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INSTRUCTOR MANUAL
INDUSTRIAL HYGIENE CHEMISTRY COURSE

LESSON NUMBER 10

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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
Atomic Absorption Spectrometry	10	1:30

BEHAVIORAL OBJECTIVE

The student will be able to list the uses, conditions, sampling constraints, instrumentation and application for atomic absorption spectrometry.

SCOPE

Definitions and description
Light sources
Wavelength selection and measurement
The flame as the atomic vapor cell
Resistively heated atomic vapor cells
Samples and standards preparation
Applications in occupational health

VISUALS	EXHIBITS
10-1 through 10-13	None

EQUIPMENT

Overhead projector
35 mm projector
Screen
Blackboard
Chalk

REFERENCES

LESSON TITLE

AA Spectrometry

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3. Walsh, A. The Application of Atomic Absorption Spectra to Chemical Analysis, Spectrochimica Acta, 7, 108, (1955).

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8. Hieftje, G. M., Holder, B. E., Maddrex, A. S., and Lim, R. Selection of Source-Modulation Waveform for Improved Signal-to-Noise Ratio in Atomic Absorption Spectrometry, Analytical Chemistry, 45, 238, (1973).

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13. Sullivan, J. V., and Walsh, A. The Application of Resonance Lamps as Monochromators in Atomic Absorption Spectroscopy, Spectrochimica Acta, 22, 1843, (1966).

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15. Keliher, P. M., and Wohlers, C. C. High Resolution Atomic Absorption Spectrometry Using an Echelle Grating Monochromator, Analytical Chemistry, 46, 682, (1974).

16. American Society for Testing and Materials. Committee E-2, Practice for Atomic Absorption Spectrometry, Practice E-2, 1, ASTM, Philadelphia, Penn. (1971).

17. Kirkbright, G. F., Sargent, M., and West, T. S. The Determination of Arsenic and Selenium by Atomic Absorption Spectroscopy in a Nitrogen Separated Air-Acetylene Flame, Atomic Absorption Newsletter, 6, 34, (1969).

18. L'vov, B. V. The Analytical Use of Atomic Absorption Spectra, Spectrochimica Acta, 17, 761, (1961).

19. Woodriff, R. Atomization Chambers for Atomic Absorption Spectrochemical Analysis: A Review, Applied Spectroscopy, 28, 413, (1974).

20. Matousek, J. P., and Brodie, K. G. Direct Determination of Lead Airborne Particulates by Nonflame Atomic Absorption, Analytical Chemistry, 45, 1606, (1973).

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28. Manning, D. C. Non-Flame Methods for Mercury Determination by Atomic Absorption: A Review, Atomic Absorption Newsletter, 9, 97, (1970).

29. Scaringelli, F. P., Puzak, J. C., Bennett, B. I., and Denny, R. L. Determination of Total Mercury in Air by Charcoal Absorption and Ultra-Violet Spectrophotometry, Analytical Chemistry, 46, 278, (1974).

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31. Orheim, R. M., and Boves, H. H. Atomic Absorption Determination of Nanogram Quantities of Arsenic in Biological Media, Analytical Chemistry, 46, 921, (1974).

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32. Fernandez, F. J. Atomic Absorption Determination of Gaseous Hydrides Utilizing Sodium Borohydride Reduction, Atomic Absorption Newsletter, 12, 93, (1973).

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34. Hauser, T. R., Hinners, T. A., and Kent, J. L. Atomic Absorption Determination of Cadmium and Lead in Whole Blood by a Reagent-Free Method, Analytical Chemistry, 44, 1819, (1972).

ADDITIONAL READINGS

LESSON TITLE

AA and AF Spectrometry

1. Christian, G. D., and Feldman, F. J. Atomic Absorption Spectroscopy, Wiley-Interscience, New York (1970).

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TITLE	LESSON NUMBER
AA Spectrometry	10

A. Definition and Description

1. In optical emission spectrometry, the atoms of an analyte are dissociated to free neutral atoms in the ground state. They are then raised to an excited state of neutral or ionized atoms by means of flames, ionized plasmas, arcs or sparks. When the electrons return to the original energy levels by numerous discrete paths, an emission spectrum is observed; its complexity is subject to the atomic structure. In atomic absorption (AA) and atomic fluorescence (AF) spectrometry, the processes of atom dissociation to the neutral ground state and of electron energy level changes are separated. First, the neutral atom is formed in a spatially isolated "cell" by means of a flame, plasma discharge or thermionic furnace. Then a separate source of known emission characteristics irradiates the atomic cell volume. At this point, the neutral atoms absorb only the ground state transitions from the known source. This decrease in intensity is measured as atomic absorption. At the same time, those analyte atoms, which have absorbed the ground state or resonance frequencies, emit that resonance frequency in all directions. The emitted intensity is measured as atomic fluorescence. Other atomic fluorescence lines may appear as the electrons return to the ground state by other transitions, but only the resonance lines are of analytical interest. Simultaneous atomic absorption and fluorescence at resonance frequencies is shown in Visual 10-1. The atomic absorption technique is similar in operation to molecular spectrophotometry, and the atomic fluorescence technique is similar in operation to molecular spectrofluorometry. (1, 2)

2. The history of atomic absorption may be dated from the dark lines observed in the solar spectrum in 1817 by Fraunhofer and confirmed in 1859 by Kirchoff as absorption spectra. But the present application in analytical spectrochemistry did not start until 1955 when Walsh and also Alkemade and Milatz published the initial two papers describing the basic approach which has not changed to the present time. Five years elapsed before there was any general acceptance of the method, although flame emission techniques had been in common use for some time. This is surprising in light of the following characteristics of AA:

   - It is highly specific because the width of the absorbed resonance line is very narrow, in the order of 0.001 to 0.005 nanometers.

   - With a flame atomizer, it is as simple to operate it as a flame emission spectrometer.

NOTES	Times (elapsed) projected	LESSON OUTLINE
	(---) 0:15	A. Definition and Description
Visual 10-1		1. Atomic to excited state, return to ground state, AA and AF
		2. History -- Fraunhofer, Kirchoff
		. Highly specific -- absorbed resonance line narrow
		. Flame atomizer

- It yields high sensitivity in relation to comparative techniques.

- Most metals and some metalloids can be measured.

- There are interferences which can be overcome when they are defined. (3, 4)

3. The basic components of an atomic absorption instrument (Visual 10-2) include:

   - One component is a narrow line atomic emission source of high stability. This is operated in a pulsed mode or with its light output mechanically interrupted. The sealed hollow cathode was used originally and is presently the most common source.

   - An atomic vapor cell capable of producing ground state atoms of the desired analyte is used. A chemical flame was used originally and is still the most common vapor cell.

   - A monochromator capable of isolating the source resonance line is another component. A quartz monochromator with a Littrow mount was used originally. Grating monochromators of about the same resolution and dispersion are presently used.

   - A phototube detector with an alternating current amplifier coupled to a read out device which indicates percent absorption or absorbance is also used. (3)

4. As the source is pulsed in an AA instrument, the alternating current detector responds to the emission source, not to the direct current flame intensity. The monochromator is between the cell and the detector so that excessive emission from the cell does not saturate the detector. (3)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		. Relative high sensitivity . Metals measured . Interference overcome
Visual 10-2		3. Basic components of AA instruments: . Emission source of high stability . Atomic vapor cell . Monochromator . Phototube detector
		4. Operation of AA instrument

5. Since flame emission and atomic absorption are complementary methods for the analysis of solutions, it is useful to compare their detection limits. In one study, 68 elements were compared on the same instrument with the same atomizer system and with the same data evaluation technique. The high temperature N_2O - C_2H_2 flame was used for all the emission work and likewise the optimum burner was selected for the atomic absorption measurement of each element. Of the 68 elements, 27 were equal in detectability, 15 were more sensitive by emission and 26 were more sensitive by absorption. Of these 26 by absorption 17 were more sensitive by a factor of 10 or more. On the other hand, flame emission has fewer chemical interferences than some of the lower temperature AA flames; and there is a greater dynamic range of analysis by emission. The 26 elements with superior detection limits have resonance wavelengths less than 300 nanometers. Therefore, AA and AF instruments should be designed to enhance the transmission efficiency in the region of 250 to 200 nanometers and even below. (5)

6. Since there are presently no commercial instruments specifically for atomic fluorescence and few applications, atomic fluorescence is discussed here only as it relates to atomic absorption and to the development of sources. A basic atomic fluorescence instrument is illustrated in Visual 10-3. (6)

B. Light Sources in Atomic Absorption

1. The basis for atomic absorption is the relation seen in Visual 10-4.

2. This corresponds to Beer's law in absorption spectrophotometry. For this relation to hold true, the half width of the emission line from the source must be less than the half width of the absorption line as shown in Visual 10-5. The half width of the lines in emission and absorption is chiefly a function of the Doppler effect given by:

$$\Delta\lambda_D = 7.162 \times 10^{-7} \left(\frac{T}{M}\right)^{1/2} \lambda_o$$

where: $\Delta\lambda_D$ = the Doppler half width
T = temperature, ^oK
M = atomic weight of the element
λ_o = resonance wavelength, A^o

For example, the Doppler half width of the sodium D line at 589.0 nm., in a 3000^{o}K flame is 0.0048 nm. Clearly the temperature is the main influence for any element; and, therefore, a stable low temperature source is required. (1)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		5. Comparison of flame emission and AA detection limits -- of 68 elements, 27 equal, 26 pro AA, 15 pro emission
AF is of interest as a potential future source of analysis. Visual 10-3		6. AF - no commercial instruments
(Transition A. -B.) From a general description to detail about light sources.	(0:15)	B. Light Sources in Atomic Absorption
	0:10	1. Basic relationship for AA
Visual 10-4		
Visual 10-5		2. Half width of emission lines, Doppler effect
Write equation on the blackboard.		

