (21)

19. A direct reading emission procedure for the determination of 13 trace metals in biological tissues has been described. A similar procedure is used for other biological samples. In this case, the sample is digested in nitric and perchloric acids. Then it is evaporated with hydrochloric acid and diluted to a volume proportional to the original sample weight. Of this volume, 0.1 ml. is evaporated in a graphite electrode with ammonium chloride. A 50 second exposure with a 10 amphere D. C. arc is used. This procedure is an example of the wide scope and range of emission analyses. (22)

NOTES Times (elapsed) projected	LESSON OUTLINE
	18. Advantages and caution of analyzing air particulates 19. Direct reading emission procedure with 13 trace metals

20. Optical emission is also used to determine specific and singular toxic metals in air, water, foods, and biological samples. Beryllium in air has been determined spectrographically for the past 25 years. The determination of arsenic and antimony is described in a procedure which combines the volatility of the hydrides of these elements with the emission sensitivity in a helium discharge. A one ml. volume of sample solution is injected into a 1% aqueous solution of sodium borohydride. The AsH_3 and SbH_3 gases which are immediately formed are swept by helium, bubbled into the reaction solution, through a drying agent into a flow-through electric discharge tube. The D. C. discharge occurs between metal electrodes across 900 volts with a power consumption of 37 watts. The ionized helium plasma efficiently excites the As and the Sb. A direct recording monochromator is used to integrate the evolved intensities of As at 228.8 nm. and Sb at 252.8 nm. One ng. of As and 0.5 ng. of Sb are detected in the 1 ml. volume of sample. These techniques show that emission spectroscopy is effective both for surveys and for quantitative analysis in the industrial hygiene field.

G. Self Test

1. Test instructions and review of questions are presented.

NOTES Times (elapsed) projected	LESSON OUTLINE
	20. Other examples of use of optical emission--Be, As, Sb
(2:05) Self Test 0:10	G. Self Test
(2:15)	1. Instruction and review

SELF TEST	Page 1 of 2
LESSON TITLE Introduction to Spectroscopy	LESSON NUMBER 9

1. Which of the following are correct statements? (Circle True or False)

[✓ T] F a. The application of spectroscopy to the quantitative chemical analysis of matter is dependent upon the physical aspects of the discrete absorption of energy by electrons and the subsequent emission of energy in discrete quanta.

[✓ T] F b. The wavelengths of the quanta, mentioned above, are the difference in the energy levels of the electrons.

2. Describe the essence of Bragg's Law:

see C.3 - C.5

SELF TEST	Page 2 of 2
LESSON TITLE Introduction to Spectroscopy	LESSON NUMBER 9

3. What is the difference between x-ray diffraction and x-ray fluorescence?

see Section D and E

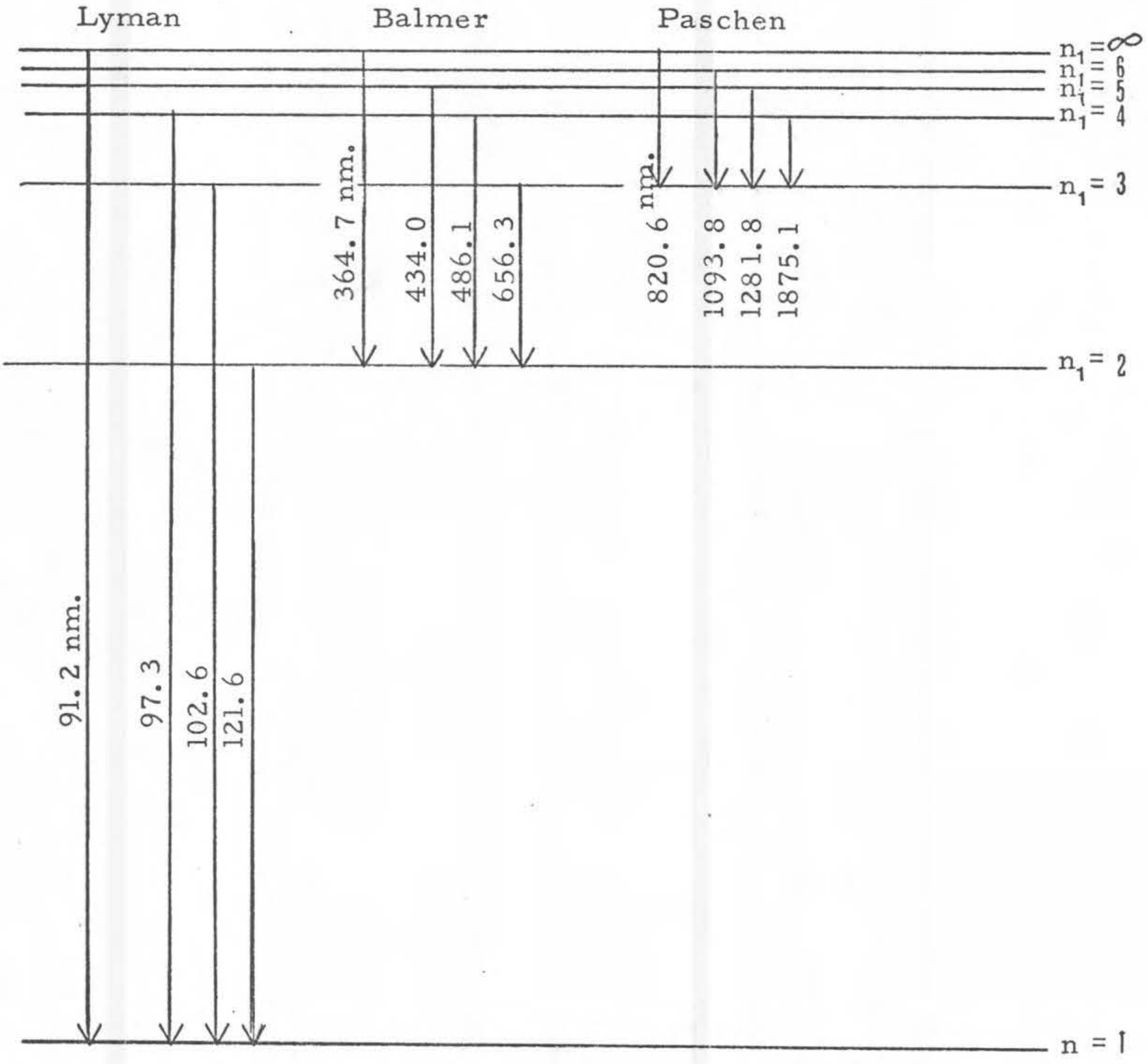
4. The principle of internal standardization for quantitative analysis originated with emission spectroscopy. With this, the concentration of the analyte is measured against the ratio of the analyte line intensity to the intensity of a line of another element.

