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INSTRUCTOR MANUAL
INDUSTRIAL HYGIENE CHEMISTRY COURSE

LESSON NUMBER 3

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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.

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- 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 Direct Reading Instruments	LESSON NUMBER 3	LESSON LENGTH 1:30

BEHAVIORAL OBJECTIVE

The student will be able to describe the general use and application of types of direct reading instruments.

SCOPE

Liquid reagents
Detector tubes
Chemiluminescence techniques
Heat of combustion techniques
Electrochemical techniques
Thermal conductivity techniques
Flame ionization techniques
Gas chromatographic techniques
Photometric techniques
Aerosol photometry

VISUALS	EXHIBITS
3-1 through 3-10	None

EQUIPMENT

35 mm. projector
Screen
Blackboard
Chalk

REFERENCES

LESSON TITLE

Direct Reading Instruments

1. Linch, A. L. *Evaluation of Ambient Air Quality by Personnel Monitoring*, The Chemical Rubber Company Press, Cleveland, Ohio (1974).

2. U. S. Department of Health, Education and Welfare, Public Health Service Center for Disease Control, National Institute for Occupational Safety and Health. *The Industrial Environment--Its Evaluation and Control*, U. S. Government Printing Office, Washington, D. C. (1973).

3. American Conference of Governmental Industrial Hygienists. *Air Sampling Instruments for Evaluation of Atmospheric Contaminants*, 4th ed., Cincinnati, Ohio (1972).

4. Department of Health, Education and Welfare, Public Health Service. Title 42, Public Health, Part 84, Certification of Gas Detector Tube Units, Procedure for Evaluation and Certification, *Federal Register*, Vol. 38, No. 88, May 1973. See also: Department of Health, Education and Welfare, Public Health Service, 42 CFR, Part 84, Gas Detector Tube Units, Proposed Approval, Federal Register, Vol. 37, No. 184, September, 1972.

5. Katz, Morris (ed.) *Methods for Air Sampling and Analysis*, Intersociety Committee, American Public Health Association, Washington, D.C., (1972).

TITLE
Direct Reading Instruments

LESSON NUMBER
3

A. Liquid Reagents

1. Some direct reading colorimetric devices incorporate a reagent on a support or use a liquid which will produce a color when in contact with an appropriate pollutant in an air sample drawn over or through a sampling system. The liquid and solid reagents usually are contained in sampling containers or supports through which a measured sample volume is drawn. Most of the paper support systems (impregnated paper) are based on the concentration times time of exposure. These detectors may be evaluated on the basis of color density (visual comparison with graded color standards) or on the basic gas titration (time for appearance of first detectable color). (1)

2. Papers impreganted with color forming reagents have been widely used for many years for the detection of toxic gases and vapors in air. Mercuric bromide papers for the detection of arsine, lead acetate for H_2S, nitrobenzyl pyridine reagent for phosgene, etc. serve as examples. When exposed to a contaminated atmosphere, the observed reaction time to produce a detectable color change can be equated to the concentration. In the case of the o-tolidene-cupric acetate paper, a 5 second response time indicates an HCN concentration of 10 ppm. (2)

3. Liquid reagents in sealed ampoules or in tubes are available in kit form for field use (Visual 3-1). Kits for direct estimation of toluene-di-isocyanate, nitrogen dioxide, chlorine, lead (both organic and inorganic) and unsaturated perfluoroalkenes have been applied successfully in Industrial Hygiene surveys. Methods based on liquid reagent systems are inherently more accurate than those methods based on solid reactants due to greater precision and accuracy of color measurements carried out in liquid systems. Field kits designed for water analysis can be adapted to air analysis. After the contaminant has been collected in a liquid reagent, the system becomes amenable to water analysis techniques. Sophisticated permanent color standards in rotatable continuous color visual comparators and portable electronic photometers are commercially available for a large number of pollutants. (1, 2)

NOTES Times (elapsed) projected	LESSON OUTLINE
(---) 0:05	A. Liquid Reagents
	1. Direct reading colorimetric devices---in general
	2. Papers impregnated with color forming reagents
Visual 3-1	3. Liquid reagent kits

B. Detector Tubes

1. Small glass tubes filled with granular silica gel which has been treated with a color forming reagent are the most widely used portable toxic gas or vapor detectors currently employed by Industrial Hygienists and Governmental Compliance Officers for evaluation of industrial exposure hazards. An example is shown in Visual 3-2. The first detector tube was developed in 1917 for the detection of carbon monoxide, and depended upon depth of color formation rather than stain length. The first length of stain tube appeared in 1935 for the estimation of H_2S.

2. The technique for using detector tubes is quite straightforward. First, both ends of the sealed tube are snapped off in the recess provided in the side of the pump (Visual 3-3); the tube is inserted into the pump adapter (orientation is indicated on the tube); and the specified air sample volume drawn through the tube by squeeze bulb, bellows or piston by manual activation. Adequate time is allowed for each stroke, if more than one, to draw the sample through the tube, then the concentration of the contaminant determined:

   - By comparing the shade of color visually with a set of color standards. Accuracy is determined by the visual ability of the observer.

   - By relating the length of stain obtained to a calibration chart. The scale may be affixed directly on the detector tube or on a chart provided with the tubes.

   - By gas titration, i.e., relating the sample volume required to produce the first observable color change to a calibration chart. Visual acuity becomes the controlling factor in this technique. (1)

NOTES Times (elapsed) projected	LESSON OUTLINE
(0:05) (Transition A. -B.)	B. Detector Tubes
From liquid reagents to reagents sealed in tubes. 0:30 (Visual 3-2)	1. Detector tubes -- widely used
(Visual 3-3)	2. Technique for using detector tubes
	. Color shade
	. Length of stain
	. Gas titration

3. The major use of detector tubes has been traditionally for the detection of hazardous gases and vapors in the work place. However, this application is governed by the limitations imposed by grab sampling unless the tubes are recalibrated for continuous sampling over extended time periods. The concentration of pollutants (gas vapor or aerosols) in the industrial atmosphere is highly variable with respect to both time and place. Grab sampling is appropriate for scoping surveys and detection of peak concentration excursions (ceiling TLV's).

4. If detector tube analysis is to be considered for evaluation of industrial environments for compliance with governmental regulations, then the statistical criteria recommended by NIOSH and OSHA should be followed. The results of samples have to be collected at random intervals during the workday with a mean m (average of all results) and a range (difference between least and greatest) r. If, for from three to ten samples, m is greater than the total of:

   - the standard

   - the percentage of systematic instrument error multiplied by the standard

   - $\frac{t \times r}{n}$

     where:

     n = number of samples taken

     t = value taken from the following table

NOTES Times (elapsed) projected	LESSON OUTLINE
	3. Uses of detector tubes 4. Compliance with OSHA using detector tubes; m greater than: • standard • % instrument error • $\frac{t \times r}{n}$

n	t (student's "t" test value)
3	2.35
4	2.13
5	2.01
6	1.94
7	1.89
8	1.86
9	1.83
10	1.81

5. This procedure may be used by compliance officers to determine the statistical significance of a sampling strategy. The error is determined in the direction of preventing an under-estimation of the true value of the hazard. This will give the employer the benefit of the doubt. If, however, one wants to be sure that the environmental hazard does not exceed the standard, the error should be calculated in the other direction. The margin of error should be subtracted from m.

