MANUAL OF RECOMMENDED PRACTICE FOR COMBUSTIBLE GAS INDICATORS AND PORTABLE, DIRECT READING HYDROCARBON DETECTORS

first edition

AMERICAN INDUSTRIAL HYGIENE ASSOCIATION

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MANUAL OF RECOMMENDED PRACTICE FOR COMBUSTIBLE GAS INDICATORS AND PORTABLE, DIRECT READING HYDROCARBON DETECTORS

First Edition

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FOREWORD

This manual was prepared to summarize the techniques for field use of the direct reading combustible gas indicator, the most widely used and misused of this class of instruments. Therefore this manual lists many of the practical types of situations encountered along with the misconceptions that have been observed. In addition the measurements are placed into context with the Threshold Limit Values as well as with explosive limits. This necessitated an introduction to instruments that are sensitive in the TLV levels. Field checks and means to verify the instrument are described and designed for every user. Recognition of the instrument's capabilities and limitations should enable the user to proceed with competence and confidence.

Most of the numerical data reported in industrial hygiene literature has been given in metric units. As a result, it is expected that few changes will be made in the basic presentations. Where English units have been previously used, both the English and metric systems will be noted in this work. References will be made and conventions adopted from the American National Standards Institute, Standard for Metric Practice, ANSI Z210.0 (ASTM E380-76).

Many of the examples of instrument misuse would not have been included in this manual had not the members of the committee actually witnessed a specific misuse. These experiences brought together by the committee are limited. Expansion of these experiences can be achieved by drawing from individuals outside of the committee. It is for this reason that the committee welcomes further information of a nature that would make subsequent revision of this manual more meaningful.

It is the committee's intention that the basic outline of this manual be a valuable guide in completing subsequent related manuals. Thus suggestions regarding the organization of this manual will assist future committee activities.

The large number of references cited in this manual are designed to provide both the reader and the instrument user with additional information about an instrument and conditions of its use. The most common reference available to an instrument user is the manufacturer's instruction manual. This work is not intended to be a substitute for this manual, which focuses on the mechanics of instrument operation, but rather, it is an in-depth presentation of practical instrument applications.

A second need for adequate reference material is best illustrated in the area of statistics, which occupies only a small portion of this manual. One chapter touches upon the variation involved in the use of instruments and their measurements. It is intended that both user's experience and guidance from this text can create an awareness of the importance of variations. The reference list then provides a means for a more extensive statistical follow-up. Certainly the literature available for a study of statistics is many orders of magnitude greater than can be covered in this manual. To meet the purposes of this publication, statistics and other areas are interfaced, not enlarged upon.

VAB.0001024178

PREFACE

The Committee on Gas and Vapor Detection Systems was preceeded by the "Ad Hoc Committee for Direct Reading Gaseous Detecting Systems". The committee functioned at that time as a joint committee with the American Conference of Governmental Industrial Hygienists. The Group published the *Direct Reading Colorimetric Indicator Tubes Manual.* Following this publication, the committee was reorganized as a standing technical committee of the American Industrial Hygiene Association. This manual was initiated during the American Industrial Hygiene Conference in Atlanta, Georgia, May, 1976. It is to be the first in a series on direct reading instrumentation.

The combustible gas indicator was chosen to be the first in the series of instruments since it is probably the most used – and misused – of the direct reading devices. Their current application in industry is greatly different from their use in the mines for which they were first developed. Therefore an introduction is made to models sensitive in the TLV and ppm ranges. Other terms may be applied to these devices. "Hydrocarbon analyzers" is one such term. These instruments are often used by many who are inexperienced and unfamiliar with their limitations. Even users who possess a high level of technical skill, such as professional industrial hygienists, fire prevention groups as well as technicians, may not always recognize the limitation of the device used. Committee members have related many examples of unwarranted and also dangerous conclusions derived from data obtained during improper use of these instruments. It is hoped that this manual will relate enough of these experiences to assist the new user.