3. The hollow cathode has been used as a spectroscopic light source since first described by Paschen in 1916. Essentially it is a low pressure discharge device operating at a few mm. pressure of mercury in the presence of an inert noble gas. The discharge is termed a glow discharge, and the hollow cathode is a special case of the glow discharge. At a certain pressure, related to the inner diameter of the cavity of the cathode, the negative portion of the glow discharge is confined within the cavity. With proper design there is no evidence of other discharges in the source. The negative glow discharge in the crater contains positive ions which bombard the inner walls of the cathode and sputter cathode atoms into the discharge. These atoms are then excited by collisions with ions and electrons, and they strongly emit the resource lines. Because the temperature is low the Doppler half width is small. Most spectroscopists used the hollow cathode in the demountable form with a purifier gas recirculation system. Other people have made hollow cathode sources in a sealed form. Hollow cathode lamps are now available for more than 70 elements, and demountable hollow cathode sources are available for special purposes. (7)

4. The sealed hollow cathode cannot be operated at currents greater than 20 or 30 milliamperes for very long because either the cathode material melts or the noble gas is absorbed in sputtered material and the pressure changes to an inoperable level. Also, an excessive amount of ground state atoms are formed in front of the cathode crater, and atomic absorption occurs before the resonance energy ever leaves the source. Therefore hollow cathode sources for AA should be operated at the minimum current to obtain a full scale range of the instrument without excessive gain on the detector system. For many elements the Doppler half width of the emitted line will increase with increased current and, thereby, decrease the sensitivity of the determination. When the hollow cathode is pulsed by the power supply for system modulation, the source should not be completely turned off. That is, the direct current pulse should operate above a minimum constant direct current. (8)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		3. Hollow cathode -- description and operation, demountable, application 4. Sealed hollow cathode not operated above 20-30 Ma

5. Although the sealed hollow cathode is used almost universally for atomic absorption, electrodeless discharge lamps (EDL) are used as sources in the determination of some elements, notably As, Se, Cd and Te. These lamps, which are also used in atomic fluorescence, consist of a sealed quartz tube containing a volatile halide, or other compound, of the element of interest with a few mm. pressure of an inert gas. Microwave radiation is coupled to the lamp for excitation. These lamps are often not as stable as sealed hollow cathodes. Also, atomic absorption or self reversal within the quartz tube occurs in many cases and diminishes the peak intensity of the resonance wavelengths. (9)

6. For the AA determination of sulfur, iodine, arsenic, selenium and mercury, a demountable hollow cathode source has been used in preference to EDL sources due to excessive self reversal of the resonance lines in the EDL's. Sulfur and iodine had sensitivities of 1.0 and 14 microgram per ml. respectively. These determinations are unusual in AA since the resonance lines at 180.7 nm. for S and at 183.0 nm. for I were used. These wavelengths are in a region where the oxygen in the air absorbs them Therefore the instrument, the optional path and the burner of the instrument all had to be flushed and shielded with oxygen free gas. Sensitivity in AA is defined as that concentration which absorbes 1% of the intensity of the resonance wavelength. (10)

C. Wavelength Selection and Measurement

1. The monochromater in AA serves to pass the resonance line to the detector with the greatest possible transmission of energy, without including any other line intensities that have not been absorbed by the analyte in the cell. For example, the absorption line of cobalt at 240.725 nm. is close to the nonabsorbing ion line at 240.767 nm. A monochromator with a dispersion of 3.3 nm./mm. requires slit widths of about 20 μm to isolate the absorption line. Fortunately the cobalt hollow cathode can tolerate a high current without loss of sensitivity. Then the detector amplification system need not be used at high gain to give excessive noise. With this narrow slit, the analytical working curve will remain more nearly linear. Since most monochromators are accurate only to 0.1 nm., the absorbing line would have to be carefully selected. Thus, the reduction of the monochromator band-pass and the source lamp current both contribute to the performance of the analysis.

NOTES	Times (elapsed) projected	LESSON OUTLINE
		5. Electrodeless discharge lamps, disadvantage
		6. Demountable hollow cathode vs. EDL
	(0:25)	C. Wavelength Selection and Measurement
(Transition B. - C.) From a description of light source to the selection of appropriate wavelengths.	0:15	1. Monochromator passes resonance line to detector

2. The Ebert and the Czerny-Turner grating monochromators shown in Visual 10-6 are the most commonly used designs in AA.

3. AA instruments are produced in single beam and double beam configurations. Visual 10-7 shows a double beam instrument in which the emission source beam is split to pass through the vapor cell as well as around it for reference, thus compensating for source fluctuations. No compensation is made in this case for cell or analyte variations. Most AA instruments now use synchromized AC amplifiers which are locked in phase with the current pulsing of the emission source or the mechanical chopping. (1)

4. In addition to atomic absorption, some of the incident source energy may be absorbed by molecular species in the flame or other vapor cell. Such background absorption may be corrected by alternately passing a continuum source through the optical paths of the instrument. Automatic background correction is included as a dual beam in many instruments. The continuum source is generally a hydrogen or deuternun discharge lamp, which is also pulsed or chopped out of phase with the line emission source. (Visual 10-8) (11)

5. The principle of internal standardization as practiced in emission spectrocopy has been used in atomic absorption as well, and some instruments are made with two monochromators. If two line sources are alternately pulsed through the straight dual beam configurations or through the split double beam configuration, the absorbed or reference beams may be measured in two monochromators at two separate wavelengths. Also, the absorption and the emission intensities of the same analyte in the vapor cell may be measured. (12)

6. As depicted in Visual 10-9, sources A and B are pulsed in phase with the dual mechanical chopper. Each monochromator may then see two sequented pulses of the sources, first through the vapor cell and then through the reference path. This type of instrument has been shown to drastically reduce variables in the vapor cell. The application of an internal standard will usually increase the precision of a determination two to four fold. (12)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 10-6		2. Shows common types of monochromators
Visual 10-7		3. Single and double beam AA instruments
Visual 10-8		4. Background absorption, automatic background correction
		5. Internal standardization with two monochromators
Visual 10-9		6. Schematic of dual channel atomic spectrometer

7. Atomic fluorescence of the resonance wavelengths suggests that a confined atomic vapor cell can act as a resonance detector and thus eliminate the monochromator. As shown in Visual 10-10, the beam from a pulsed single element hollow cathode is absorbed at the resonance wavelengths by the analyte in the flame cell. This then irradiates a cloud of neutral atoms in the resonance detector. The multiplying phototube then responds only to the pulsed resonance wavelengths as in AF analysis. This then is an instrument dedicated to the AA analysis of one element. Several have been used in industry for the determination of Ca, Mg, Cu and Ni. However, the limited life of the resonance detector due to gas clean-up has prevented further application of this simple system. (13)

8. In a further extension of this principle, the hollow cathode source is operated in the direct current mode. The resonance detector is replaced by a mechanical chopper and a concave mirror. Then, when the chopper is open, the absorbed beam is returned through the flame cell and focused near the aperture of the hollow cathode. Now the ground state atoms which have escaped from the hollow cathode behave as a resonance detector. The chopped fluorescence signal is observed at a 90^{o} angle through a second window on the sealed hollow cathode source. The determination of Cu and Ni have been demonstrated. It has been estimated that at least 22 elements have resonance spectra suitable for this type of dedicated instrumentation. (14)

9. If the resolution and dispersion of the monochromator were sufficiently high so that the band-pass for a given slit width was less than the absorption width, then any source could be used, even a broad continuum source. Echelle monochromators, which feature a high angle grating with a special groove shape, are operated at high orders, typically from the 40th through the 100th order. A direct comparison between a 150 watt xenon (continuum) lamp and hollow cathode lamps was made using an echelle monochromator. The results for 32 lines of various elements indicate that the continuum source was less sensitive by a factor of two to five. Such a system, illustrated in Visual 10-11, could be used for routine analysis with a continuum source. (15)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Visual 10-10		7. Resonance detecting AA instrument
		8. Use of hollow cathode and chopper
Visual 10-11		9. Comparison of hollow cathode with broad continuum source

D. The Flame as the Atomic Vapor Cell in AA

1. Flame atomization has been used for 20 years because it is very convenient, fast in operation, and is applicable to a wide range of analyses. On the other hand, the flame is not the best way to produce the ground state. (3)

2. Analytically, two types of flames can be used -- the diffusion flame and the premixed flame. In a diffusion flame, the fuel is mixed with the oxidant external to the burner. Nebulization of a sample solution takes place at the entrance to the reaction zone. This has been called a total consumption burner. Although all the solution passes through the reaction zone, studies have shown that much of the sample is not dissociated. Total consumption burners are no longer in general use in AA and AF. (1)

3. The premixed burner consists of a chamber to mix the fuel and oxidant with the nebulized solution. The mixed gases and fine aerosol of solution ignite and burn as they leave the exit port, which is formed as a long narrow slot. Usually only 5 to 10 percent of the solution passes into the flame. The remainder is rejected. The length and width of the slot is based upon the burning velocity of the mixed gases and the desired length of the cell path. The three common gas mixtures which are used in premixed or laminar burners are: H_2 - Ar, entrained air; C_2H_2 - Air; C_2H_2 - N_2O. (16)

4. A greater degree of nebulization can be attained by the addition of an organic solvent to the solution. Also, a higher population of the fine aerosol particles which enter the flame have been made by ultrasonic action. Ultrasonic nebulization with subsequent evaporation of the aerosol solvent has yielded the greatest sensitivities for the laminar or slot burner. (16)

5. The nitrous oxide - acetylene flame and the air-acetylene flame are suitable for most elements determined by AA. The low temperature hydrogen-argon entrained air flame is reserved for elements such as tin and arsenic. The temperature of the N_2C - C_2H_2 flame approaches 3000° K and this flame is used with a slight excess of fuel to prevent the formation of refractory metal oxides in the flame:

$$ALO \rightleftharpoons AL^{o} + (O)$$

NOTES	Times (elapsed) projected	LESSON OUTLINE
(Transition C.-D.) From a discussion of wavelength selection to flame atomization.	(0:40) 0:10	D. The Flame as the Atomic Vapor Cell 1. Flame -- advantages, disadvantages 2. Diffusion and premixed flames 3. Burner description -- parts, combustion, gas mixtures 4. More nebulization by adding organic solvants and ultrasonic action 5. Nitrous oxide -- acetylene flame; hydrogen argon; N_2O - C_2H_2

However, at this high temperature much of the population of the ground state refractories exists as an excited species or as ions. Elements, such as La or Ba are added to the sample as in an ionization suppressant (spectroscopic buffer); therefore, more of the refractory metal is available for atomic absorption or fluorescence. There are many chemical effects documented, and some may be due to the excess oxygen from the air which diffuses into the reaction zone. A separated or shielded flame has been formed to reduce the flame background and improve the direct determination of arsenic and selenium. (17)

6. The process in the premixed flame may be summarized as:

   - Nebulization produces aerosols of the ions in the host solvent. Only 6 to 10% accompany the mixed gases into the flame.