6. In addition to testing atmospheres within enclosures for flammable gases and vapors and oxygen content, detector tubes serve a useful function for detection of toxic components such as H_2S, SO_2, nitrogen oxides, etc. A 50% safety factor (1/2 the TLV) should be applied for clearance to enter autoclaves, tanks, sewers, mine shafts, etc. The rapidity with which approximate results can be obtained with detector tubes is a strong recommendation for delineating the high risk areas created by chemical spills, accidental release of toxic gases or vapors, abnormal operating conditions and leakage of process materials from manufacturing operations. (1)

NOTES Times (elapsed) projected	LESSON OUTLINE
	5. Other calculation -- to be safe
	6. Detector tubes -- testing air prior to entering enclosure

7. Inaccessible locations can be sampled by introducing the detector tube connected to one end of a flexible (rubber) tube of the same inner diameter as the detector tube. The other end then is connected to the hand pump to draw the sample through the detector tube. In no case should the sample be drawn through the tubing before entering the detector tube as serious errors can ensue from adsorption and reaction on the tubing wall. Lengths up to 20 meters can be used, but more time must be allowed between pump strokes to compensate for the reservoir effect and obtain full sample volume. (1)

8. Hot gases from stacks or engine exhausts must be cooled before passing into the detector tube as otherwise the calibration will be invalid and the sample volume uncertain. Usually a glass or metal probe is attached to the inlet of the detector tube with a short length of silicone or polytetrafluorethylene (PTFE) tubing. As little as a 10 cm. of probe length will cool the sample from 250°C to about 30°C. Serious adsorption losses can be encountered and this technique cannot be employed when condensable vapors are present (dew point above ambient temperature. (3)

9. Very wide and unpredictable variations in physical and chemical properties in successive batches are the rule in the manufacture of silica gel. Silica gel is the typical granular support used in detector tubes. The reaction rate of the color forming reagent is highly sensitive to traces of impurities on the gel surface (active centers). The manufacturer must exercise very close quality control on the purity and activity of the materials going into the process, the method of preparation and cleanliness in the production areas as well as particle size distribution. (1)

10. Moisture may contribute a significant effect on the formation of the color complex as well as the physical properties of the gel. Example: mercuric chloride adsorbed on silica gel for the detection of arsine. The length of stain increases as the water content is increased and the color changes from yellow to dark brown. However, above 120% H_2O the gel tends to shrink in storage. A compromise between maximum stain length and gel shrinkage was reached at 120% H_2O content. (1)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		7. Remote sampling using tubing
		8. Sampling hot gases
		9. Silica gel -- problem with accuracy of tubes
		10. Moisture -- problem for accuracy

11. As a general rule a narrow column yields better definition of the stain front and less risk of channeling. However, the advantage is gained at the expense of increased ΔP. Therefore, a compromise with grain size, column diameter and ΔP is accepted. One manufacturer has successfully reduced the internal tube diameter to 2 to 4 mm., while the others have continued to employ diameters in the range 8 to 10 mm. I.D. Small variations in the diameter of the narrow tubes causes relatively large variations in cross sectional area that produce errors as great as 50%. The differences in cross sectional area will be associated with differing column lengths when a constant weight of indicator gel is used. One manufacturer supplies a correction chart to compensate for column variations which reduces this error to ±5%. (1)

12. Pressure drop is not only influenced by particle size of the silica gel, but also by the skill exercised in filling and packing the tubes, and inserting the cotton or glass wool retainer plugs. These variables which control ΔP are more important for those tubes which depend up ΔP to control the critical flow rate than those systems which incorporate a critical orifice in the pump inlet to control sampling rate. However, these fine orifices are subject to plugging - partial or complete - by dust, grease, or corrosion and enlargement by careless reaming and cleaning. These manual pumps do not deliver a uniform, constant sample flow rate through the detector tubes. (1)

13. Sampling pumps should deliver repetitive sample volumes with less than ± 5% deviation from the volume used in calibrating the detector tubes. Hand pumps should be checked for leakage frequently in the field. This is accomplished by placing an unopened detector tube in place on the pump, retracting the piston for piston type pumps, or depression of the bellows in the bellows type, locking in position, and noting after 3 minutes the return of the piston or the expansion of the bellows during this period. Less than 5% leakage should occur. In the laboratory actual leakage can be determined by connecting the hand pump to a water monometer. The soap film flowmeter also furnishes reliable rate data. (3)

14. Since the total volume sampled and the rate of sampling are the critical variables controlling the detector tube's performance, no deviation from the manufacturer's instructions are permissable unless the tubes are recalibrated for the revised conditions. Tubes of one manufacture should not be interchanged with a pump from another source. (1)

NOTES	Times (elapsed) projected	LESSON OUTLINE
		11. I. D. consistency -- critical to accuracy
		12. Δ P -- effected by density of silica gel, critical orifice
		13. Sampling pump -- leakage
		14. Follow manufacturer's instructions

15. Temperature is a very important variable for tube calibration and use. The effect is different for different types of tubes. Since the color change type of tube depends upon degree of reaction, sensitivity is greater than encountered with length of stain types. The original color change carbon monoxide tubes required a correction factor of two for each deviation of 10° C from calibration conditions. If the temperature coefficient is significant, the manufacturer supplies a corrective chart. Most length of stain tubes do not require correction within normal temperature ranges. A notable exception is the CO length of stain tube which requires stain length corrections for temperature below 15°C or above 40°C. (1)

16. A shelf life of at least two years is highly desirable for practical purposes. Small variations in impurities - especially water content - frequently have a significant effect upon the thermal and shelf life of the tubes. Since the temperature greatly effects deterioration rate, storage in a refrigerator is highly recommended (Visual 3-4); in fact, reduced temperature is mandatory for tubes such as those intended for detection of benzene, xylene, toluene, etc. Shelf life is stated in terms of the time within which the calibration accuracy is maintained within ± 25%. Each box or lot of tubes should carry an expiration date beyond which recalibration is required before use. Decomposition usually manifests itself by characteristic color changes. (1)

17. Few detector tubes are specific for the trace gas or vapor for which use is intended. For example, more than 30% of all detector tubes are based on the reduction of either a chromate salt or chromic acid to a differently colored (green) chromium salt. Therefore, most reducing agents will produce a positive reaction. The investigator must determine before sampling is attempted what components would be expected to be present from an inventory of chemicals entering the area under investigation. The same reagent system is employed for the detection of benzene, toluene and xylene. A true reading will not be obtained if two or all three are present together. Negative interferences also can be expected. For example, in the presence of ammonia, mercury vapor produces no color change in the mercury vapor detector tube. Other interferences are well enough established and recognized to appear as warnings in the instructions for proper use of the detector tubes. In some cases, guard layers are incorporated directly in the detector tube or furnished as an accessory to be attached to the inlet end of the detector tube. Examples include, ethylene in the presence of CO, nitrogen oxides present with CO, SO_2 in the presence of H_2S, benzene in mixtures with other hydrocarbons, removal of water from systems which are humidity sensitive, etc. A limited number of detector tubes incorporate a preliminary reaction

NOTES	Times (elapsed) projected	LESSON OUTLINE
		15. Temperature correction
Visual 3-4		16. Shelf life of tubes
		17. Chemical interferences -- positive, negative, guard layers, preliminary reaction zone

zone to convert the pollutant to a detectable derivative. The chlorinated hydrocarbons are representative. The preliminary reaction usually involves a strong oxidizing agent to convert combined chlorine atoms to elemental chlorine which produces a color in the following color-forming reagent (dianisidine or tolidine). Multilayer tubes frequently possess a short shelf life due to diffusion between the two layers. (1)