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Committee:

1976 [A]Joseph W. Klinsky*, Chairman
1976 Newell E. Bolton*, Ph.D., Adm. Board Representative
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1976 [A]Patrick R. Frazee*
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ACKNOWLEDGMENTS

A manual of recommended practice, such as this one, is truly a cooperative work with input from a great number of people. Appreciation is expressed directly to the committee members as listed. To these we add not only those consultants who are listed, but also many contributors too numerous to mention. Their experiences are most vital to illustrate various specific points.

Manufacturers have contributed much to the report, both by the photographs and the direct contribution of several committee members. Indirect assistance has been given through instruction manuals. These have not been specifically quoted, but form an enormous fund of knowledge. When contacted by phone, manufacturers provided information freely. Their research has provided today's users with much more sophisticated instruments than were available even a short time ago.

The vision of management and wives of the committee members and contributors has been far seeing enough to support this work, an effort that will probably help them only indirectly, or at a philosophical level. Their recognition of the importance of advancing industrial hygiene has made this publication possible.

During the period of writing, committee members and assignments have changed. Therefore, a complete roster is listed, including members that have retired prior to the 1977-1978 year. The list, together with the date the assignment was accepted, follows:

1976	Joseph W. Klinsky*, Chairman until May, 1980, Editor of the Manual.
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VAB.0001024181

TABLE OF CONTENTS

I. PURPOSE 1
NEEDS
1. Introduction
2. Information Gaps
3. References
4. High Sensitivity Indicators
5. Ranges
6. Unusual Applications
SUMMARY

II. COMBUSTIBLE GAS INDICATORS 3
INTRODUCTION
1. Miner's Lamps
2. Early Hot-Wire Indicators
3. Transitions
4. Cautions and Examples
5. Applications
DEFINITIONS
1. Combustable Gas Indicator
2. Flammable
3. Explosive Limits
4. Threshold Limit Values (TLV's)
5. Gases and Vapors
6. Fume

III. OPERATING PRINCIPLES 7
INTRODUCTION
MAJOR PARTS
1. Schematic
2. Orientation
a. Off Position
b. Sensor Systems
c. Battery Check
d. Scale Select
e. Zero and Span Adjust
f. External Connections
3. Summary
SENSOR SYSTEMS
1. Overview
2. Hot Wire
3. Catalytic Combustion
4. Diffusion vs Flow Through
5. Solid State
6. Flame Ionization
7. Photo Ionization
8. Infra Red
9. Other

IV. FIELD CONSIDERATIONS 15
INTRODUCTION
DEFINITIONS
1. Ladder for TLV and LEL Values
2. Description
3. Other Characteristics
4. Hazard Potential
PERSPECTIVES
1. Scale of Concentrations
2. Applications, Toluene
3. Applications, Other
MEASUREMENTS
1. Range of Measurements
2. Examples
3. Proportionality
4. Scales
5. Examples
6. Non Proportionality
LOWER LIMITS OF DETECTION
1. Introduction
2. Scales
3. Logarithmic Read Out

V. USAGE 19
INTRODUCTION
INSTRUMENT INTEGRITY
1. Instrument Controls Not Set in the Proper Operating Mode
2. Perspectives Applied from the Hazard Ladder
3. Sample Tube Free of Leaks
4. Intrinsic Safety
FIELD OPERATIONS
1. Temperature
2. Humidity
3. Condensation
4. Zero Setting Within Contaminated Atmospheres
5. Zero Adjustments
6. Liquid Contamination
7. Oxygen Depleted Atmospheres
a. Without Inerting Gas, Over the Upper Explosive Level
b. With Inerting Gas
8. Oxygen Enriched Atmospheres
9. Hypobaric, Conditions of Reduced Pressure
10. Hyperbaric, High Pressure Applications
11. Group A, B, C & D Atmospheres
12. Use in the Presence of Halogenated Hydrocarbons
13. Use with Other Compounds
14. Use with Inorganic Compounds
15. Unusual Oxidizers
16. Use in Mixtures

VI. MAINTENANCE 29
INTRODUCTION
1. General
2. Record Keeping
MAINTENANCE
1. Manufacturer's Instructions
2. Interchangeability of Components and Parts
3. Maintenance of Components and Parts
4. Field Servicing