   - Evaporation in the flame produces a dried salt particle.

   - Fusion, melting and evaporation of the salt forms a gaseous product.

   - The gas dissociates into atoms in the ground state. The process in the flame has an efficiency of <1 to 10%.

   - Thus, 1% of the original sample, or less, passes through the optical axis of the instrument, in the form of ground state atoms, at a rate of about 10 meters per second. (9)

E. Resistively Heated Atomic Vapor Cells

1. A heated graphite tubular furnace for the production of ground state atoms in atomic absorption can be modified by using a D.C. arc to rapidly evolve a dried sample residue from an electrode. This electrode is positioned midway in a 4 cm. long graphite tube which is maintained at 2000 to 3000°C in an argon atmosphere. The internal volume of the atomizer is 0.2 ml. For 12 elements it has been reported that sensitivities of 10^{-9} to 10^{-11} grams of analyte are possible. Several instrument manufacturers have now produced inert gas heated furnaces modeled after this early work with cell volumes ranging from 12 ml. to 0.07 ml. (18, 19)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		6. Process in premixed flame: • Nebulization produces ion in host solvent • Evaporation produces dried salt • Formation of gas • Gas dissociates to ground state • 1% passes through optics
(0:50) (Transition D.-E.) From a description of flames to resistively heated atomic vapor cells. 0:10 Cover this topic fairly briefly.		E. Resistively Heated Atomic Vapor Cells 1. Inert gas heated furnaces

2. In most measurements in AA with the flame cell, the sample is introduced as a solution; an equilibrium is established; and the degree of absorption or fluorescence is measured directly from a meter or recorder. The signal is integrated for a period of time to improve precision. The sensitivity is expressed in weight of the analyte per volume of solution, i.e. μg./ml. In the resistively heated cells, the solution is introduced to a surface, dried and charred if organic material is present. Then the temperature is increased to vaporize and atomize the sample residue. The heated inert gas in the cell assists in the dissociation of the analyte to neutral ground state atoms. These atoms then diffuse from the cell, and the signal peak height is measured. Greater precision and accuracy is attained by integrating the entire signal above background during the evolution period, since the matrix of the sample and the heating will affect the time of the maximum signal and the neutral atom population at that time. The matrix of the sample and its dissociated products may also produce non-atomic absorption within the band-pass of the instrument. This may be corrected for by the dynamic background compensation from a continuum source. The sensitivity for these cells is often expressed in weight of the analyte which may range from 10^{-8} to 10^{-13} grams. (19)

3. In the furnaces initially developed, the main body of the graphite tube is maintained at operating temperature and the sample residue, which is on a separate surface, is introduced at the center of the tube. In later adaptations, samples of 1 to 50 microliters are evaporated in graphite tubes, graphite rod filaments and refractory metal filaments, such as tantalum. After preliminary heating, the entire tube or filament is heated to evolve the analyte and produce the ground state atoms. The operation is faster, and the residence time in the optical path is shorter than in the long tube furnaces. This places more stringent requirements on the response of the detector-measurement system, on the integrity of the surface of the tube or filament and on the consistency of the matrix of the sample. For instance, in the case of the carbon rod or small graphite tube, if the matrix is composed of elements which readily form carbides, there is a diffusion of the carbide into the surface, with successive additions of samples. This drastically changes the response of the device. Frequent checks with standards are required during the analysis. Tubes of about 9 mm. length are frequently coated with pyrolytic graphite to prevent this diffusion. In some instances these small graphite tubes have been used as direct air samplers, with or without the insertion of a membrane filter. Sensitivity for particulate lead is 2×10^{-11} grams, which means that less than 1 liter samples of air are required to yield adequate sensitivities for the work room environment. (20)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		2. Measurement with flame cell vs. resistively heated cells 3. Use of shorted tube filaments -- advantages and examples

4. Industrial hygiene chemists do not normally need the sensitivities attained with the resistively heated cells to work within the Threshold Limit Values. However, these cells may be used to advantage when the sample is small and rapid spot checks of contaminant levels are required. Overall, the conventional flame cell is simpler in operation, has greater precision and is less subject to casual and unsuspected contamination. (21)

5. Continuing development of atomic vapor cells can be expected to produce an equilibrium of the analyte arising from the introduction of a dry aerosol of the sample, similar to recent developments in emission spectroscopy. A graphite furnace for continuous introduction of the sample has been used. A controlled amount of methane in the inert gas allows the pyrolytic protective coating to be grown and replaced in situ. The relative standard deviation varied from 2 to 4 percent, which is a considerable improvement over the 7 to 15 percent experienced with several types of furnaces with flash vaporization of residues. Carbide forming elements such as Al and Ti remained in the wall creating a high memory effect unless removed between samples by the leaching action of CCl_4 vapor. (22)

F. Samples and Standards Preparation

1. Atomic absorption techniques use solution samples almost exclusively. The preparation of a sample may require considerably more time than the instrumental analysis. However, the ability to prepare standards in solution is a great advantage. The advantage of working with solutions which are generally dilute is sometimes offset by the contamination from filters, reagents and laboratory ware and also by the losses of the analyte by absorption on the walls of laboratory ware. The integrity of standards when stored as dilute solutions must be constantly checked to maintain accuracy. (23)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		4. Usually flame cell sensitive enough in industrial hygiene applications
		5. Continual introduction of sample
Now procedures for the use of AA equipment after discussing the equipment itself.	(1:00) 0:10	F. Samples and Standards Preparation
		1. Use and advantages of preparing solution as standards

2. Chemical interferences are the major variables in AA and AF analyses. The effect of aluminum, silicon, titanium and phosphate on the determination of alkaline-earth metals has been studied extensively and a number of chelating, releasing and buffering agents have been described. In many cases, a solvent extraction procedure is the preferred way to separate an analyte or a group of them from the matrix prior to the determination. For example, ammonium pyrrolidine dithiocarbamate (APDC) is often used to complex with Fe, Ni, Co, Mn, Cu, Zn, Bi, Pb, Cd, Tl and Sb in acids, urine, water and blood samples. Once the complex is formed, it is then extracted with methyl isobutyl ketone as the solvent. The extract is then directly aspirated into the flame cell. Isolation from the matrix is the chief advantage, although there may be some concentration effected during the extraction procedure. An additional enhancement of the signal results from the use of the solvent in the flame cell. Other methods of separation include ion exchange, electrolysis, co-precipitation, liquid chromotography and gas chromotography. (23)

3. Dilute aqueous samples can often be standardized against single element or multi-element aqueous standards. Often it is sufficient to use the same type and concentration of acid in samples and standards. Where the matrix is variable and unknown due to the sample source, the method of standard additions is practiced, as illustrated in Visual 10-12. First, the approximated concentration of the analyte is determined from direct comparison with a standard. Then the sample is diluted by a known amount, so that its concentration is within a linear portion of the analytical curve. Next, incremental amounts of the analyte standard are added to separate portions of the sample in the range of 0.5 to 4 times the estimated amount in the sample. All portions, including the sample without an addition are diluted to the same volume; and the absorbance is measured for each, or the net intensity in the case of AF. The concentration of the unknown sample is then obtained by extrapolating the data to zero absorbance. These portions may be used as standards against other samples of the same concentration range and matrix. (24)

NOTES	Times (elapsed) projected	LESSON OUTLINE
Describe relevant personal experience.		2. Chemical interferences -- use of solvent extraction and example
Visual 10-12		3. Dilute aqueous samples standardized against standards -- procedure

4. The oxidation of organic and biological samples is often the most critical step in the preparation of a sample for analysis. The common practices are:

   - Dry ashing
   - Dry ashing with addition
   - Low temperature ashing
   - Wet oxidation
   - Pressurized wet oxidation

5. Dry ashing is always suspect without confirming data on recoveries. Dry ashing with sulfuric and nitric acid and magnesium acetate is useful when the ash content is low. Acid digestion with nitric and perchloric acids is the mixture which gives the most rapid and complete recovery. Only mercury loss is significant and this is specially controlled with a reflux condenser. (25)

6. Low temperature ashing is a technique where thermal energy is not applied directly. The sample is contained in a low pressure chamber fed with a small flow of oxygen. The oxygen is dissociated into nascent oxygen with radiofrequency energy. The nascent oxygen attacks the sample surface. The temperature at the surface is a function of the material and the oxidation rate. Quartz vessels are used, since metals inhibit the action. The method is 2 to 5 times slower than dry ashing at 500°C but recoveries are much greater. Losses of the most volatile elements, Hg, Se and As do occur.

7. Visual 10-13 shows a low temperature asher.

NOTES	Times (elapsed) projected	LESSON OUTLINE
		4. Oxidation of sample: . Dry ashing . Dry ashing with addition . Low temperature ashing . Wet oxidation . Pressurized wet oxidation 5. Dry ashing 6. Low temperature ashing
Visual 10-13		7. Low temperature asher

8. In wet oxidation, with nitric acid alone, the elements are recovered when the digestion takes place in a sealed pressure vessel of stainless steel lined with Teflon. One half to one hour digestion periods at 150°C are used. (25) (26)

G. Application in Occupational Health

1. Twelve atomic absorption methods are detailed in the 1974 NIOSH/U.S. HEW Manual of Analytical Methods. One of these is a general procedure for the determination of 25 elements in blood, urine and air particulates collected on membrane filters. The samples are digested with nitric acid and ashed in Pyrex at 400°C, with the exception of those samples containing arsenic where the maximum temperature is 140°C. The residue is then taken up in nitric or hydrochloric acid and diluted typically to 10 ml. at a pH of 1. Though not stated, a blank should be run with each group of samples. This direct aspiration method is adequate for air samples, but in biological samples it is not sensitive enough for Be, Cd, Ca, Cr, Mn, Mo, Ni and Sn. Since 1.5 to 2 ml. are used for each determination, a limited number of determinations can be made on each sample. As previously indicated, the flame emission with the N_2O - C_2H_2 burner would yield better or equal sensitivity for 13 of these elements. The versatility of atomic absorption is demonstrated by this procedure. (27)

2. The determination of mercury has had a long analytical history for heavy metals in occupational health. It is unique in atomic absorption and fluorescence, because it is the only metal which yields sufficient ground state atoms at normal room temperature. This allows for sensitive detections. It was determined by atomic absorption in vapor detectors long before the development of atomic absorption in the flame.