18. In order to evaluate the effect of possible interferences the observer must be able to identify the reagent in the detector tube he proposes to use. The chemical reaction will determine the significance of his observations, or determine whether available detector tubes could solve the problem. In the absence of this information the survey should not be attempted as the conclusions could be based on false information created by coexistant components that could either mask or enhance the true result. If the preliminary survey discloses apparent target compound concentrations in the 0.5 to 1.5 TLV region, then a survey based on a specific, quantitative method such as charcoal tube sampling followed by gas chromatographic analysis should be carried out. (1)

19. Most detector tubes have been converted from color change to length of stain basis to avoid the problems inherent in shade matching. A fixed volume of air sample is drawn through the tube and the stain length related to concentration either on a scale placed directly on the tube itself or by reference to a chart. If the stain front is not well defined (diffuse), or is not perpendicular to the tube sidewall, then observational variability contributes to the uncertainty factor. Experience gained from sampling known concentrations will assist the observer in his decision relative to measurement of stain front at the leading or trailing edge and what portion of an irregular edge will be considered as a limit. Reading should not be delayed beyond the suppliers' recommendation as some stains change with time. Precision can be involved by averaging four or five readings, or better, averaging readings by two or more observers. (1)

NOTES Times (elapsed) projected	LESSON OUTLINE
	18. Evaluate possible interferences; if cannot use more precise method
	19. Reading length of stain tubes

20. Repeated use of a single detector tube as a routine practice should be avoided. This practice cannot be condoned on either the basis of economy or experience. There are certain tubes which can be used again when a negative result is obtained, but the investigator must be thoroughly familiar with the reagent system involved, and the effects of interferences which may be present in the atmosphere sampled. Water vapor especially may alter the reagent system involved. Tubes which require a guard layer to remove interferences are vulnerable when reused. Tubes filled end to end with a homogenous reagent composition can be reversed in some cases for a second determination if estimation of concentration from stain length on a chart is provided. Tubes with printed calibration directly on the tube require a second scale for reading. Repetitive sampling to increase the sensitivity, unless recommended by the manufacturer, should be approached with caution. In some cases - carbon monoxide and benzene, for example - two successive aliquots can be drawn through the tube, if taken in quick succession, and the result divided by two. With at least one tube, benzene, an interval of more than 15 minutes between samples will produce errors greater than 15%. A third successive sample may create errors of more than 20%. Any deviation, such as repetitive sampling or using a second tube to remove interferences or for multiple determinations (H_2S and phosgene tubes in series), from supplier's instructions should be confirmed by recalibration under identical conditions. (1)

21. As a consequence of findings relative to the poor performance of a number of gas detector tubes a Federal Certification Agency was established within NIOSH during 1971. Since that time a number of tubes, as well as sampling equipment have received performance certification. When obtainable, only certified tubes and equipment should be used, especially if conformance with governmental standards is involved. Tubes for CO, SO_2, NO_2, H_2S, CO_2, NH_3, CCl_4, trichloroethylene, Cl_2 and benzene have been certified. Calibration criteria require accuracy within ±25% at 1.0, 2.0 and 5.0 times the TLV and ±35% at 0.5 times the TLV.

NOTES	Times (elapsed) projected	LESSON OUTLINE
		20. Repeated use of same tube, reversing, increasing sensitivity 21. Certification of detector tubes

C. Chemiluminescence Techniques

1. Chemiluminescence produces a distinctly colored glow which accompanies the oxidation of decaying wood, of luciferin in fireflies and yellow phosphorous. This principle has been adapted to the reaction of ozone with reducing gases such as ethylene and nitric oxide for the measurement of ozone and nitrogen oxides in the ambient atmosphere. (2)

2. Detection of ozone in the concentration range 0.001 to 1 ppm is based upon the photometric (photo multiplier tube) measurement of the chemiluminescence produced by the flameless gas phase reaction in the air sample with ethylene gas metered through capillary tubing into a reaction chamber. Similarly, NO measurements from 0.01 to 5,000 ppm are based upon the chemiluminescent reaction of NO and ozone to produce NO_2 and O_2. The ozone is synthesized from bottled oxygen by an in-line silent electrical discharge generator. Analysis for NO_x is accomplished by means of the reduction of NO_2 to NO in a catalytic converter which operates in a bypass line on a timed sequence basis. The NO_2 concentration is obtained by difference. The selectivity of these instruments is further improved by incorporating narrow-band optical filters into the optical circuit which provide negligible interference effects from other co-existing atmospheric contaminants. Although designed for ambient air applications, these instruments are adapted easily to in-plant fixed station monitors. (2, 3)

D. Heat of Combustion Techniques

1. Almost without exception the portable explosive and flammable vapor detectors are based on the principle of controlled combustion over a filament heated above the ignition temperature of the combustible materials in the air sample drawn through the instrument. The filament usually is one arm of a Wheatstone bridge circuit. The resulting heat of combustion changes the resistance of the filament (usually platinum), and the measurement of the imbalance is related by a dial meter to the concentration of gas or vapor in the sample. This method is non-specific; but some selectivity can be attained by selecting filament temperatures which correspond to the ignition temperature of an individual component, or by using an oxidation catalyst for the desired reaction such as hopcalite for carbon monoxide. Unless factory pre-set, most meters are not suitable for methane which requires a higher filament temperature than do the other hydrocarbons for combustion. (2)

NOTES Times (elapsed) projected	LESSON OUTLINE
(0:35) (Transition B.-C.) From details on detector tubes to direct reading devices using chemiluminescence. 0:05	C. Chemiluminescence Techniques 1. Chemiluminescence in general
	2. Applications -- ozone, NO_x
(0:40) (Transition C.-D.) From chemiluminescence to heat of combustion 0:10	D. Heat of Combustion Techniques 1. Principle, specificity of technique

2. The super-sensitive instruments can be operated in the range - 0 to 1000 ppm. However, the most useful scale for these instruments is the explosive range application (Visual 3-5). Many are calibrated in terms of percentage of lower explosive limit (L. E. L.). Since the possibility of operation in the explosive range is present, these instruments must always be fitted with flashback arrestors. Combustible gas meters must be calibrated in the laboratory for their response to anticipated individual test gases and vapors, such as benzene, toluene, hexane (for hydrocarbons in general, gasoline, naphtha, etc.), carbon monoxide, acetone and styrene (Visual 3-6). These instruments are easily portable and are a valuable survey meter which must be available to the industrial hygienist for the evaluation of explosion hazards. However, the investigator must recognize that industrial atmospheres rarely contain a single gaseous contaminant and that these meters will respond to all combustible components present. Also, the concentrations of concern are far above the upper permissable limits for toxic hazard control. For example, the lower explosive limit for toluene is 1.2%. The control point is usually 25% L. E. L., or 3% toluene which is equivalent to 3000 ppm. The TLV for toluene = **100 ppm.** Therefore: 25% L. E. L. is 30 times higher concentration than the permissable health control standard. Hence, supplementary sampling and analytical techniques must be employed to define the total airborne hazard. (3)