VISUALS, TABLES, FIGURES AND EXHIBITS

ELEMENT	NM.	NM.	IONIZATION POTENTIAL (EV)
Cs	852.110	894.350	3.87
Rb	780.023	794.760	4.16
K	766.491	769.898	4.32
Na	588.995	589.592	5.12
Li	670.784		5.36

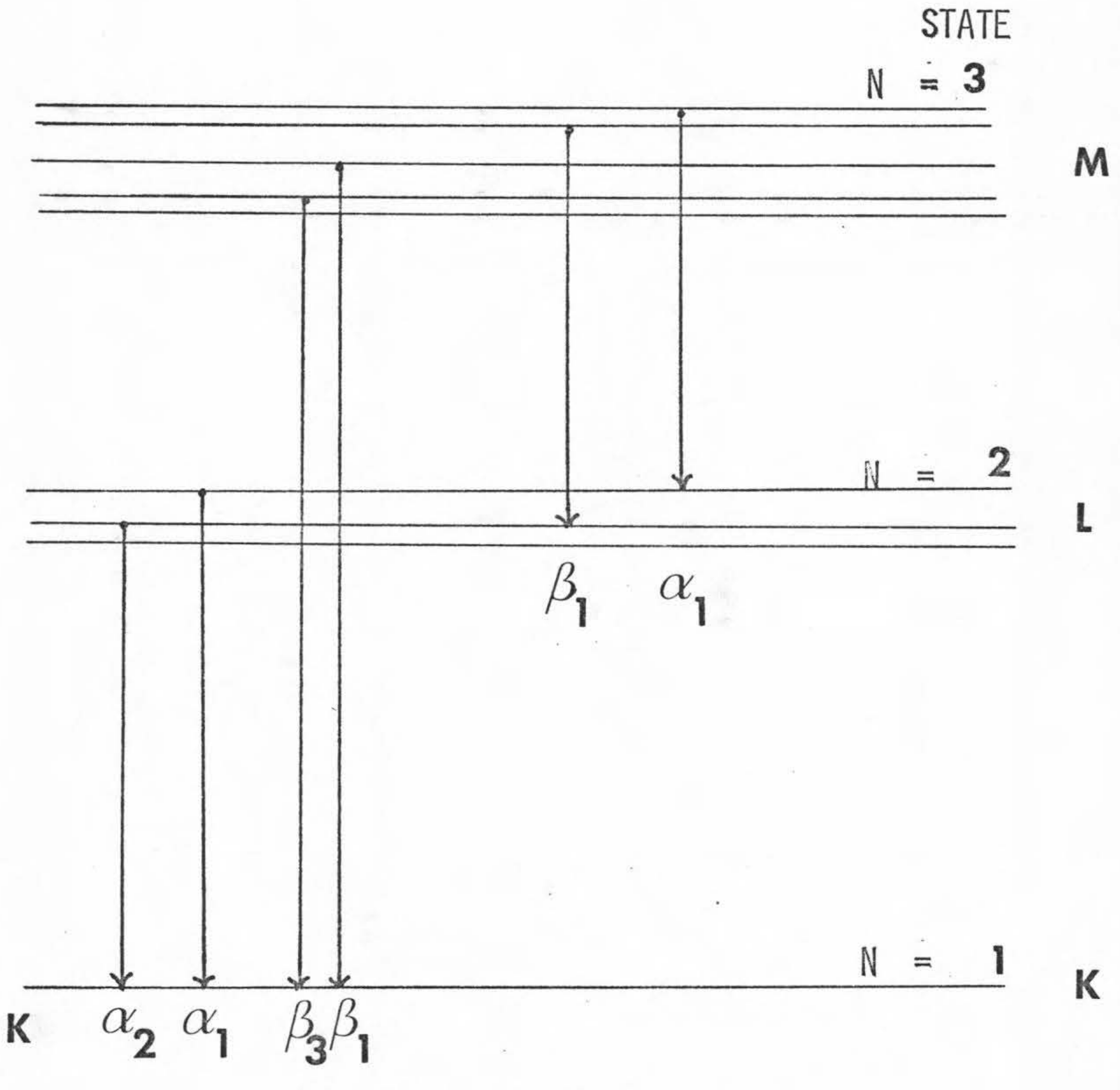
RESONANCE LINE WAVELENGTHS FOR THE ALKALI ELEMENTS

Visual 9 - 1



Energy Level Diagram of Hydrogen Atom