3. Mercury has been separated for analysis by many means including:

   - Exchange with CdS
   - Electrolytic reduction

NOTES	Times (elapsed) projected	LESSON OUTLINE
		8. Wet oxidation
(1:10) From the preparation of standards for application of AA to its application.	0:10	G. Applications in Occupational Health
Go through these examples to give the students a feel for practical applications.		1. General procedure for 25 elements
		2. Mercury determination very sensitive
		3. Mercury separated: . Exchange with CdS . Electrolytic reduction

- Amalgamation on metal powders and foils
- Dithizone extraction
- Reduction with stannous chloride

4. Mercury may then be evolved from each of these preparations by heating in a flow of gas. The absorption of the mercury vapor is then measured in a 10 to 20 centimeter cell with a sensitivity of 0.2 to 1.0 nanograms on the absorption line at 253.7 nm. There are more sensitive lines, but they are in the vacuum ultraviolet region below 200 nm. Mercury determinations suffer interference from water vapor, combustion products, organic vapors and water, which give a positive bias to the data. These can be eliminated by trapping the interferences and allowing the mercury to pass through to the vapor cell or by retaining the mercury on gold or silver wire and foil. The gold or silver is subsequently heated to release the mercury for measruement. Interferences may also be eliminated by dynamic background correction. Due to the large demand for analyses, several dedicated laboratory instruments have been produced for the determination of mercury. Most of these do not provide dynamic background correction. (28)

5. Mercury exists in air and other media as condensed particles, in a metallo-organic compound such as methyl mercury, or in the free vapor state. Total mercury in air may be determined by collecting in an activated charcoal trap. Mercury and its compounds are then thermally released from the charcoal, passed through a reactor to convert all forms to mercury vapor and then amalgamated on silver. Again the mercury is subsequently evolved for measurement. The collection efficiency is 97% at flow rates up to 1 liter per minute, for 430 nanograms of mercury in a 15. cm. length of activated charcoal. (29) (30)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		. Amalgamation . Dithizone extraction . Reduction with stannous chloride 4. Mercury measured at 253.7 nm., interferences 5. Mercury particles in air, collected in charcoal trap, amalgamated on silver, measured

6. Particulate mercury, mercury vapor and organic mercury vapor may be separately analyzed in air by a three component sampling system composed of:

- A membrane filter for particulates
- A Carbosieve B absorbent in a tube for organic mercury vapor
- A silver coated support in a tube for free mercury vapor

7. The particulate mercury on the filter is digested with nitric acid in a Teflon decomposition vessel and released with stannous chloride reduction for analysis. The organic mercury vapor and the mercury vapor are thermally released separately for analysis. All mercury releases are retained on gold particles mixed with sea sand for the removal of interferences. Two absorption cells of different length are used in tandem to obtain a wider range of analysis. The first cell covers the range of 1 to 200 ng. and the second 10 to 2500 ng. (30)

8. Although arsenic can be determined directly in an air acetylene flame, more sensitive determination is made by reducing the arsenic in solution to the trivalent state and then releasing arsine gas (AsH_3). The arsine is collected and then passed to an argon-hydrogen flame with entrained air. Measurement of the absorption at 193.7 nm. yields a sensitivity of 50 nanograms. By using a non-flame cell of Vycor at 700°C the sensitivity is reduced to 5 nanograms. The collection can be made in an expanding rubber balloon or by trapping the arsine at liquid nitrogen temperature. Zinc metal is added to the acid solution to form the hydride of arsenic and the zinc may often contain as much arsenic as is being determined. A more consistent release agent with little discernable blank is sodium borohydride ($NaBH_4$). When the $NaBH_4$ is introduced as a 5% solution in alkaline water, the release of AsH_3 is rapid and consistent so that the arsenic can be immediately sent to the absorption cell. The use of $NaBH_4$ also allows the determination of Bi, Sb, Se, Te and Ge by the hydride evolution method. (31 (32)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		6. Particulate mercury and organic vapor system: . Membrane filter . Carbosieve B absorbent . Silver support 7. Process for system 8. Arsenic to trivalent state, measured at 193.7 nm.

9. An example of the AA analysis with the resistively heated cell is the determination of chromium in biological samples. The heated graphite cell is a modified Massman tube, programmed to dry a 10 to 50 µl. sample at 100°C, dry ash for 30 seconds at 1400°C and atomization at 2400°C. The sensitivity is 44 picograms (10^{-12} grams). With a scale expansion of 20 fold, the detection limit is 2 picograms. Chromium was determined in blood plasma in the range of 3 to 7 nanograms per milliliter with a relative standard deviation of 1.3%. Although the analysis can be performed directly on the blood plasma with a longer ashing cycle, the acid digestion of the sample reduced the analysis time and increased the useful life of the graphite tube from 40 to 150 sequential firings. (33)

10. Cadmium and lead are determined in whole blood by atomic absorption with a tantalum boat-flame technique. The sample is first vacuum dried and then ashed in a low temperature radio frequency asher. The residue in the tantalum boat is then inserted into an air-acetylene flame directly under the optical axis. Using 500 microliter samples the detection limits are 0.2 ng. per ml. for cadmium and 2 ng. per ml. for lead. Automatic background correction is used. The flame-boat vaporization technique is simple, direct and does not use contaminating reagents, as in the digestion-extraction methods. The flame-boat vaporization method is limited to the volatile elements which will evolve from the metal surface as heated in the flame. The evolution is also slower than from the resistively heated devices. The technique is a useful compromise between the solution fed flame and the residue resistively heated devices.

H. Self Test

1. Test instructions and review of questions are presented.

NOTES	Times (elapsed) projected	LESSON OUTLINE
		9. Chromium in biological samples with resistively heated cells
		10. Chromium and lead in blood with tantalum boat-flame technique
	(1:20)	
Self Test	0:10	H. Self Test
		1. Instructions and review
	(1:30)	

LESSON TITLE	LESSON NUMBER
AA Spectrometry	10

1. Circle those of the following characteristics as true or false in regard to AA spectrometry:

   T (F) Few metals can be measured by AA spectrometry.

   (T) F It is simple to operate an AA instrument as a flame emission spectrometer when it has a flame atomizer.

   (T) F AA spectrometry yield high sensitivity in relation to comparative techniques.

2. What gas mixture is not used in premized burners?

   a. C_2H_2 - N_2O

   b. C_2H_2 - Air

   c. H_2 - Air, entrained air

   (d.) H_2 - N_2O

3. What advantage does the resistively heated cell have for the industrial hygiene chemist?

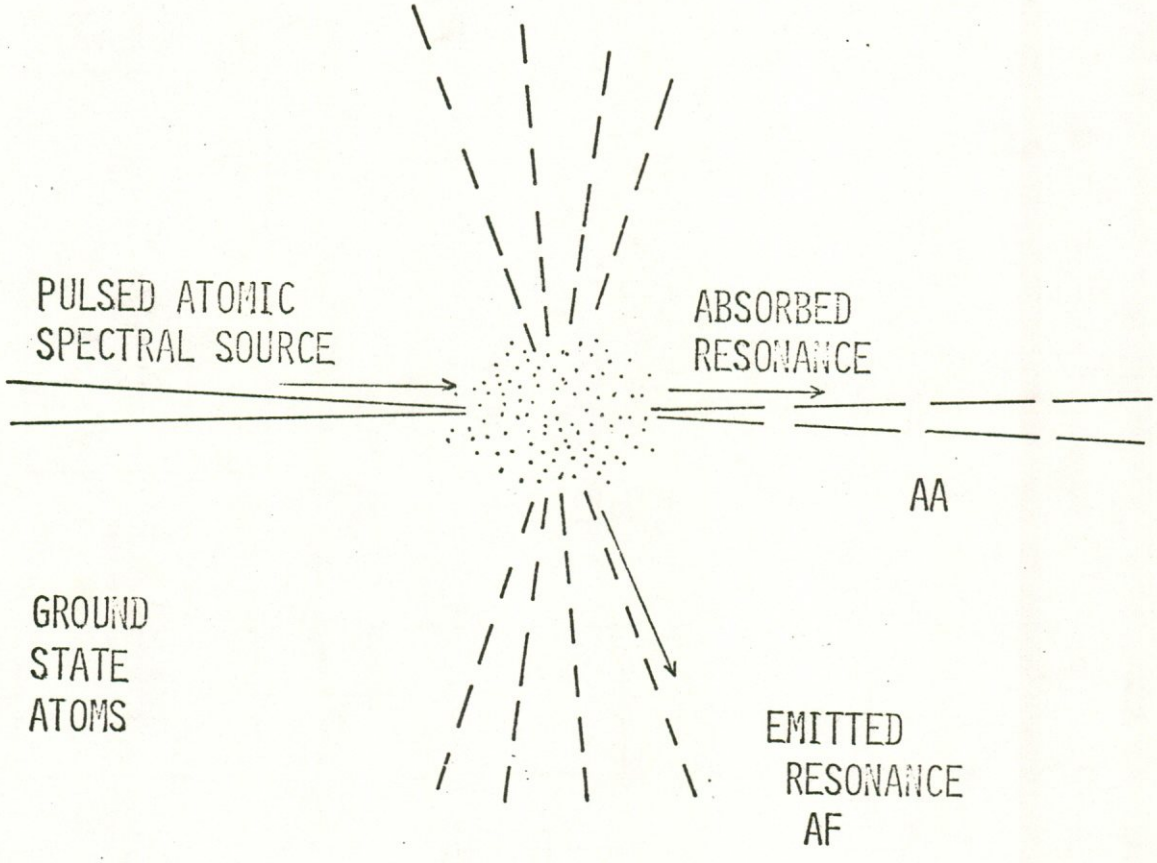
   (See E. 4)

4. Fill in the blanks:

   A solvent extraction procedure is the preferred way to separate an analyte or a group of them from the matrix prior to the determination.