3. Like all instruments the combustible gas meter has its limitations and precautions. Operation of the filament at a high temperature for the higher ignition point vapors and gases shorten the filament life. Chlorinated (halogens in general)hydrocarbons such as carbon tetrachloride will produce a false response and rapidly shorten the filament life through corrosion of the platinum. Lead and mercury compounds (tetraethyl lead) will "poison" the filament. Increasing the filament temperature will vaporize the lead, but at the expense of shortened filament life. The portable meters are battery operated - either expendable dry cells or rechargeable nickel cadmium batteries. Battery life must be considered when undertaking field surveys. Most combustible gas meters have built-in battery charge indicators which present a warning when the battery charge has dropped below operational limits. Frequent calibration checks should be carried out on a routine schedule to ensure reliable functioning. Field kits for this purpose are supplied by several of the suppliers. (2)

NOTES Times (elapsed) projected	LESSON OUTLINE
Visual 3-5, Visual 3-6	2. User -- survey and explosion hazards; calibration
	3. Precautions and limitations -- high temperature, substances damaging to filaments, batteries, calibration

4. Several portable carbon monoxide monitoring instruments based on catalytic combustion are available. A typical assembly contains a pump to draw the atmospheric samples through the cell containing beads of active hopcalite. Two thermistors are imbedded in the catalyst and are part of a Wheatstone bridge circuit. The oxidation of CO to CO_2 in the insulated cell produces heat which imbalances the resistance of the thermistor legs of the bridge and produces a proportionate meter reading. The cell temperature is held constant by a solid-state proportioning controller despite variations in the ambient temperature. Therefore, only the heat of combustion produces a change in the thermistor resistance. A drier to absorb the moisture which also will produce heat in the catalyst bed is an essential unit in the instrument. The dryer life is approximately 10 sampling hours under normal humidity conditions. (3)

E. Electrochemical Techniques

1. Those gases which will produce electrolytes when absorbed in an aqueous solution will manifest themselves by increasing the electroconductivity of the system. The effect is a summation of all of the ions present; therefore, the method is not specific unless interferences can be eliminated, or if only a single component which ionizes in water is present in the air sample, or if all other ionizable components can be held constant. Temperature control is extremely critical in conductivity measurements; therefore, the detector cell must be either thermostatically or electrically compensated. The temperature coefficient for conductivity is 2% per degree centigrade on the average for many gases. The major application for this method has been for continuous monitoring of SO_2 in ambient atmospheres. A light-weight portable battery powered analyzer which uses a peroxide absorber to convert H_2SO_3 ($SO_2 + H_2O$) to H_2SO_4 is available for field surveys. Readings over the 0-1 ppm range are obtained within one minute. (2, 3)

NOTES Times (elapsed) projected	LESSON OUTLINE
	4. CO devices based on catalytic combustion
(0:50) (Transition D. -E.) From heat of combustion to electrochemical techniques. 0:05	E. Electrochemical Techniques 1. Electrical conductivity -- basis and use

2. Gases that react with reagents in solution to alter the pH of the solution produce a potentiometric change which is proportional to the concentration of absorbed gas. This change is sensed by a galvanic cell commonly referred to as the pH electrode. In the pH electrode energy associated with chemical reactions is converted to electrical energy manifested by an electromotive force (emf) which depends primarily on the concentration of the substances involved in the electrode reactions. The electrode must come to an equilibrium which is not disturbed while measuring the developed emf. Therefore, null balance potentiometers are used to prevent the flow of any current through the electrode circuit. In principle the pH change is non-specific unless reagents that are most conductive to the desired reaction for the gas are selected. Selective electrodes for ions other than hydrogen have been developed and include fluoride, nitrates, sulfates, etc. (3)

3. Coulometry is based on the measurement of the number of electrons in terms of coulombs transferred across an electrode-solution interface to carry to completion the reaction of a substance in a sample. In principle there is no restriction in coulometry relating to the volume of the sample or to the concentration of the substance in the sample. Furthermore, since the basic method involves measurement of the number of coulombs required for a particular reaction, provision for locating the end point of the reaction is not included. Therefore, any of the known methods for end-point detection may be utilized. The sensitivity of the end point determination may become the limiting factor in the ability of the system to detect very low concentrations. It has been used for the determination of O, ozone, CO and SO_2 (Visual 3-7).

F. Thermal Conductivity Techniques

1. Detection of the thermal properties of a gas is a widely used method for gas analysis. The specific heat of conductance is a physical method for quantitative measurement which is non-specific for a mixture of gases. However, when mixtures are resolved in gas chromatography, the technique has found widespread application. For a mixture of a few components in which one gas has a relatively high coefficient of thermal conductivity and occurs in relatively high concentration, thermal conductivity can be used with some success. Frequently, a differential measurement will balance out the effects of the other gases, leaving the concentration of the target gas a measurable quantity. If a combustible hydrocarbon in air is burned, and the CO_2 is determined before and after combustion, then the CO_2 differential is related to the hydrocarbon content. The by-product water must also be considered. (3)

NOTES Times (elapsed) projected	LESSON OUTLINE
	2. Potentiometry -- basis and uses
(Visual 3-7)	3. Coulometry -- basis and uses
(0:55) (Transition E.-F.) From electro-chemical to thermal conductivity techniques. 0:01	F. Thermal Conductivity Techniques 1. Description and general use

G. Flame Ionization

1. The hydrogen flame ionization detector (FID) is a stainless steel burner in which hydrogen is mixed with the sample in the base of the unit. Air or oxygen for combustion is introduced axially and diffused around the hydrogen jet which carries the sample to the cathode tip where ignition takes place. A loop of platinum serves as the collector electrode which is set above the burner tip. The current carried across the electrode gap is proportional to the ion concentration generated during combustion. The detector responds to all organic compounds except formic acid. Response is greatest with hydrocarbons and decreases with increasing substitution of other elements, especially oxygen, sulfur and halogens. The system does not respond to water, permanent gases and most inorganic compounds. Usefulness extends to both laboratory and field models of gas chromatographs as well as hydrocarbon analyzers which can be used as fixed station monitors for ambient atmospheres in the field. (2)

H. Gas Chromatographic Techniques

1. Gases or vapors are absorbed in a porous medium in a column. The components of the gas migrates differentially through the porous medium. These separations are the result of various affinities of the sample components for the material in the column, the rate of carrier gas flow, and operating temperatures of the column. As a result of the varied affinities exhibited by the components, the components are eluted sequentially and produce a spike on a chart. The height and area of the peak are proportional to the concentration of the sample component. The time of retention on the column and supporting analytical techniques will identify the individual peaks and when compared with knowns yield positive identification of the compound. Sensitivity to fractional parts per million of organic substances is readily attainable. Rugged battery operated, portable GC's have been developed to a degree which justifies use in the field. These instruments are available with a choice of thermistor-type thermal conductivity, flame ionization and electron capture detectors. The lecture bottles containing carrier gas provide 8 to 20 hours of operation in the field, depending on flow rates. (2, 3)

NOTES Times (elapsed) projected	LESSON OUTLINE
(0:56) (Transition F. -G.) From thermal conductivity to flame ionization techniques. 0:02	G. Flame Ionization Technique 1. General description and uses
(0:58) (Transition G. -H.) From flame ionization to gas chromatography as utilization in direct reading instruments. 0:02 Chromatography is covered in detail in lessons #12 and #13.	H. Gas Chromatographic Techniques 1. Basic principle of operation, general uses