VII. CALIBRATION 33
INTRODUCTION
1. General
2. Record Keeping
VERIFICATION
1. General
2. Leak Test
3. Flow Rate
4. Span Gas Calibration
5. Batch Calibration
6. Dynamic Systems
CALCULATIONS
1. Introduction
2. Equations
3. Tables and Sources
4. Mixtures

VIII. MEASUREMENT PROPERTIES 45
INTRODUCTION
1. Variations
2. Mistakes
3. Error

VAB.0001024182

ACCURACY, BIAS AND PRECISION
1. Introduction
2. Measurements
a. Accuracy, Bias and Precision, Illus. 1
b. Accuracy, Bias and Precision, Illus. 2
INHERENT INSTRUMENT VARIABILITY
1. Examples
2. Linear Response Curves
3. Nonlinear Response Curve
4. Noise Level
5. Sensitivity
6. Other Errors
TIME RELATED RESPONSE
1. Theoretical Concentrations
2. Measured Concentrations
3. Definitions
CONCLUSIONS

IX. SUMMARY OF LIMITATIONS 49
INTRODUCTION
SUMMARY
1. Quantitative Characteristics
2. Halogenated Hydrocarbons
3. Purpose of Use
4. Flash-back Arrestors
5. Intrinsic Safety
6. Contaminants
7. No Interchangeable Parts
8. Maintenance
9. Verification
10. Zero Drift

X. APPROVAL AND CERTIFICATION 51
INTRODUCTION
GOVERNMENTAL AGENCIES
1. National Institute for Occupational Safety and Health (NIOSH)
2. Mining Enforcement Safety Administration (MESA)
2a. Mining Safety and Health Administration (MSHA)
3. Environmental Protection Agency (EPA)
4. United States Navy (USN)
5. United States Coast Guard (USCG)
ORGANIZATIONS
1. Factory Mutual Research Corporation (FM)
2. Instruments Society of America (ISA)
3. Underwriters Laboratories (UL)

XI. REFERENCES 53

XII. INDEX 55

VAB.0001024183

I. PURPOSE

NEEDS

1. As the need for the use of direct reading instruments becomes greater, individuals with a broad range of professional and nonprofessional backgrounds may be required to use them. This manual is designed to provide information which would allow instrument users to become skillful in the operation of combustible gas indicators. For a user with some technical background, it should provide a means to use the instrument quickly and with good understanding. To the non-technical user, the manual provides comprehensive information essential to proper instrument use. For any user, the guidelines provide a perspective and explanation of instrument pitfalls which are not often explained but do have disasterous consequences if not recognized and observed.

2. Information gaps exist in the available literature on combustible gas indicators. This manual is designed to provide information in these areas. Some limited illustrations include the following:

   a. Few instruction manuals that describe the operation of the indicator measuring from 0 to 100% LEL include a statement of the lower limit of detection typical of that instrument. This is an important property which most of chapter IV on Field Considerations addresses. (Reference 14)

   b. Advanced texts on Industrial Hygiene, such as Industrial Hygiene and Toxicology by F. A. Patty, provide in-depth interpretation and advanced techniques for the use of combustible gas indicators. The problems associated with measurements made before entering confined spaces, the complications involved with measurements where there is a lack of oxygen, and other measurement difficulties are described.

   c. Information is presented on the need for instruments to be calibrated, sample tubing not leaking, etc.

   d. Instrument, operator and environmental variations must be considered. Chapter VIII concerns error analysis and applies the important concept of variability to the problems of reading the indicator during calibration and field measurements.

3. References are cited where information is available to satisfy needs beyond the scope of this manual. One of the best sources is the reference published by the National Institute for Occupational Safety and Health (NIOSH) entitled "Evaluation of Portable Direct Reading Combustible Gas Indicators" (Reference 5). That publication describes results of tests carried out on several instruments including quantitative results on drift, stability, circuitry, etc. Chapter X, Approval and Certification, provides information on other organizations which carry out tests on combustible gas indicators.