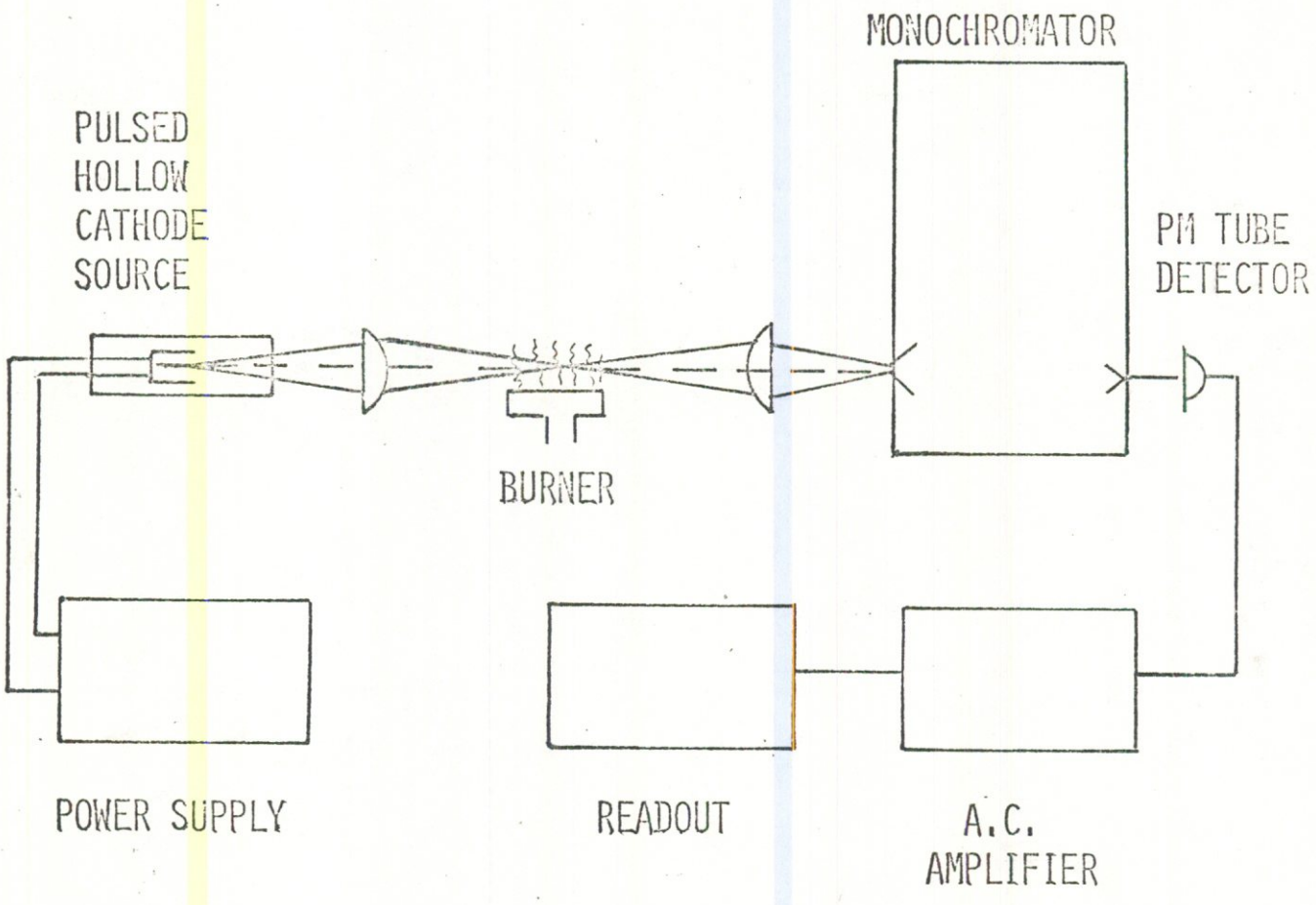
   Low temperature ashing is a technique where thermal energy is not applied directly for the oxidation of organic and biological samples.

VISUALS, TABLES, FIGURES AND EXHIBITS



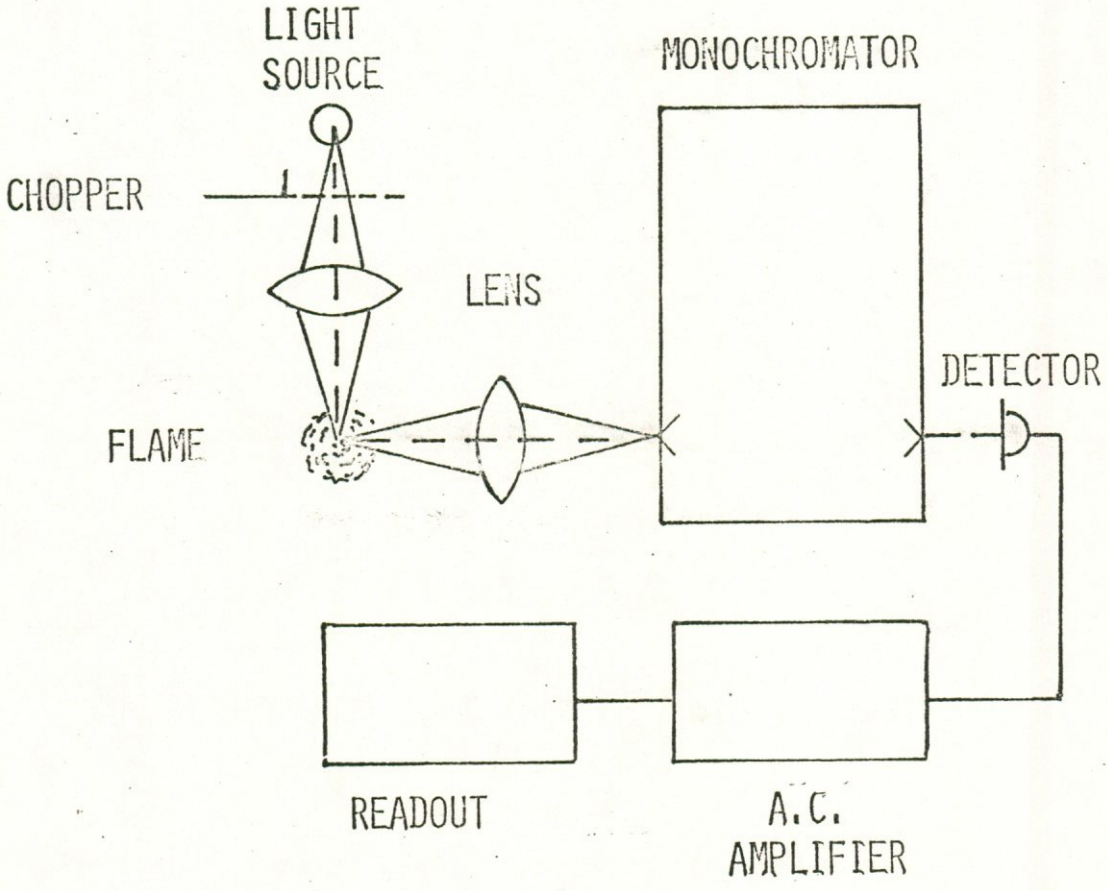
ATOMIC ABSORPTION AND FLUORESCENCE
AT RESONANCE FREQUENCIES

Visual 10 - 1



BASIC ATOMIC ABSORPTION INSTRUMENT

Visual 10 - 2



BASIC ATOMIC FLUORESCENCE INSTRUMENT

Visual 10 - 3

BASIC RELATIONSHIP FOR ATOMIC ABSORPTION

$$\text{LOG } \frac{I_O}{I} = K_{\lambda_o} n l$$

WHERE:

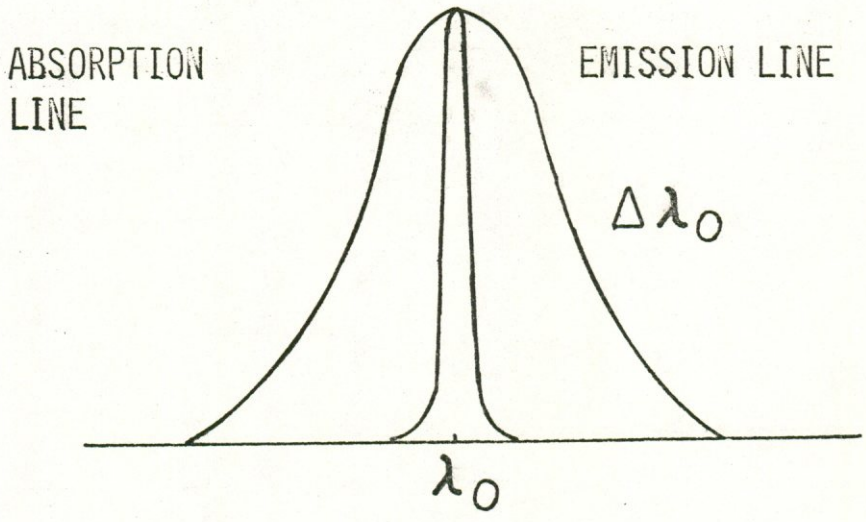
I_O = THE INTENSITY OF THE RESONANCE WAVELENGTH FROM THE SOURCE

I = THE TRANSMITTER RESONANCE WAVELENGTH INTENSITY

K_{λ_o} = A PROPORTIONALITY CONSTANT FOR THE WAVELENGTH

n = NUMBER OF ATOMS PER UNIT VOLUME OF THE CELL

l = LENGTH OF THE CELL

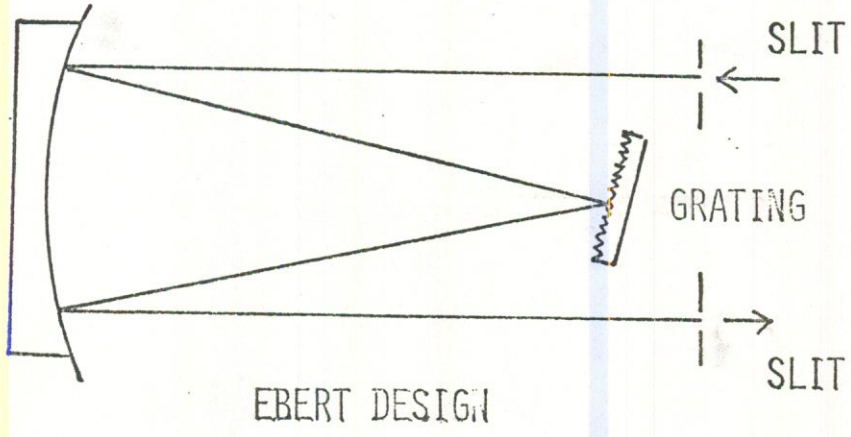


WHERE:

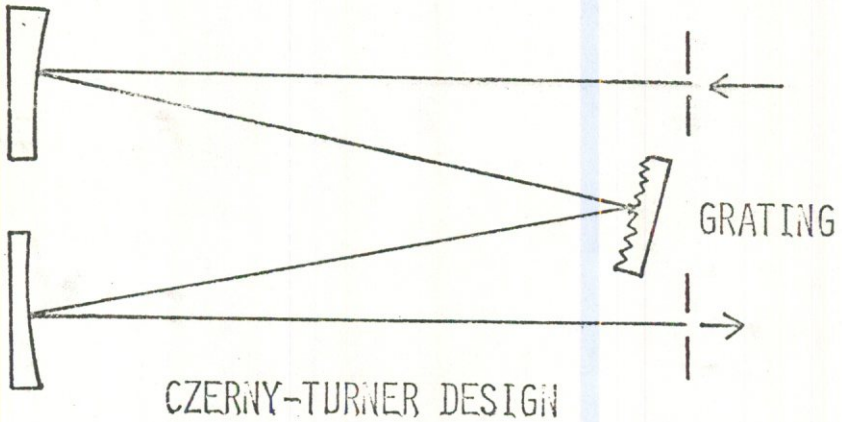
$\Delta\lambda_o$ = DOPPLER HALF WIDTH

λ_o = RESONANCE WAVELENGTH

REQUIRED EMISSION AND ABSORPTION
LINE PROFILES



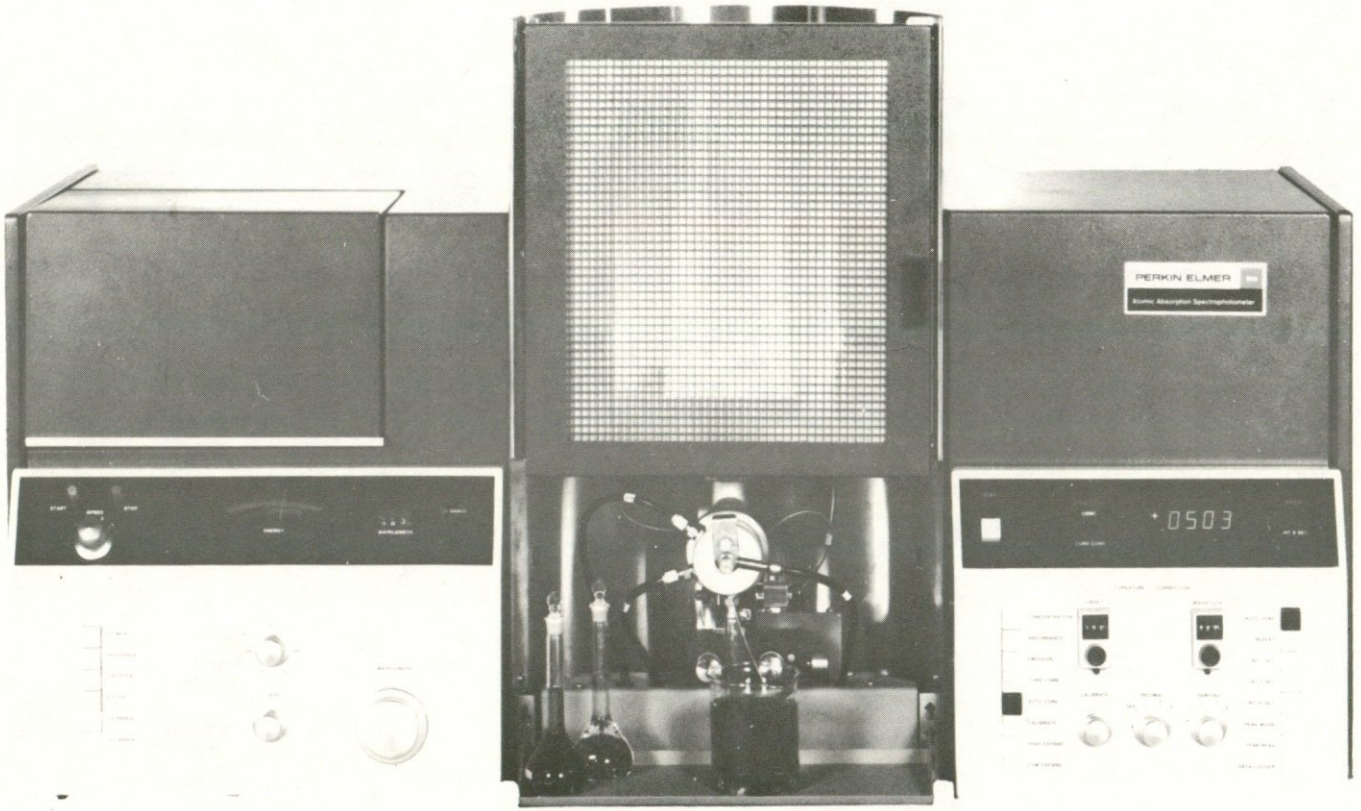
EBERT DESIGN



CZERNY-TURNER DESIGN

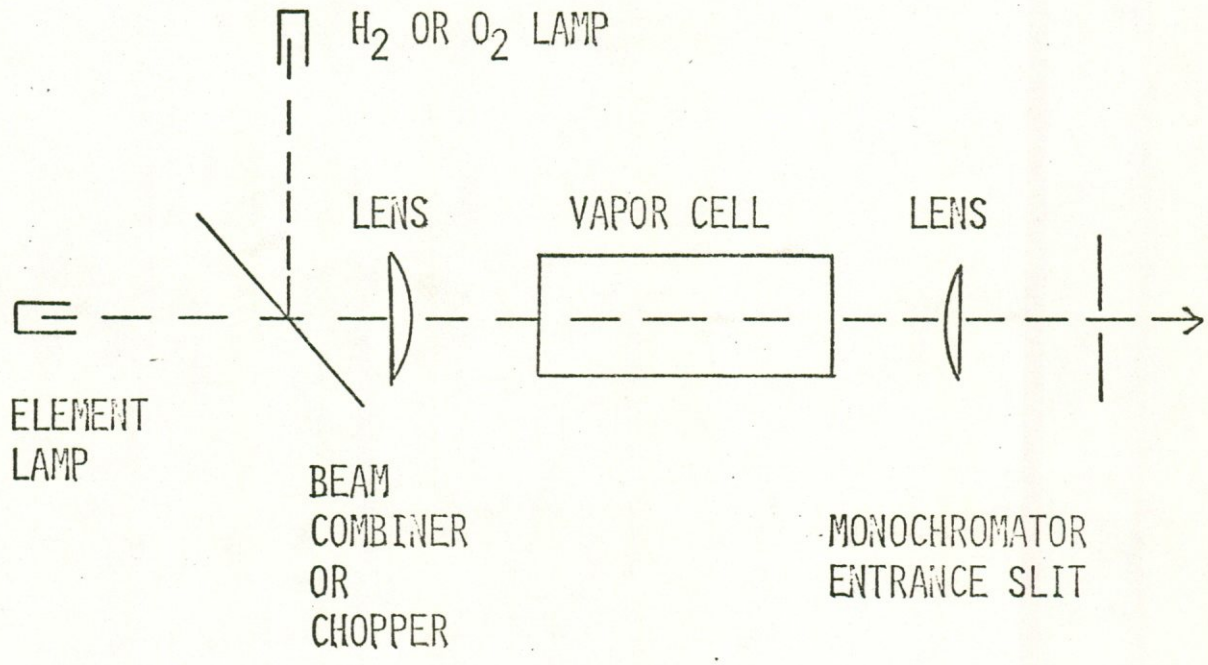
COMMON TYPES OF MONOCHROMATORS
FOR AA AND AF

Visual 10 - 6



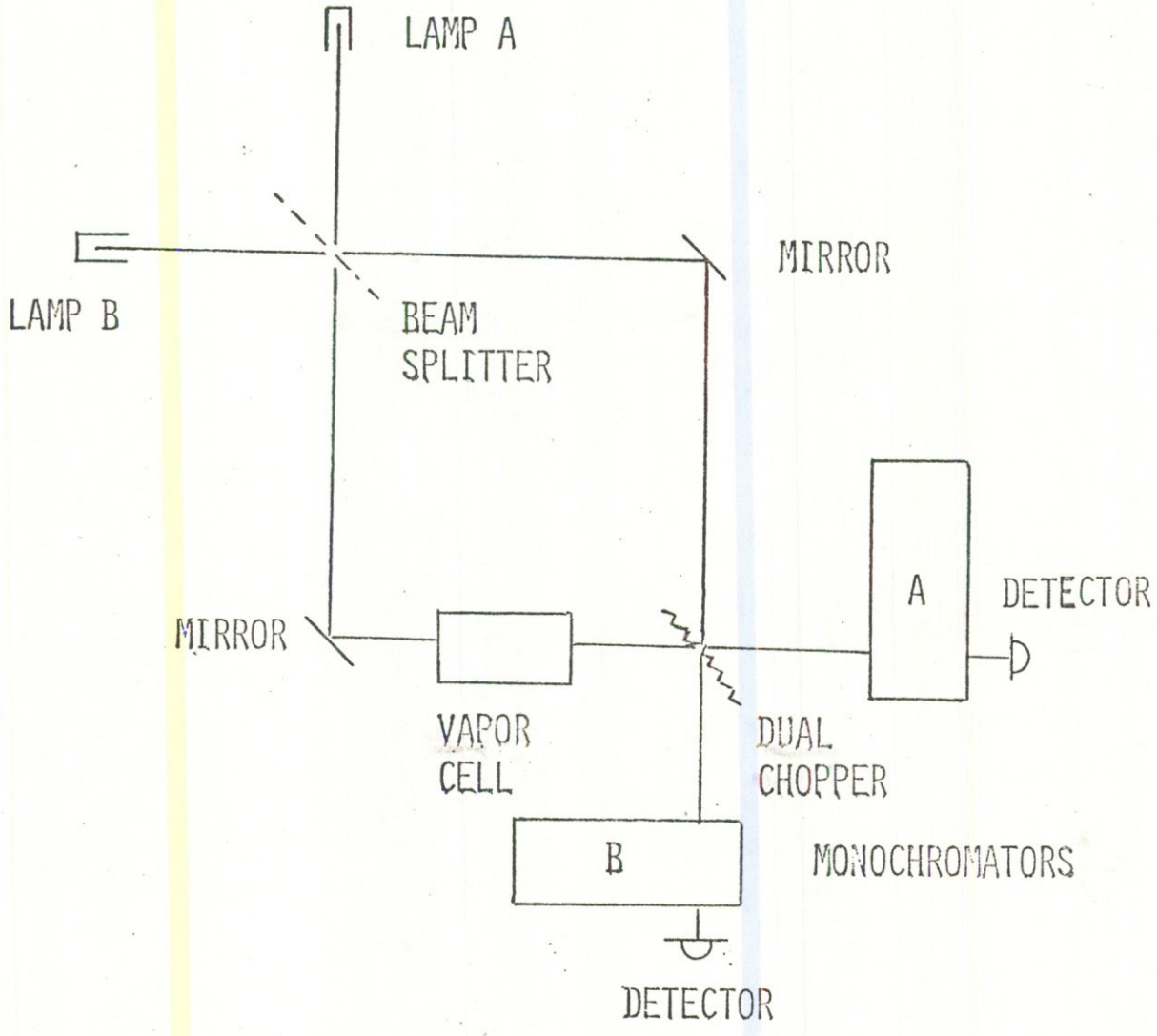
Atomic Absorption Spectrophotometer

Illustration Courtesy of The Perkin-Elmer Corporation
Norwalk, Conn.