I. Photometric Techniques

1. Photometry is the measurement of the relative radiant power of a beam of radiant energy in the visible, ultraviolet (UV) or infrared (IR) region of the electromagnetic spectrum, which has been attenuated by passing through a solution or a gas in air mixture such as mercury vapor, ozone or benzene in air. A spectrophotometer contains a prism or grating in place of optical filters in photometers to provide essentially monochromatic light. Such instruments are capable of high specificity and precise analytical results. The UV spectrophotometer uses a quartz prism which transmits UV efficiently. Most portable UV photometers operate at a fixed wave length for a specific gas or vapor in the atmosphere. (2)

2. One of the major applications has been for the detection of mercury vapor which absorbs strongly at 253.7 nanometers. Several portable hand held survey instruments are commercially available. A calibration filter is included in the assembly to serve as a reference standard. Ozone also absorbs strongly in the UV region of the electromagnetic spectrum. Therefore, a fixed wavelength UV photometer can be used for analysis of ozone in the atmosphere. Sophisticated circuits have been developed to increase both the specificity and sensitivity. A stack gas analyzer employs UV absorption spectroscopy to monitor for SO_2, NO and NO_2. Since aromatic ring structures absorb strongly, the portable UV photometer can be adapted to detection of compounds such as benzene, aniline, alcohol, illuminating gas, acetone, pyridine, toluene, xylene, etc. by selection of the maximum absorption band in the UV spectrum. (3)

3. The infrared region can be used as a powerful analytical tool based on its specificity, sensitivity, versatility, speed and simplicity. The spectra provide the information for identifying and quantitating the components present in a solid, liquid or gaseous system. IR radiation is passed through a chamber in which the sample is contained. The beam is then dispersed and detected. Each compound absorbs the radiation in its own characteristic pattern. A graph of absorption versus wavelength can be used to identify the component, and the amount of radiation absorbe is proportional to the concentration of the component. Like the UV photometer, direct reading IR photometers measure absorption at a fixed wavelength which is appropriate for the air pollutant sought. The major application of IR photometry has been for the non-dispersive detection of carbon monoxide. (5, 3)

NOTES Times (elapsed) projected	LESSON OUTLINE
(1:00) (Transition H.-I.) From gas chromatographic to photometric techniques.	I. Photometric Techniques
0:05 Photometry and spectrophotometry are covered in detail in lesson #6 and #7.	1. Photometer vs. spectrophotometer
	2. Uses of U V photometry
	3. IR photometry -- operation and use

TITLE Direct Reading Instruments	LESSON NUMBER 3

J. Aerosol Photometry

1. An aerosol is an airborne solid or liquid which has been dispersed into the atmosphere as a result of man's activities or natural causes. Aerosols are generated by fire, erosion, sublimation, condensation or the abrading action of friction on minerals, metals, organic and inorganic substances in construction, manufacturing, mining, agriculture, transportation and recreational activities.

2. When the particle concentration in a dust cloud is not adequate for direct light absorption (extinction) photometry the light scattering properties of suspended particles can be used. A wide variety of such instruments is available commercially. In common, all incorporate a light source, a sensing zone which contains the sample and a photoelectric receptor, usually a photo multiplier unit, so arranged that the light scattered by the particles at an angle from the incident beam is collected by the receptor. (3)

3. Multiparticle sensing zone instruments with conventional light source are commonly referred to as aerosol photometers or tyndallometers. Forward scattering photometers (Visual 3-8, 3-9) utilize an optical arrangement similar in principle to the dark field microscope. A narrow cone of light passes through the dust cloud, but is prevented from reaching the photo receptor directly by black stops. Only light scattered in the near forward direction from the particulate is sensed. These instruments display either the concentration in terms of mass (mg. /$M.^3$) or number of particles per unit volume. The calibration will vary according to the composition and size distribution found in the aerosol cloud. The primary advantage of forward scattering vs. angular scattering is a relative insensitivity to refractive index and light absorbancy of the particles. (3)

4. Commercial photometers for angular dispersion - usually at 30°, 45° and 90° - from the incident beam also are available. The integrating photometer designed to determine atmospheric visual range has a large detector volume illuminated by a flash lamp. The photomultiplier picks up light scattered by particles throughout the angular sensing zone from 8° to 170° from the light beam. Construction is simple; no lenses are involved; and the instrument is suitable for visibility surveys. Good correlation of visual range and aerosol mass concentration has been demonstrated. (3)

NOTES Times (elapsed) projected	LESSON OUTLINE
(1:05) (Transition I.-J.) From use of photometry for measurement of gases to use for particulates. 0:15	J. Aerosol Photometry 1. General description of aerosol
	2. Light scattering instruments in general
Visual 3-8 Visual 3-9	3. Forward scattering photometers
	4. Angular dispersion photometers

5. For extremely small particles, the condensation nuclei counter has been developed on the principle of adiabatic expansion of a saturated vapor chamber in which water condenses on the particles, thereby enlarging them to detectable size. The counter can be calibrated directly for nuclei concentration as the water droplet size is essentially independent of nuclei concentration and size. (3)

6. Some commercially available instruments are designed to count and size suspended particulate by scattered light pulses. The sample volume is small and a dilution system is built in to reduce optical coincidence of two or more particles to a minimum. The sensing photo multiplier counts the particles as light pulses and the size by pulse height (amount of light). The useful size range includes 0.3 µm. to 10 µm. The major advantage presented by this technique is in the speed with which aerosol size distribution can be obtained. The instrument should be calibrated with the same or closely similar matrix to avoid errors due to different surface composition, refractive index and transparency. (3)

7. Laser beams also have been incorporated in the particle size concentration meters (Visual 3-10). Very small sample volumes (0.05 ml.) are required which allows particle concentrations up to 1000/cm.^{3} to be evaluated without coincidence error. Application to the determination of the surface area of coal mine dusts has been described. (3)

8. The interaction between aerosols and airborne electrical (static) charges provides a basis for two types of direct reading meters. Particulate matter tends to acquire a static charge, and when charged, particles will migrate in an electrical field. In the first type of samples the particles pass through a cloud of unipolar ions to induce a charge on each particle before passing into an electrical field. In this field, the number of charges, and quantity of charge which is directly related to particle size can be measured. Particles in the aerodynamic size range of 0.015 - 1.0 µm. can be determined. The mobility section of the instrument operates as an electrostatic precipitator - high voltage rod suspended in a concentric cylinder - which records the charges as they collect on the charged rod. (3)

NOTES Times (elapsed) projected	LESSON OUTLINE
	5. Condensation nuclei counter
	6. Single particle instruments
Visual 3-10	7. Particle counters using laser beams
	8. Instruments which charge particulates through cloud of unipolar ions

9. The second type of analyzer is based on the interception of ions by the aerosol particles as they flow past by a spiral wire coated with radioactive cobalt (60C source). The electrical current generated by this capturing process then is read-out in terms of particle concentration and mean radius of the particles. A knowledge of the amount of charge on the particles before introduction into the ion chamber must be available as highly charged aerosols cannot be analyzed by this technique. (3)

10. The resonant frequency of a vibrating piezoelectric crystal is changed when the mass increases, i.e., dust deposits on the face of the crystal by electrostatic precipitation or by mechanical impaction. The mass concentration-frequency relationship is linear, and sufficient sensitivity for measuring ambient particulate mass concentration in a 0.5 liter air sample (3 l./min. for 10 sec.) can be attained. (3)

K. Self Test

1. Test instructions and review of questions are presented.

NOTES Times (elapsed) projected	LESSON OUTLINE
	9. Instruments which intercept ions by particulates as they flow past cobalt wire
	10. Collection on piezoelectric quartz crystal
(1:20)	
Self Test	K. Self Test
0:10	1. Instruction and review
(1:30)	

SELF TEST	Page 1 of 2
LESSON TITLE Direct Reading Instruments	LESSON NUMBER 3

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

[✓ T] F — a. Analytical methods based on liquid reagent systems are inherently more accurate than those methods based on solid reactants due to greater precision and accuracy of color measurement carried out in liquid systems.