Exhibit 9 - 1



THE MOST INTENSE LINES OF THE
K AND L SPECTRA

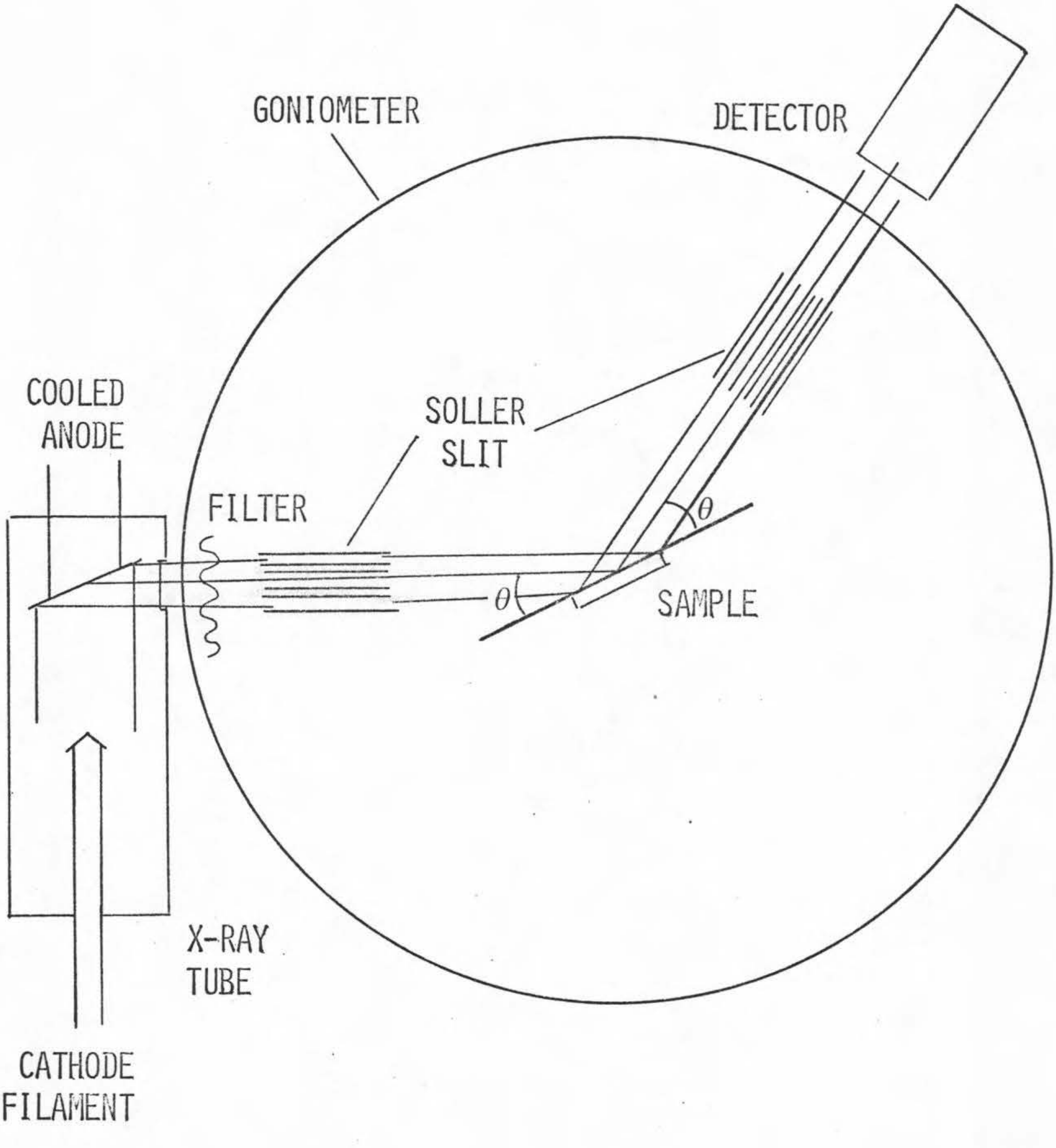
K, L AND M X-RAY ENERGY LEVEL DIAGRAM

Visual 9 - 2

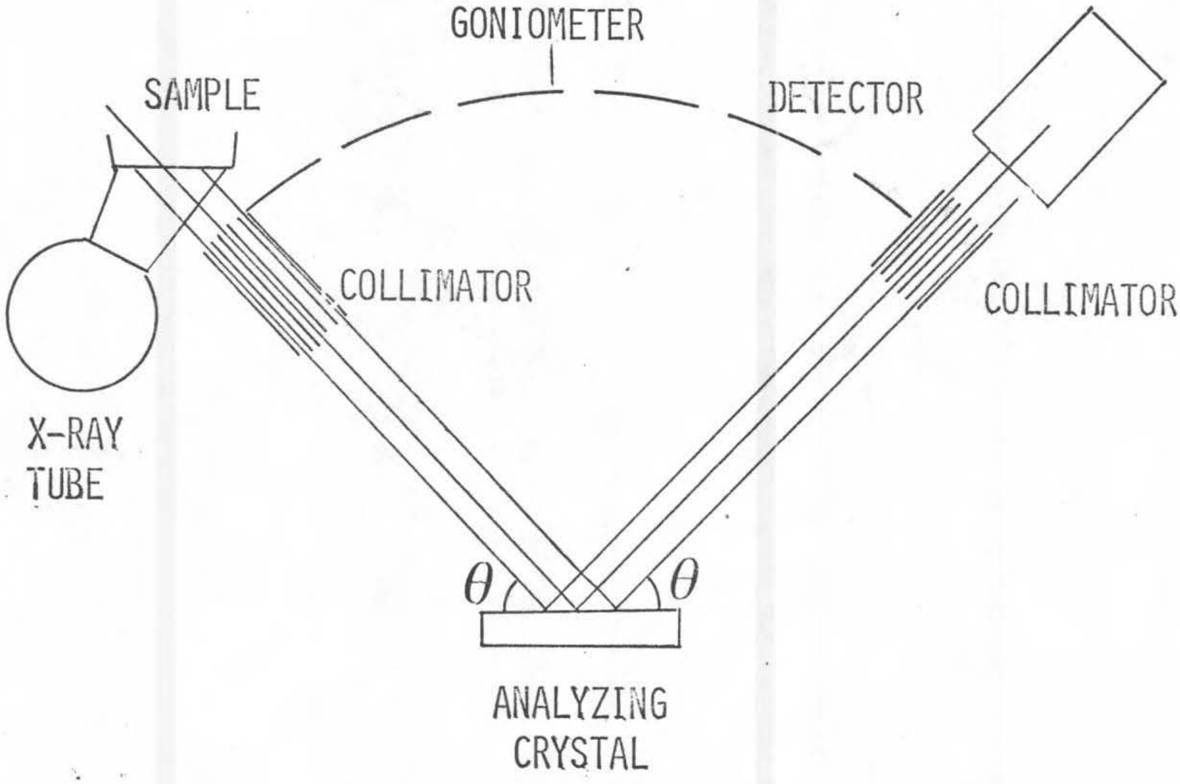
ELEMENT	TIME	λ	N	N λ
Cu	Kα	.1542	1	.1542
Zr	Kα	.0786	2	.1572
Zr	Kα	.0791	2	.1582
In	Kα	.0512	3	.1536
In	Kα	.0517	3	.1551