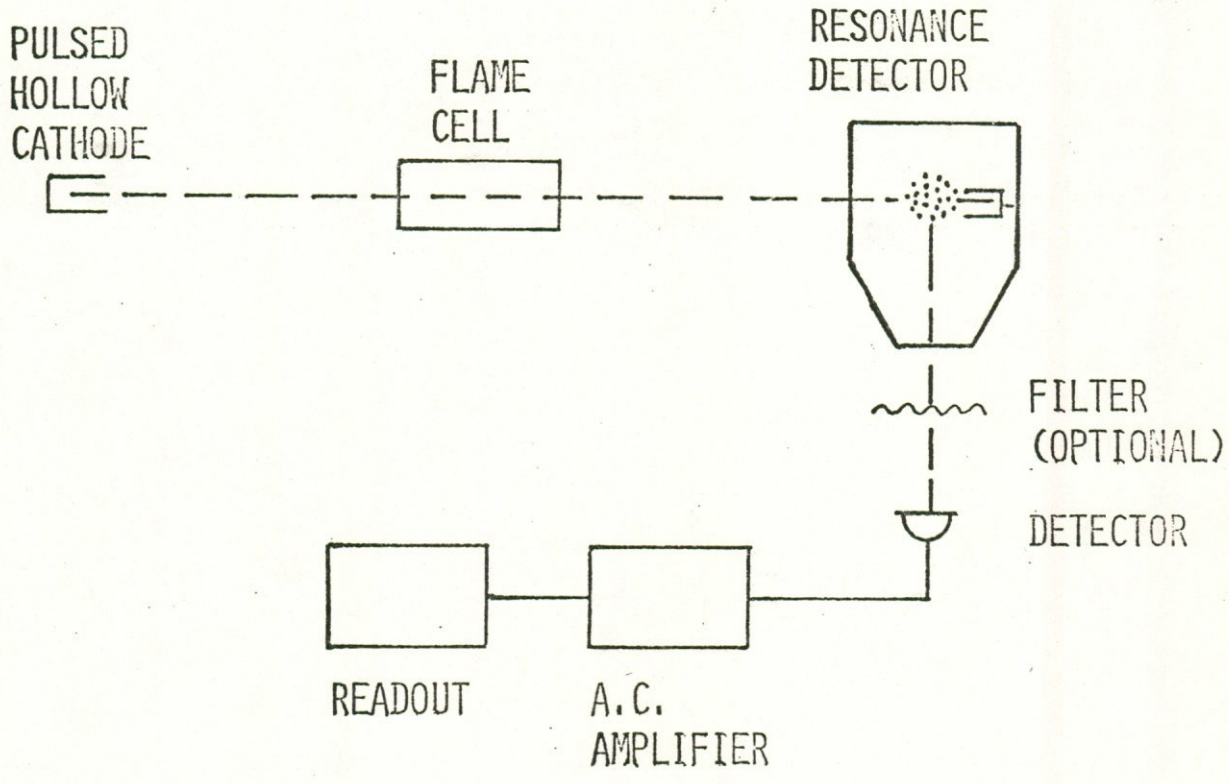
BACKGROUND CORRECTION FOR VAPOR CELL
NON ATOMIC ABSORPTION

Visual 10 - 8



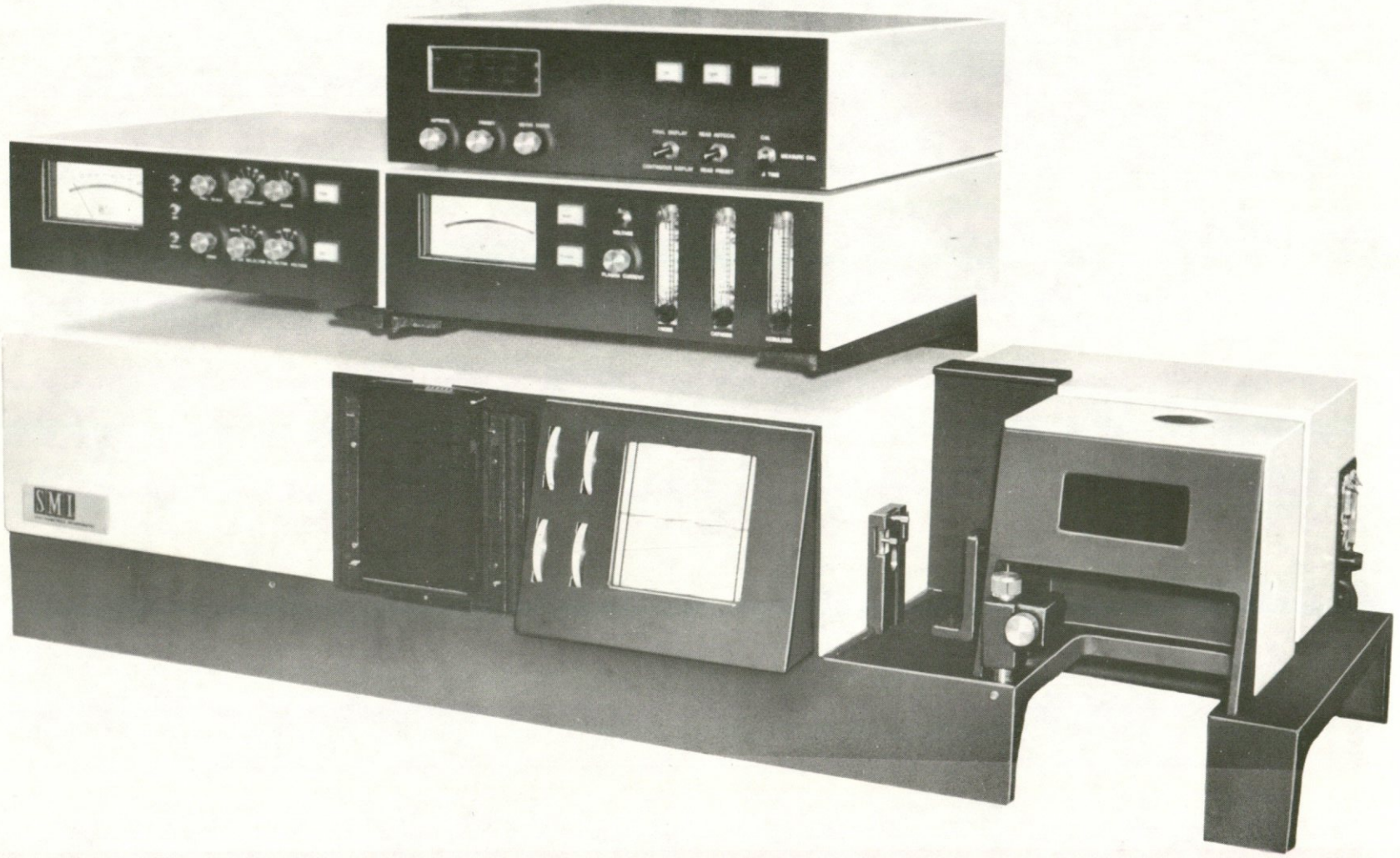
SCHEMATIC OF DUAL CHANNEL
ATOMIC SPECTROMETER

Visual 10 - 9



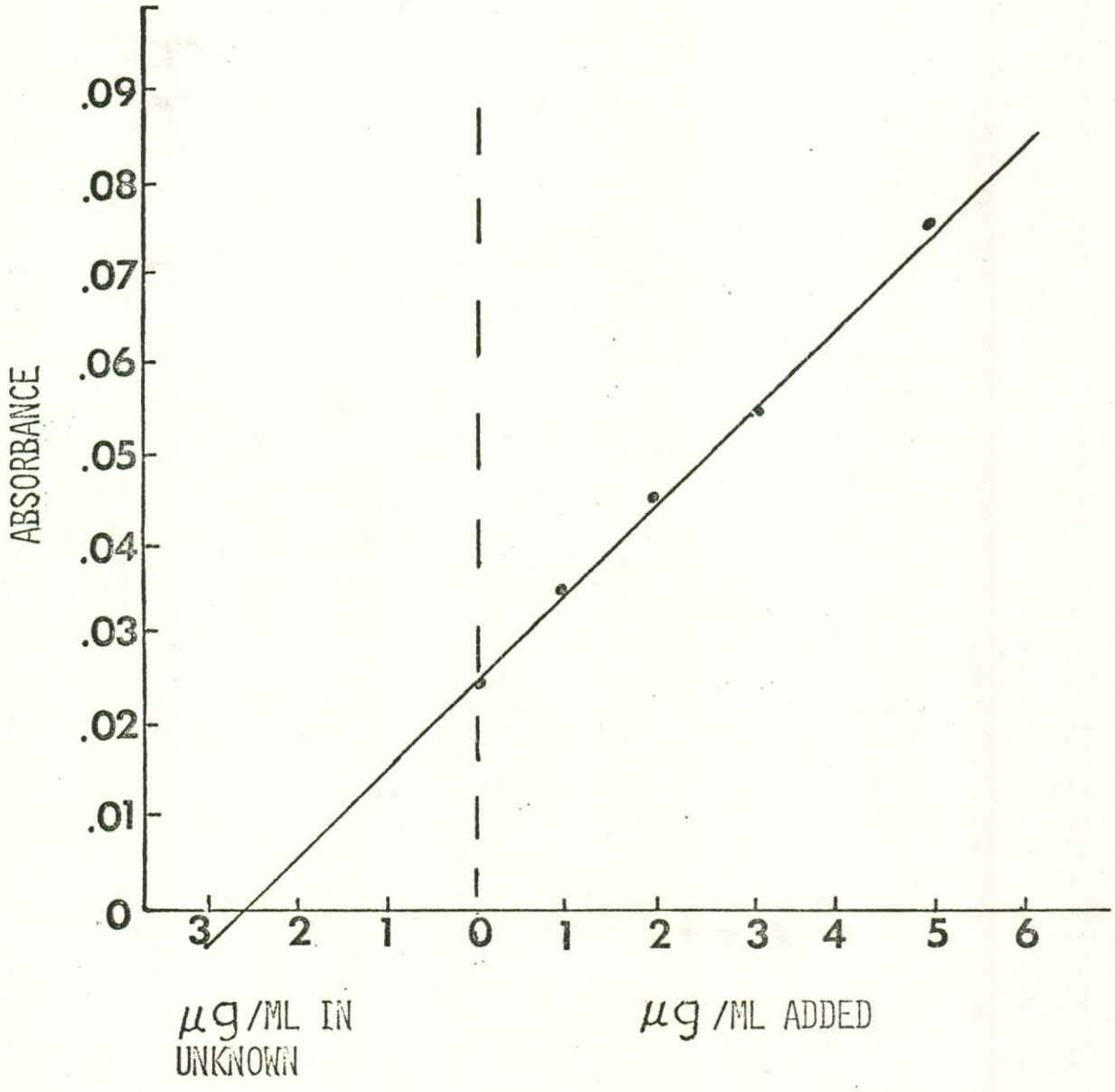
SCHEMATIC RESONANCE DETECTING
ATOMIC ABSORPTION INSTRUMENT

Visual 10 - 10



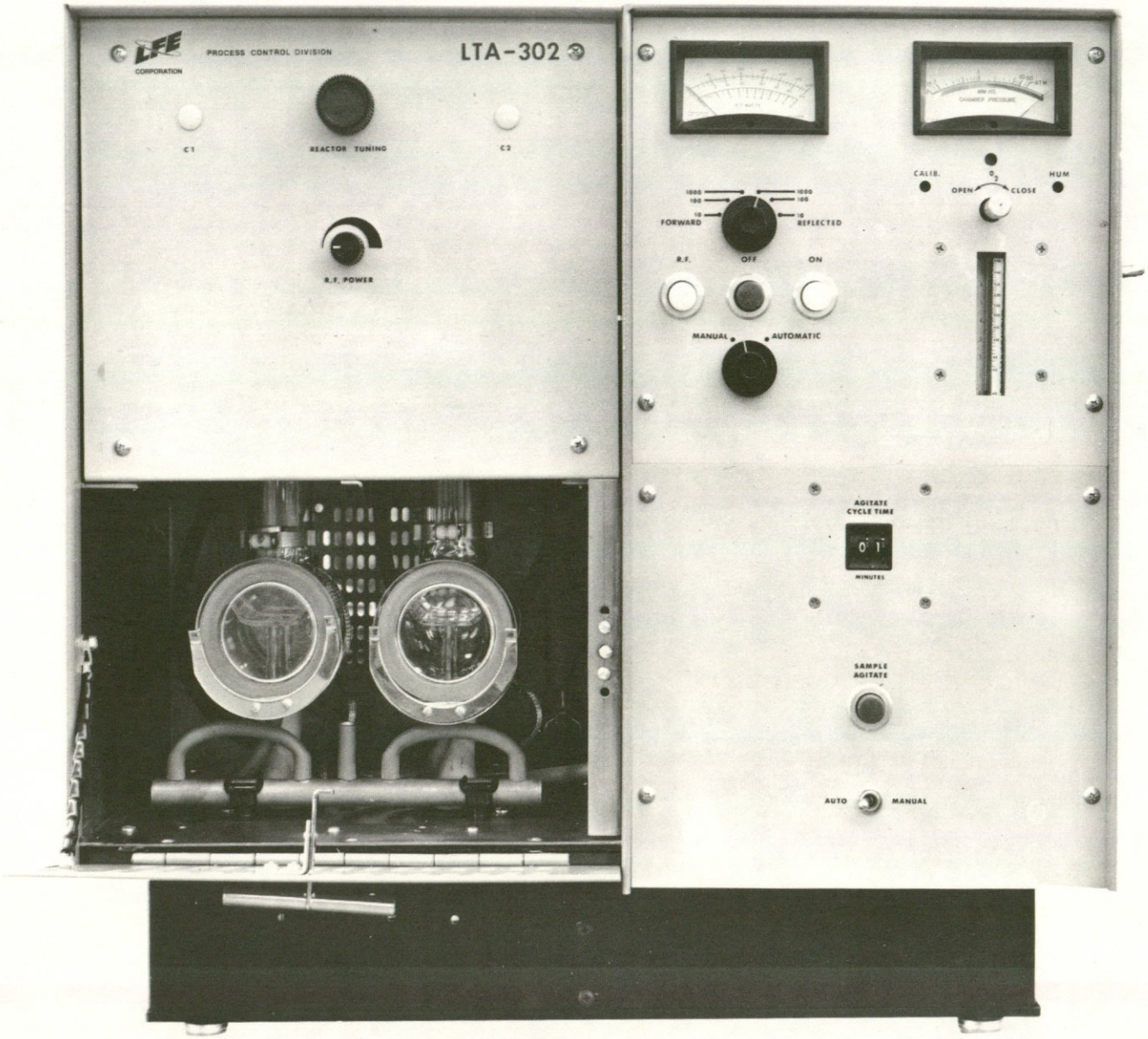