T [✓ F] — b. The application of detector tubes is governed by the limitations imposed by integrated sampling unless the tubes are recalibrated.

[✓ T] F — c. No more than 5% leakage is allowed for sampling pumps used with detector tubes.

T [✓ F] — d. Most sampling pumps used with detector tubes can be interchanged.

T [✓ F] — e. Most detector tubes are specific for the trace gas or vapor for which they are intended.

2. What are heat of combustion type devices usually used for?

See D.

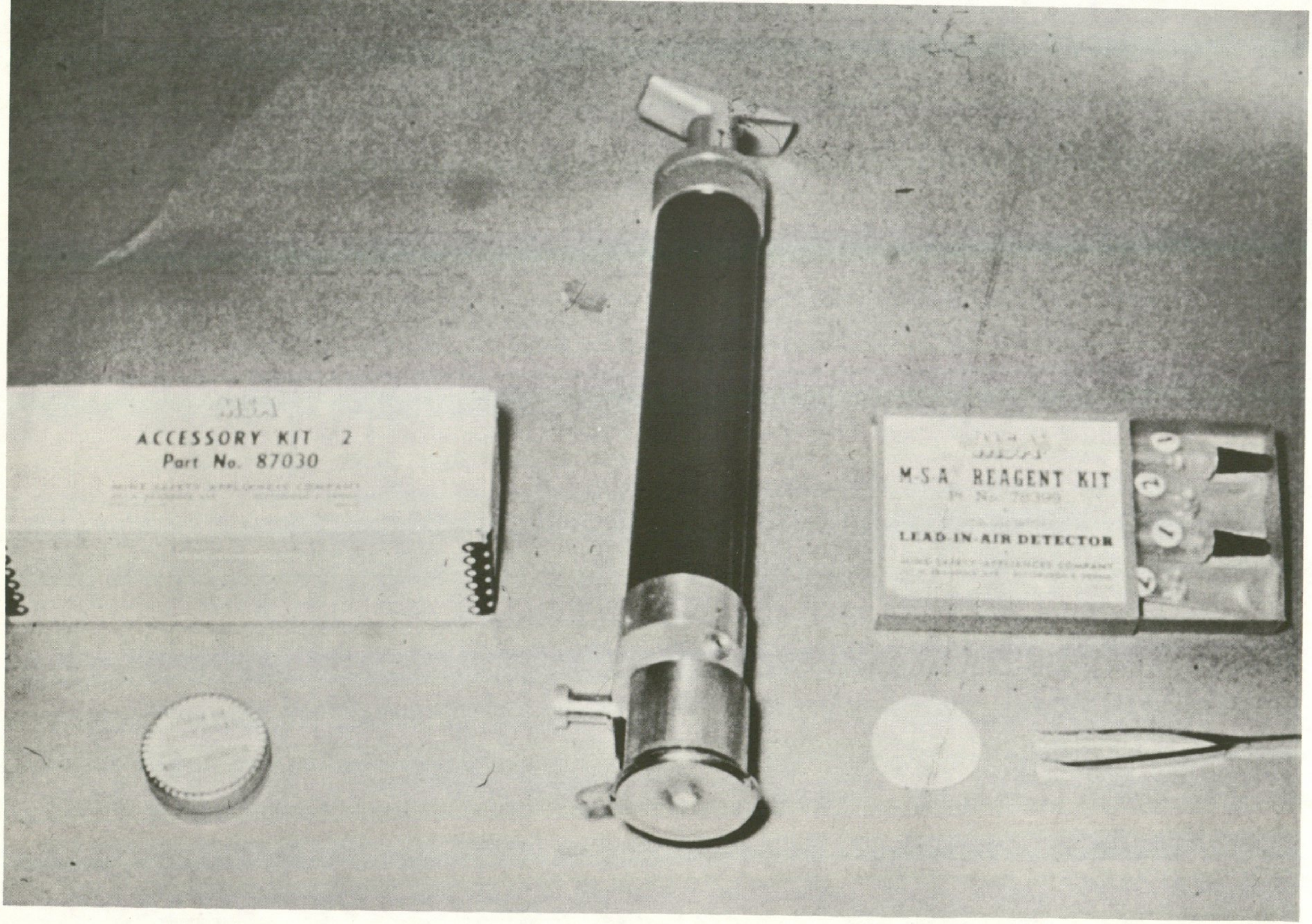
SELF TEST	Page 2 of 2

LESSON TITLE	LESSON NUMBER
Direct Reading Instruments	3

3. Very generally, how is light scattering used in aerosol photometry?

See J. 2 - J. 4

VISUALS, TABLES, FIGURES AND EXHIBITS



Liquid Reagent Kit

Illustration Courtesy of Mine Safety Appliances Company
Pittsburgh, Penna.

Visual 3 - 1

OPERATING INSTRUCTIONS FOR
THE GASTEC ANALYZER

SAMPLING & MEASUREMENT

1. Break both tips of a fresh analyzer tube by bending each tube end in the tube tip breaker.
2. Insert the tube into the pump so that the arrow points toward the pump.
3. Make certain the pump handle is all the way in. Align the red dots on the shaft and back plate of the pump.
4. Pull the handle to desired stroke (50 ml – 1/2 stroke, 100 ml – full stroke).
5. Read concentration at end of color stain when staining stops. Turn the pump handle slightly before returning it.
6. If the indication is low, take additional samples by making a number of strokes until color stain attains the lowest scale. Obtain true concentration by dividing the reading by the number of strokes made.
7. If the gas concentration is expected to be greater than indication on the tube, stop the handle at the half stroke (50 ml) and obtain true concentration by doubling the reading.