INTERFERENCES DUE TO OVERLAPPING ORDERS OF N

Visual 9 - 3

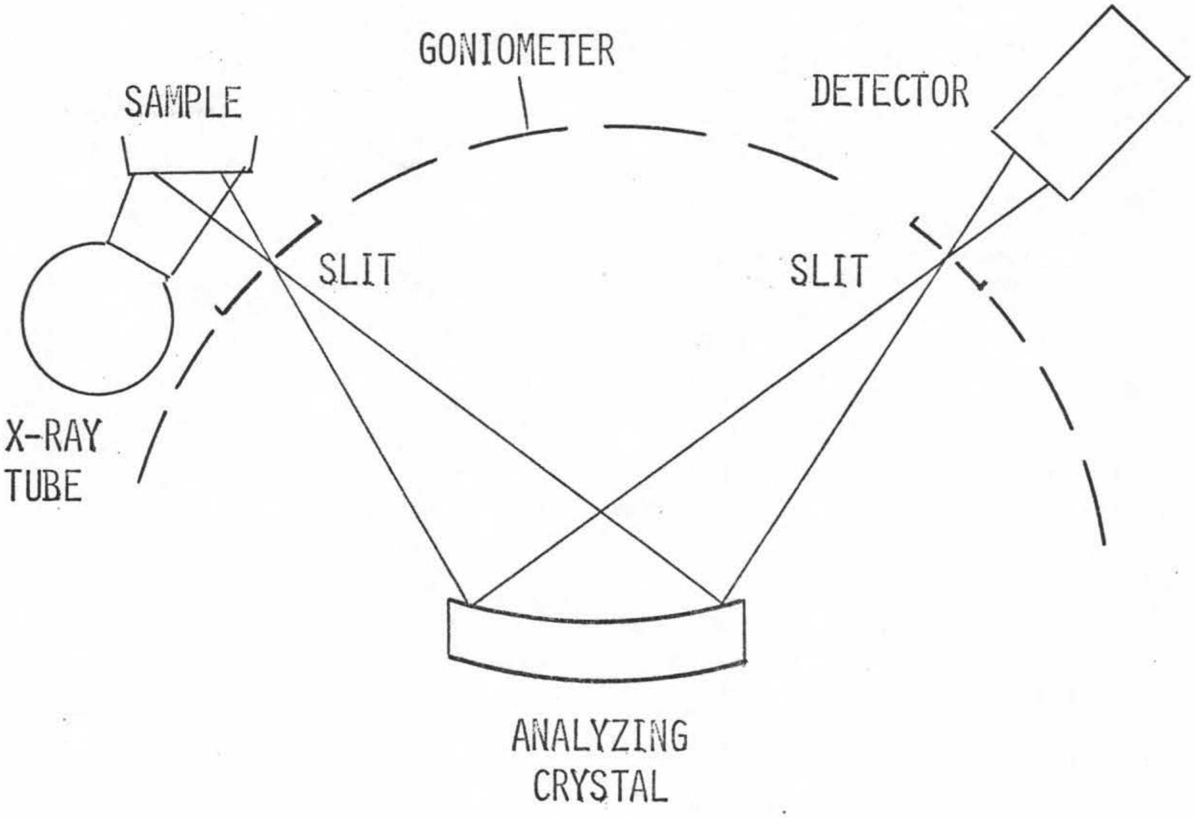


SCHEMATIC OF X-RAY DIFFRACTION SPECTROMETER



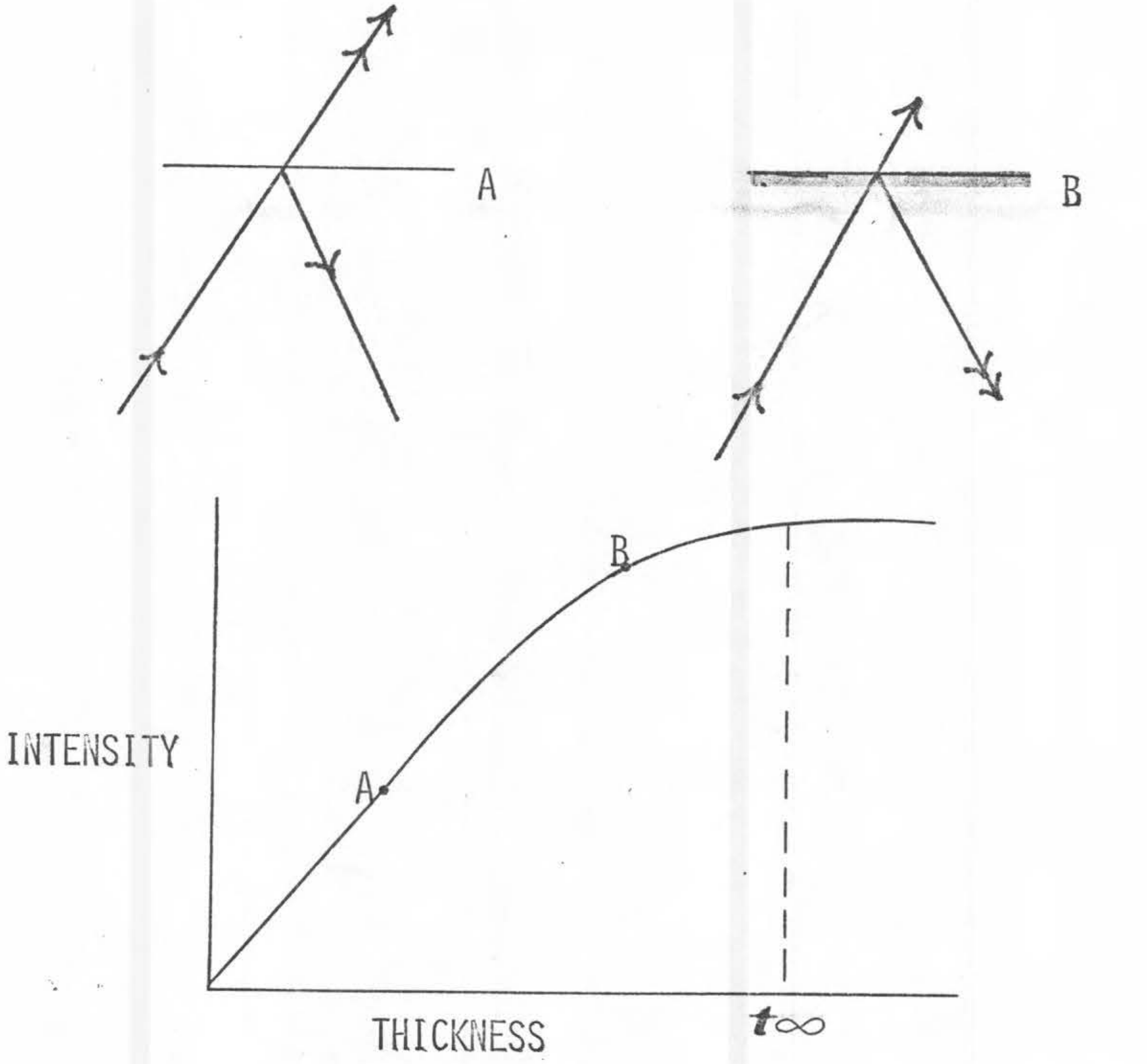