4. The need for instruments that have a greater sensitivity than the traditional combustible gas indicator has necessitated the use of amplifiers. For the hot wire types and most of those with catalytic sensors, increasing measurement sensitivity at the low end of the range introduces response variability which limits application of the instrument. This is due to several factors. One is simply that changes in moisture content of sampled air also has an effect. Variations in air flow across the sensor surface becomes important and changes affect the results. For the catalyst type of sensor, the temperature changes that are measured are so small that other effects, such as the variation in air temperature of the sampled air, mask the readings.

5. In general, the instruments that respond in the parts per million range have sensors with very different response characteristics than the "work-horse" instruments previously used to detect combustibles in the explosive range.

6. The combustible gas indicator may be used under conditions that vary substantially. Common examples include measurements made above the upper explosive limit (UEL), at low oxygen levels (inert atmospheres), to determine leaks, for fugitive emissions, surveys, etc. One unique type of meter has been designed to measure combustible gases where the oxygen level is substantially below normal concentrations. These and other applications are described. The experiences of others are made available so that they do not have to be inadvertently repeated.

SUMMARY

This AIHA manual provides information on the following:

a. Instrument applications, including examples.
b. Orientation for the manufacturer's directions and operating principles.
c. References to other technical manuals and relevant information.
d. Information that is useful for choosing an instrument appropriate for a given use.
e. Functions and limits of the tests and test programs that have been carried out by the various agencies and organizations that certify instruments and provide specifications for their use.

VAB.0001024184

II. COMBUSTIBLE GAS INDICATORS

INTRODUCTION

1. *Miner's Lamps*

Perhaps underground miners were among the first to become aware of the need for a device to detect the presence of gases in concentrations which were hazardous in some manner. In their environment a host of gases could be present. However the miner would normally be interested in a limited number of these gases and their variations with respect to "typical" air. The gases might include methane, carbon dioxide, carbon monoxide, lack of oxygen and others. These terms are the ones in use today, and not the colorful ones such as "black damp", and "white damp" of yesteryear. Of these gases methane has often been present in sufficient quantities to explode. It is not a systemic toxicant and has no warning odor. Explosive levels can accumulate before a worker realizes the potential risk. With high methane concentrations, any source of ignition, including those in the original miner's lamps worn at the time, could readily set off an explosion. It is in this setting that the use of the first "combustible gas indicator", the Davie's Lamp, provided a significant step forward in mine safety. The visible characteristics of the flame of the Davie's Lamp could inform the experienced user of much more than just the presence of methane. In fact, refinements of the Davie's Lamp are in use today.

In this manual we will focus only on the electronically operated instruments used for detecting the presence of combustible gases.

2. *Early Hot-Wire Indicators*

Early developments in portable direct reading instruments included the first modern direct reading combustible gas indicator. This type of instrument worked on the principle that a heated wire located in the gas sample stream became hotter when the composition of the gas approached a measurable fraction of the combustible level. As resistance of the wire changed with temperature, the effect was measured electrically. These temperature changes were detected by an electrical unbalance in a Wheatstone bridge circuit. This device was introduced shortly after the turn of the century. The success of the hot wire type of instrument has been demonstrated by the fact that it has been the "workhorse" of the industry. It is still being used, especially in mines. Only recently has this type of instrument begun to be supplemented by other types of devices.

3. *Transitions*

The success of the hot wire combustible gas indicator in mines eventually brought it out onto the surface for use in other industries. It is this new role to which this manual is addressed. The new industrial atmosphere is very different from the mine environment. Thus we should consider the following questions related to the applications and limitations of the instrument under these new conditions.

a. Does one interpret meter response the same for any gas as for methane? If not, how does one obtain meaningful information?
b. Are there any gas concentrations of importance which are below the range of response of the meter? If so, what are these examples?
c. Do some industrial gases suppress instrument response, resulting in erroneous readings? If so, which ones and how?
d. Are there some situations in which certain models of combustible gas indicators can initiate an explosion? If yes, which ones and under what circumstances?
e. What new principles are being applied to the design of the new models of combustible gas indicators? How do they differ in their response and applications?