SEE WHITE TECHNICAL INFORMATION SHEET FOR EACH TUBE IN BOX

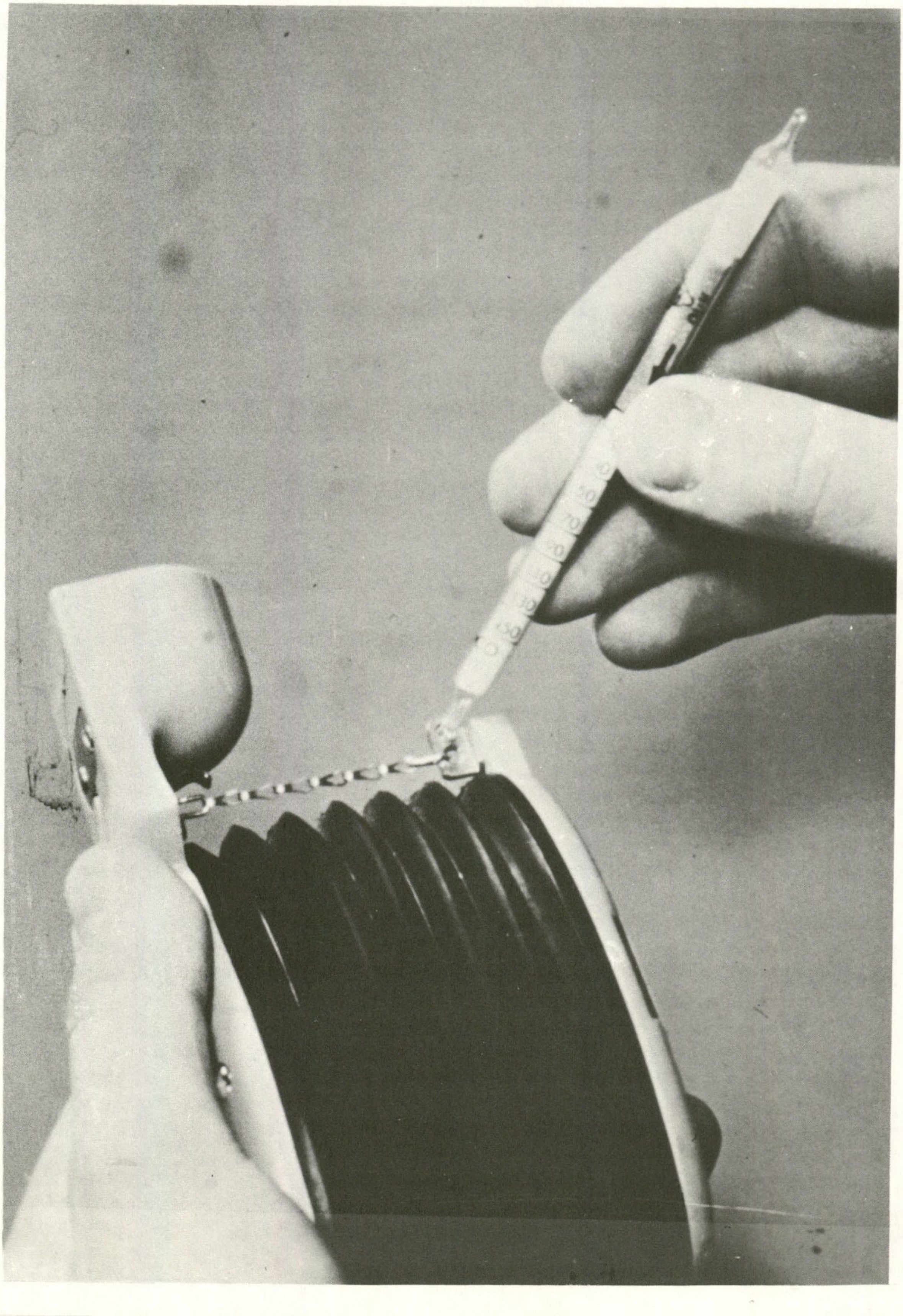
TEMPERATURE CORRECTION

1. No temperature correction is normally needed at tube temperature of 0° – 40° C (32° – 104° F).
2. Where temperature correction is needed, a table is provided on the box of analyzer tubes. The indication on the tube must be corrected according to the table.

Detector Tubes with Pump

Illustration Courtesy of Bendix
National Environmental Instruments, Inc.
Warwick, Rhode Island

Visual 3 - 2



Breaking Tip of Indicating Tube

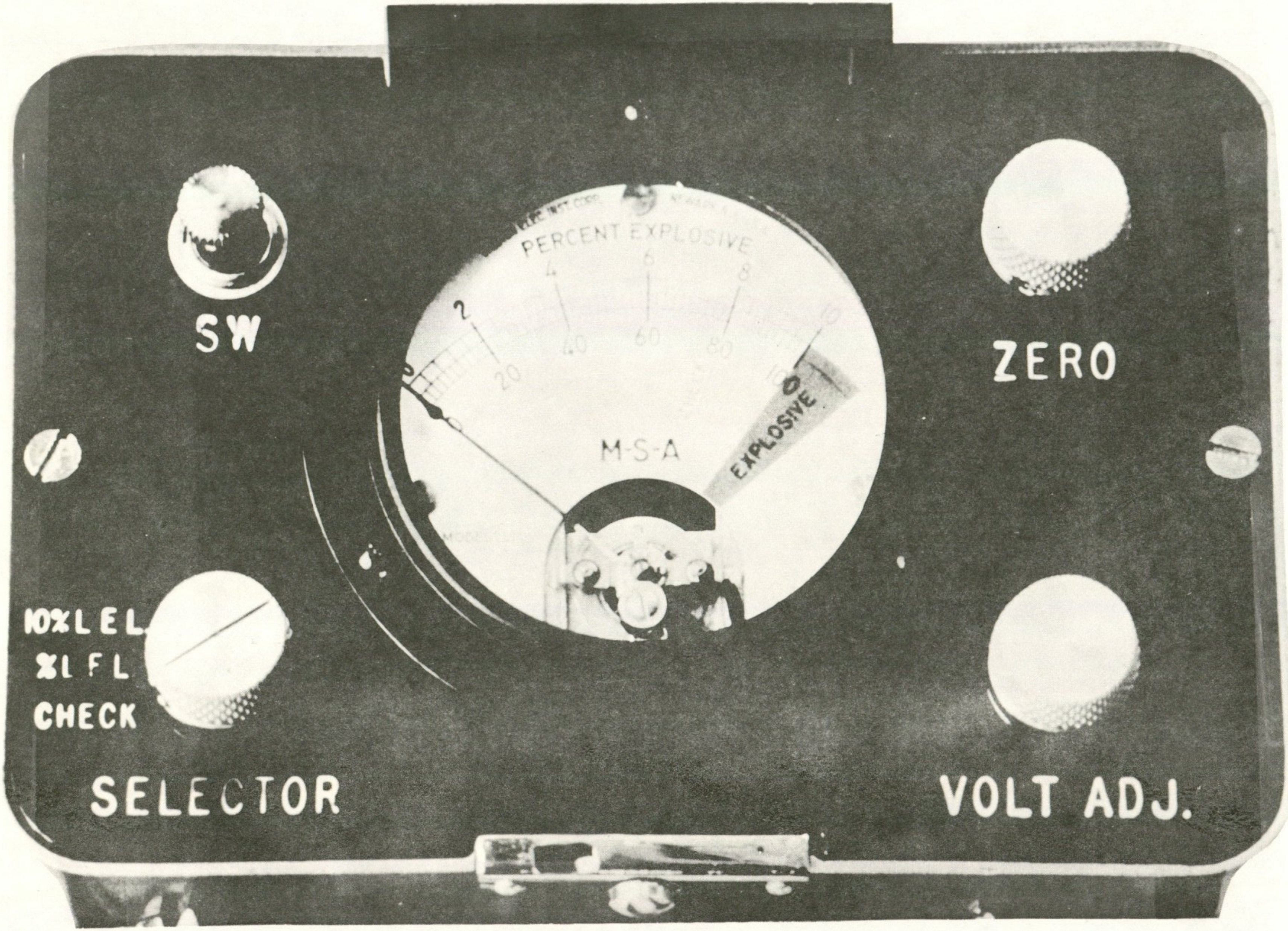
Illustration Courtesy of Mine Safety Appliance Company
Pittsburgh, Penna.