FLAT CRYSTAL X-RAY SPECTROMETER

Visual 9 - 5



CURVED CRYSTAL X-RAY SPECTROMETER

Visual 9 - 6



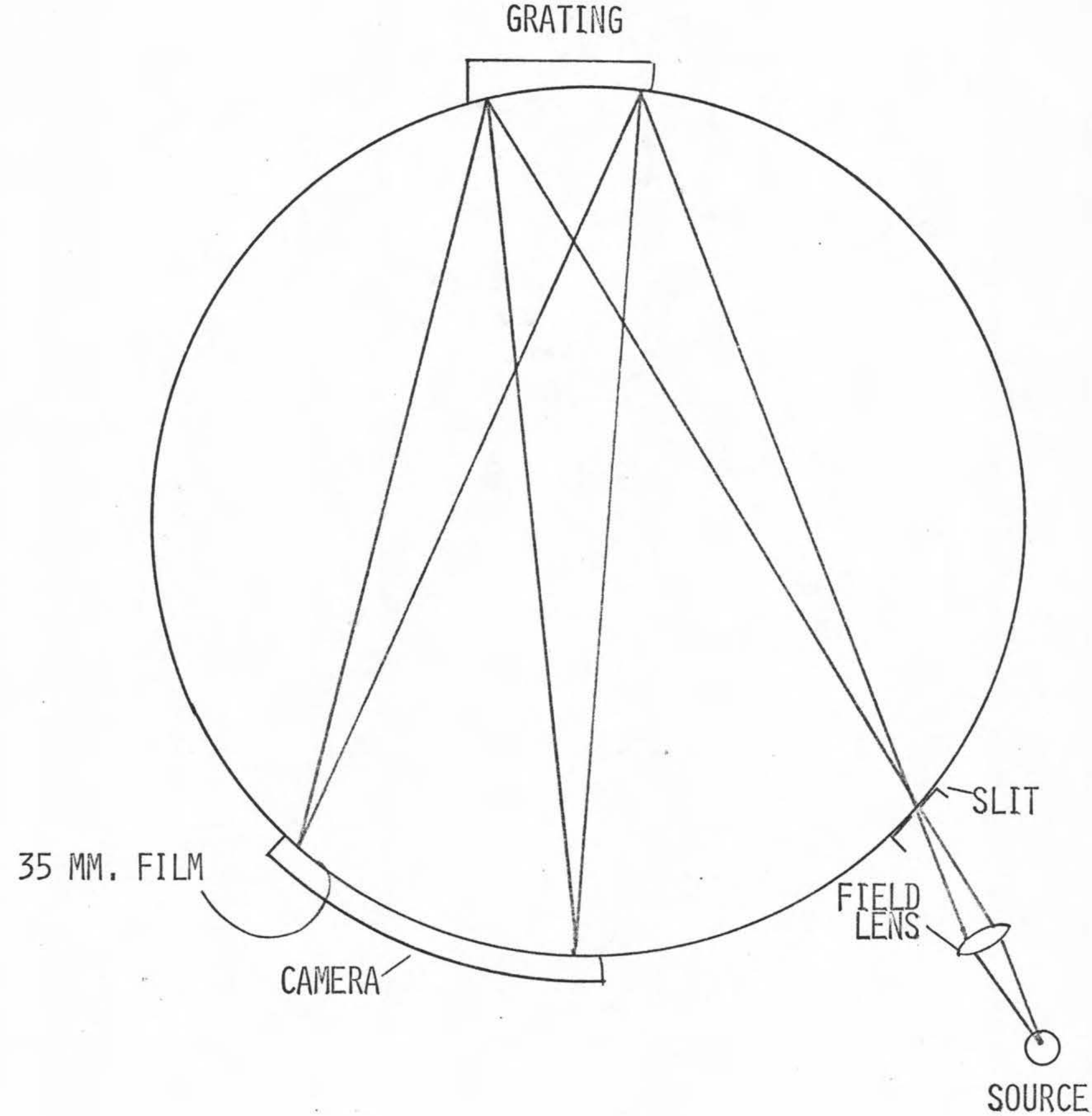
INFINITE THICKNESS IN THIN FILM ANALYSIS