4. *Cautions and Examples*

Limitations of some combustible gas indicators exclude their use in many situations, however, new types are available. As with the original type, these still measure the ability of a mixture of gas or vapor in air to burn. Whatever the type of sensing mechanism, similar information will be obtained for each. Most precautions for use apply to all combustible gas types of instruments.

One traditional use of combustible gas indicators is to detect leaks in gas heating systems, for example propane. Resulting measurements can provide information of a significant leak and of the potential for a fire to occur where combustible vapors are released. At a small operation, a minor explosion alerted the group to a problem. A combustible gas indicator was used to detect the path of the gas escape. Once traced to its source, the situation was readily corrected.

Combustible gas indicators are routinely used by personnel in refineries and petrochemical plants to determine the potential for a fire or explosion in areas where work is to be carried out. A permit to allow work to proceed will not be issued until a gas test is carried out and the risk is judged to be acceptable, based in large measure on the combustible gas indicator readings.

5. *Applications*

Chapter V (Usage) is dedicated to the specific use and application of combustible gas indicators. One should refer to this section for more examples than have been given to this point. Once the cautions are defined and

VAB.0001024185

recognized by the user, the indicator will become most valuable for detecting a wide variety of combustible gases and vapors.

DEFINITIONS

1. *COMBUSTIBLE GAS INDICATOR (See Figures II - 1 through II - 4):* Combustible gas indicators are direct reading field instruments that measure those pollutants in the gas phase which "will burn". This definition must extend to and apply to the gases that may be present when such instruments are relied on during industrial hygiene operations. Therefore the use and discussions include the TLV and ppm regions. Other texts may use the terms "heat of combustion instruments" or "hydrocarbon analyzers" for some of these devices. The gases reviewed are therefore not limited to the vapors from combustible and flammable gases as defined by NFPA in Codes 30 and 325M (Reference 1).
2. *FLAMMABLE:* This term is derived from the Latin and French word "flammere" meaning to burn. It has been universally used to refer to materials which will burn. This usage has been standardized since World War II. Prior to that, the term "inflammable" had also been used commonly. Since the prefix meant either *non* flammable or *highly* flammable according to the interpretation of the prefix *"in"*, confusion resulted. To eliminate this ambiguity and prevent accidents due to the misunderstanding of terms, the U. S. Bureau of Mines conducted a series of demonstrations on the control of flammables. They stressed the use of the term "flammable" without any prefix.
3. *EXPLOSIVE LIMITS:* In situations where gases or vapors form explosive mixtures with air, there is a minimum concentration of vapor below which the flame does not propagate when in contact with a flame or surface that is above its ignition temperature. This minimum concentration is known as the "Lower Explosive Limit" (LEL) or as the lower flammable limit (LFL). There is also a maximum proportion of gas or vapor in air, which, if ignited, will not propagate flame, although the flame may burn at the gas-air interface. This maximum concentration is known as the "Upper Explosive Limit" (UEL), or upper flammable limit (UFL). In popular terms, a mixture below the LEL is too "lean" to burn. Above the UEL, the mixture is too "rich" to burn or explode. At the LEL the combustible gas indicator reads 100% LEL, by definition and design. The gas concentrations can be expressed as either % gas in air or % LEL for concentrations below the LEL.

   The concentrations that lie between the LEL and UEL will explode with vigor. If the mixture is large and near the optimum concentration the resulting explosion may be devastating.