Sequential Element Quantitative Analyzer with Digital Readout
using an Echelle Monochromator System

Illustration Courtesy of Spectrametrics Incorporated
Andover, Mass.



METHOD OF STANDARD ADDITIONS

Visual 10 - 12

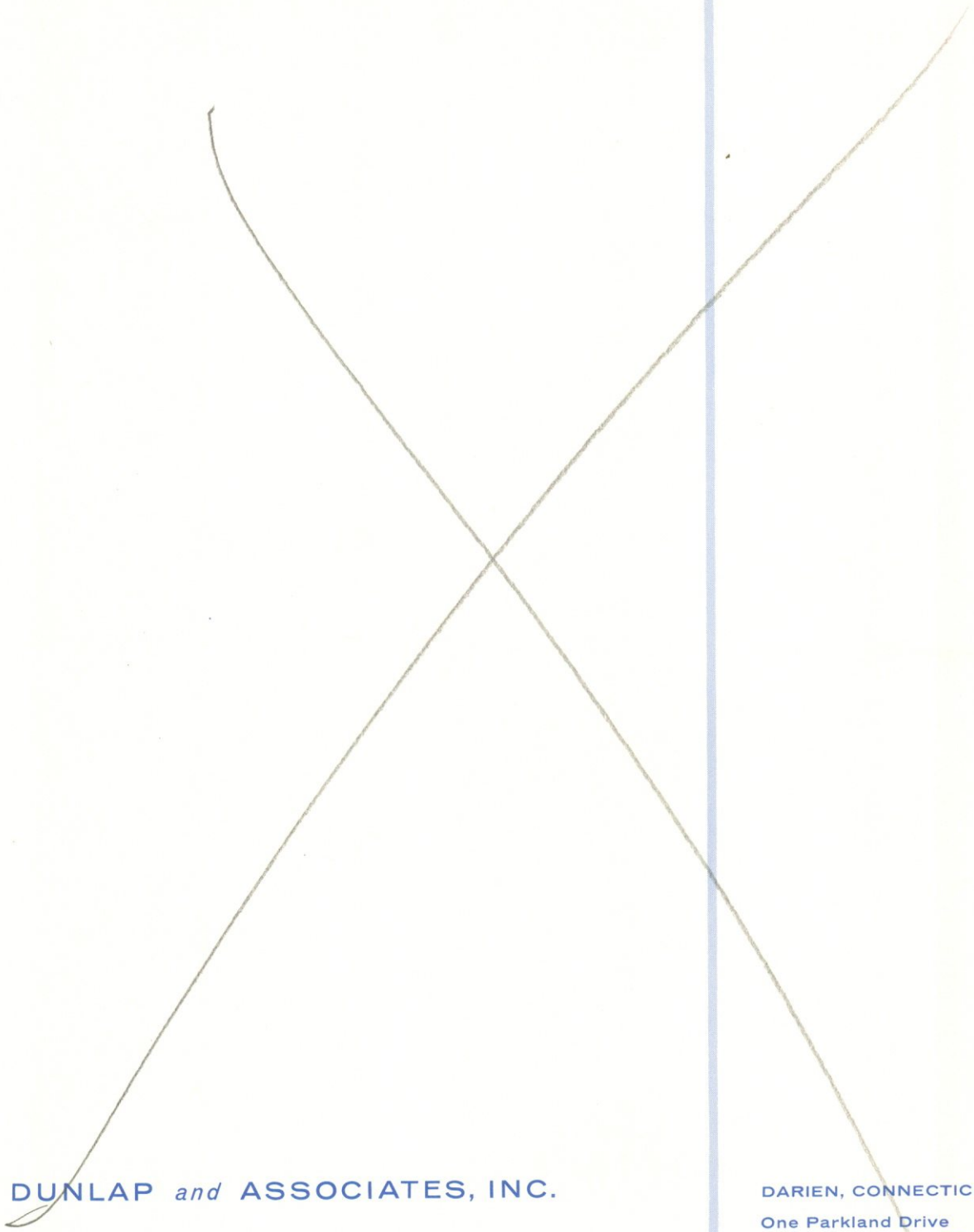


Low Temperature Asher

Illustration Courtesy of LFE Corporation
Waltham, Mass.

Visual 10 - 13

95-01



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