Visual 9 - 7

A Non dispersive X-ray Fluorescence Spectrometer

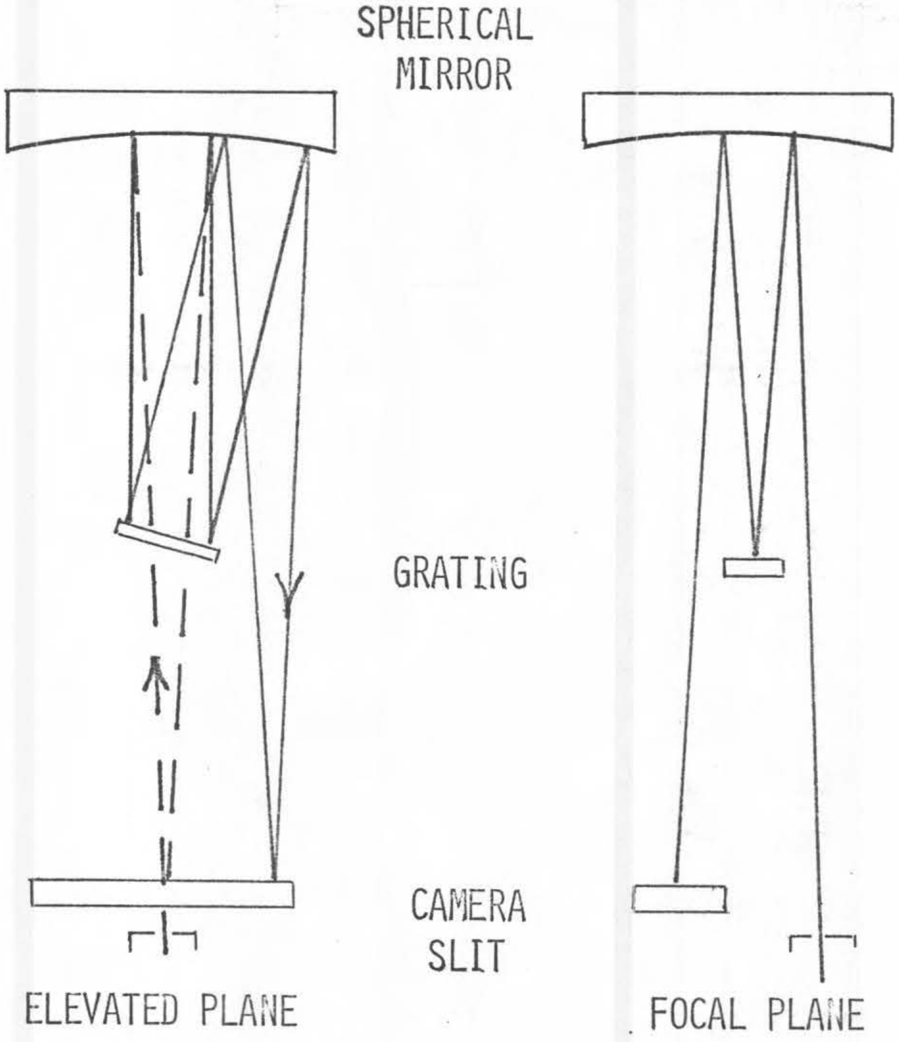
Illustration courtesy of Finnegan Corperation, Sunnyvale, Calif.