   A miniature example of the "gentle" explosion at the LEL for volatile liquids is demonstrated in the "Flash Point Test". In this test a small amount (e.g. 50 mL or 2 ounces) of solvent half fill a covered cup. The contents are gradually warmed, evaporating progressively more liquid. At the same time a small flame (hotter than the ignition temperature) is passed over the opening in the cover. When the temperature is reached where the evaporating vapor fills the space to the LEL concentration, the flame propagates (explodes). The temperature at which this occurs is known as the Flash Point (Reference 1).
4. *THRESHOLD LIMIT VALUES (TLV's):* TLV's refer to airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be exposed eight hours a day for a forty-hour week over a working lifetime without adverse effect. To meet these requirements, the concentrations of gases vary from 1000 ppm down to below 0.1 ppm. (Reference 2)
5. *GASES AND VAPORS:* All discussions in this manual apply to the measurement of materials in the gaseous state. If the material is a gas in its normal physical state at room temperature and atmospheric pressure, it is called a gas. If it is normally a liquid at these conditions, the material in the gaseous state is called a vapor. Furthermore, a gas may be defined as a formless fluid which tends to occupy an entire space uniformly at ordinary temperatures and pressures. (Reference 15).
6. *FUME:* This term will not be used in this manual. A dictionary definition of common usage defines fume as "a smoke, vapor, or gas, especially when irritating (e.g. engine exhaust)". This application is nonspecific and can refer to more than one state. Thus non-technical usage would not preclude describing vapors from a tank. A technical definition of fume is "the particulate resulting from the evaporation of hot metal". The indicators discussed reject such particulate essentially completely. (Reference 15)

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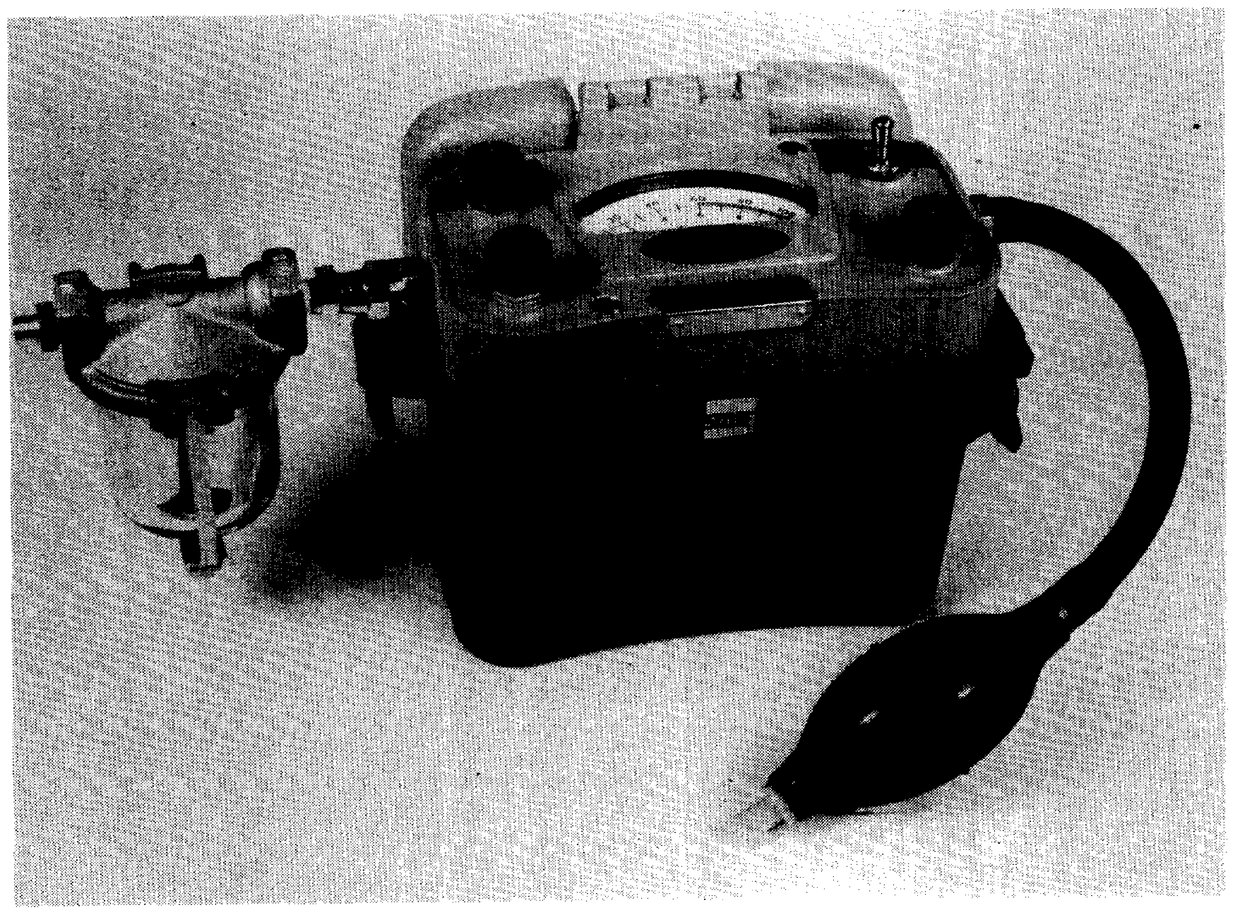