Visual 3 - 5

TYPICAL SHELF LIFE OF AN INDICATOR TUBE

TEMP °C	SHELF LIFE
25	> 2 YEARS
50	> 1/2 YEAR
100	1 WEEK
150	1 DAY

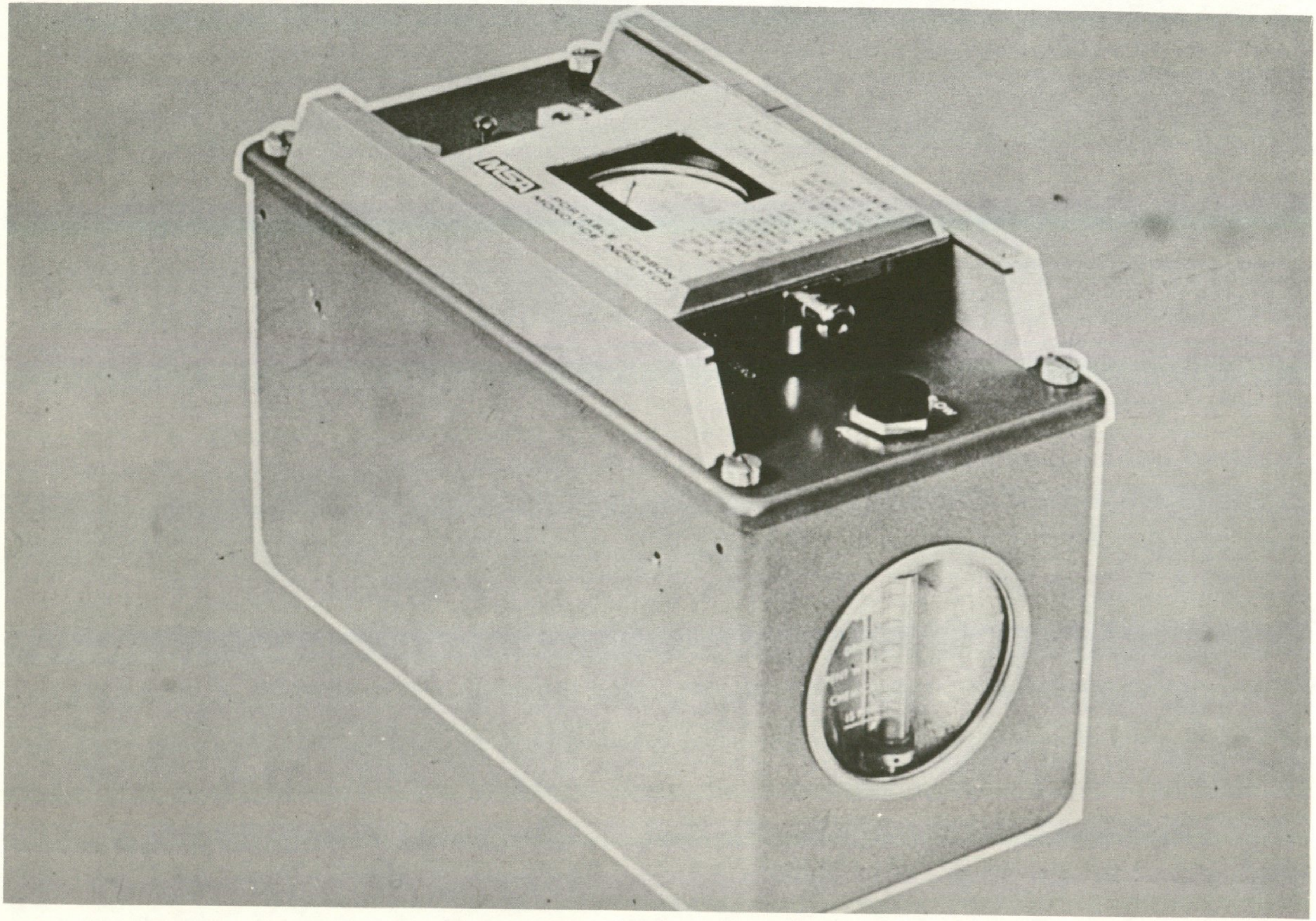
Visual 3 - 4



Combustion Gas Meter

Illustration Courtesy of Mine Safety Appliances Conpany
Pittsburgh, Penna.

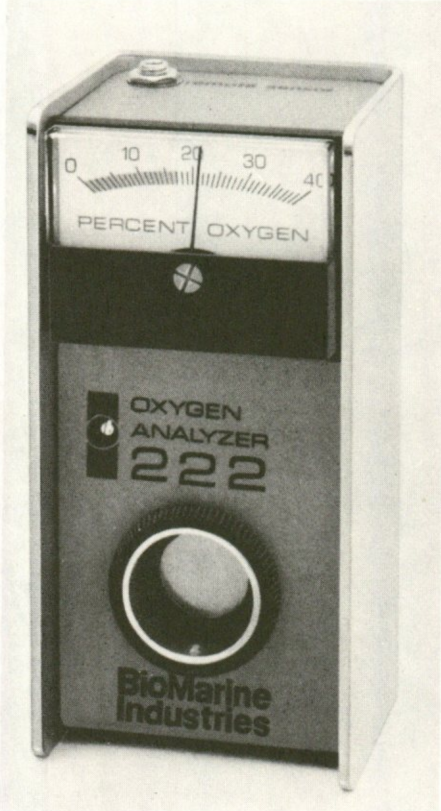
Visual 3 - 5



Direct Reading C O Indicator

Illustration Courtesy of Mine Safety Appliance Company
Pittsburgh , Penna.

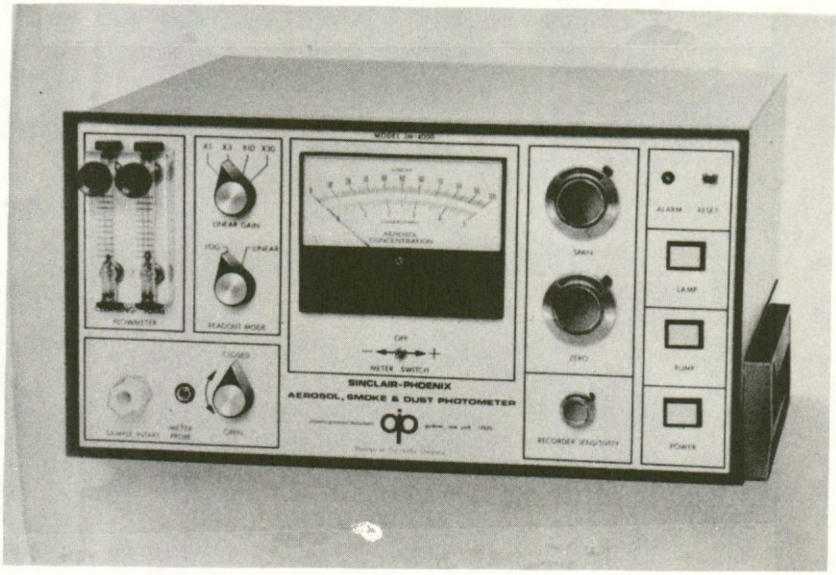
Visual 3 - 6



Direct Reading O Meter Using Coulometry

Illustration Courtesy of Biomarine Industries Inc.
Devon, Pennslyvania

Visual 3 - 7



Forward Light Scattering Photometer

Illustration Courtesy of Phoenix Precision Instrument
Gardiner, New York

Visual 3 - 8

Forward Light Scattering Photometer

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

Visual 3 - 9

Particle Counter Using a Scanning Laser Beam

Illustration Courtesy of Nuclepore Corporation
Pleasanton, Cal.

Visual 3 - 10