Visual 9 - 8



PASCHEN-RUNGE MOUNTING SPECTROGRAPH

Visual 9 - 9

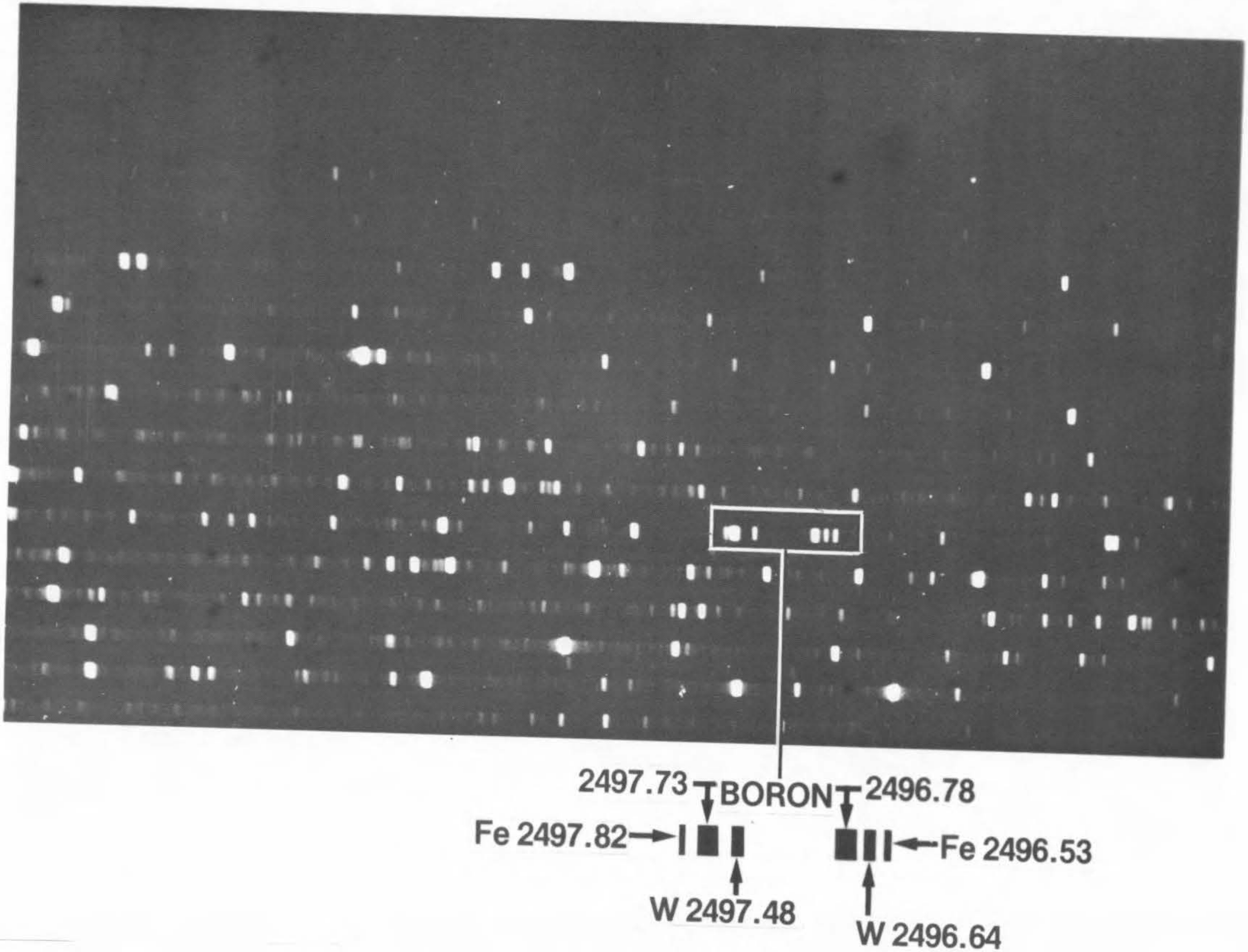


EBERT-FASTIE MOUNTING SPECTOGRAPH

Visual 9 - 10

Eschelle Spectrometer

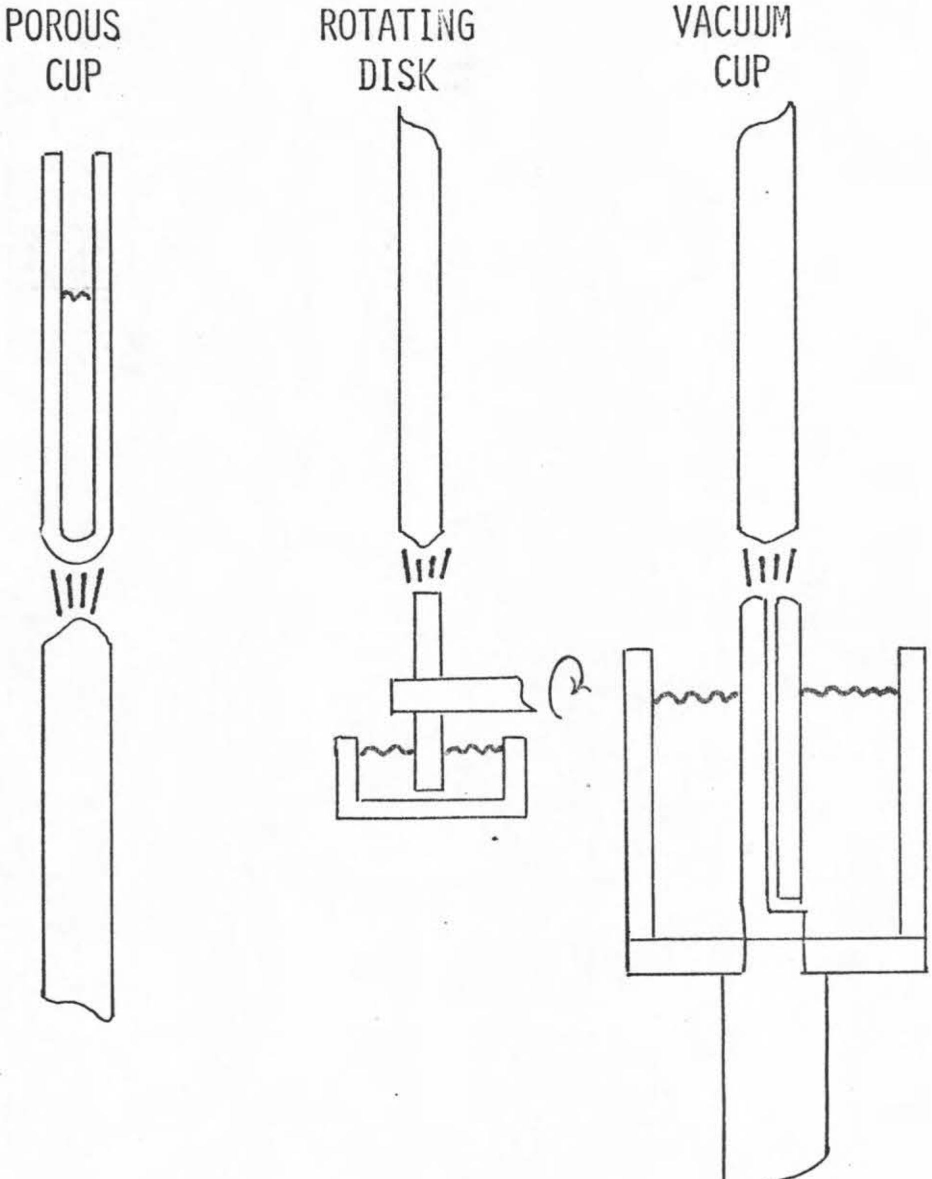
Illustration courtesy of Spectrametrics, Inc. Andover, Mass.
Visual 9 - 11



Eschellogram

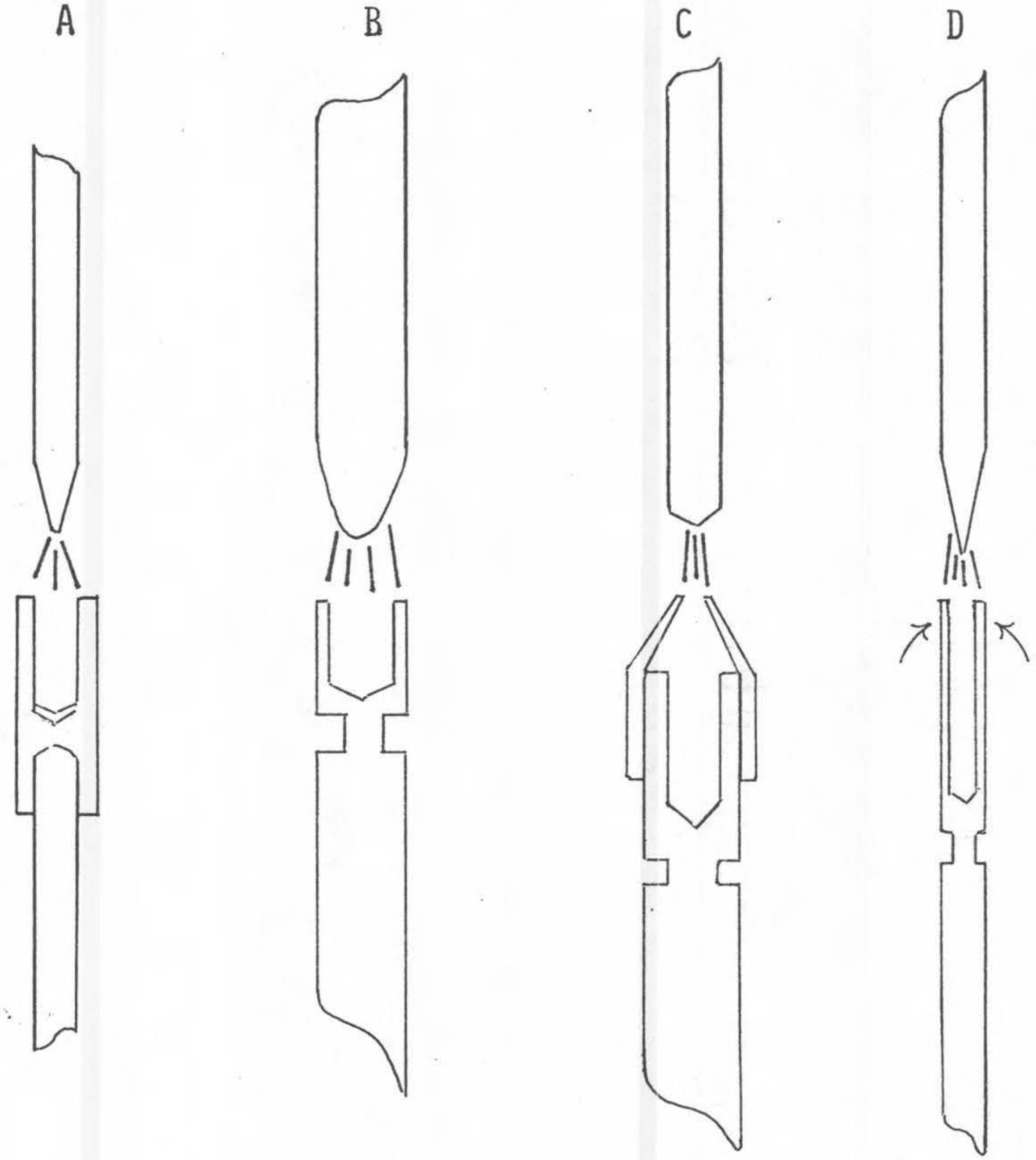
Illustration Courtesy of Spectrametrics, Inc.
Andover, Mass.

Visual 9 - 12



GRAPHITE ELECTRODES FOR DIRECT SOLUTION ANALYSIS

Visual 9 - 13



GRAPHITE ELECTRODES FOR DIRECT
CURRENT ANALYSIS

Visual 9 - 14