Figure II - 1 — Example of combustible gas indicator, with dual ranges, 0 to 100% LEL and 0 to 10% LEL, a dryer/trap is provided. (Photo courtesy SCOTT, Vapotester, Model D-16.)

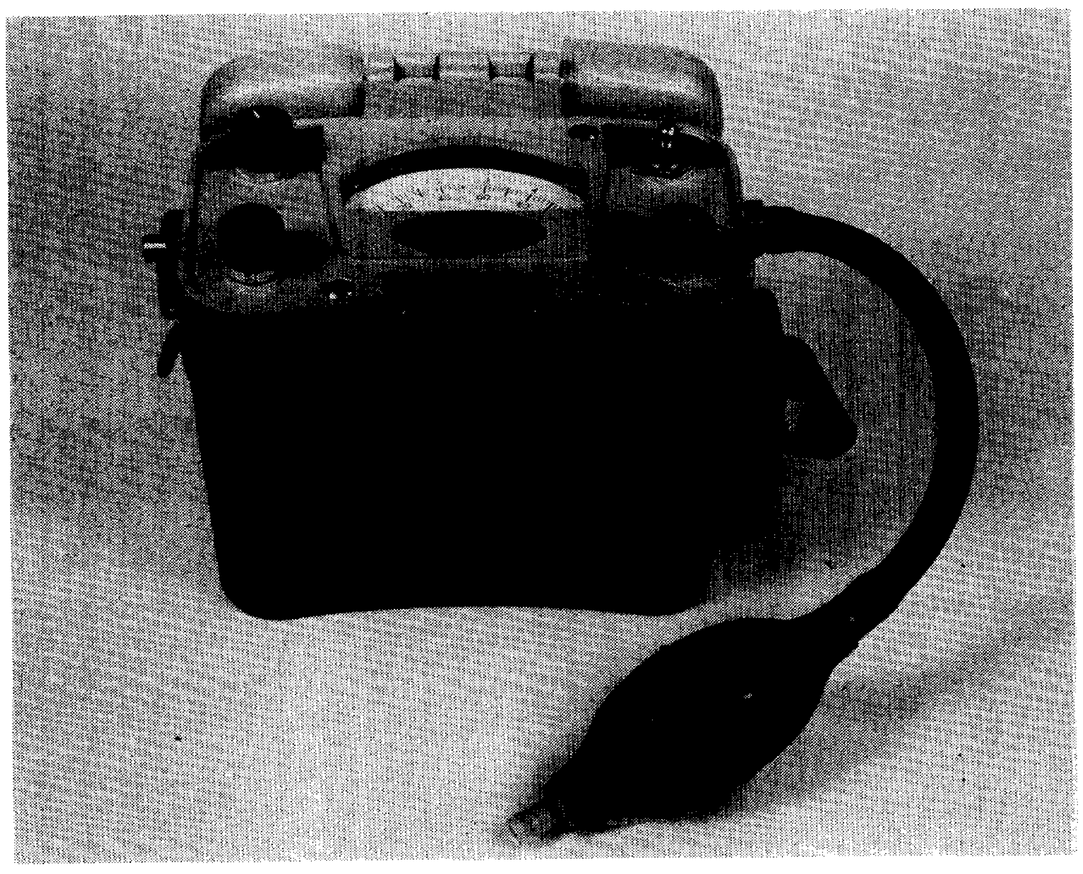

Figure II - 2 — Example combustible gas indicator, dual range 0 to 100% LEL and 0 to 10% LEL. (Photo courtesy SCOTT, Vapotester, Model D-15.)

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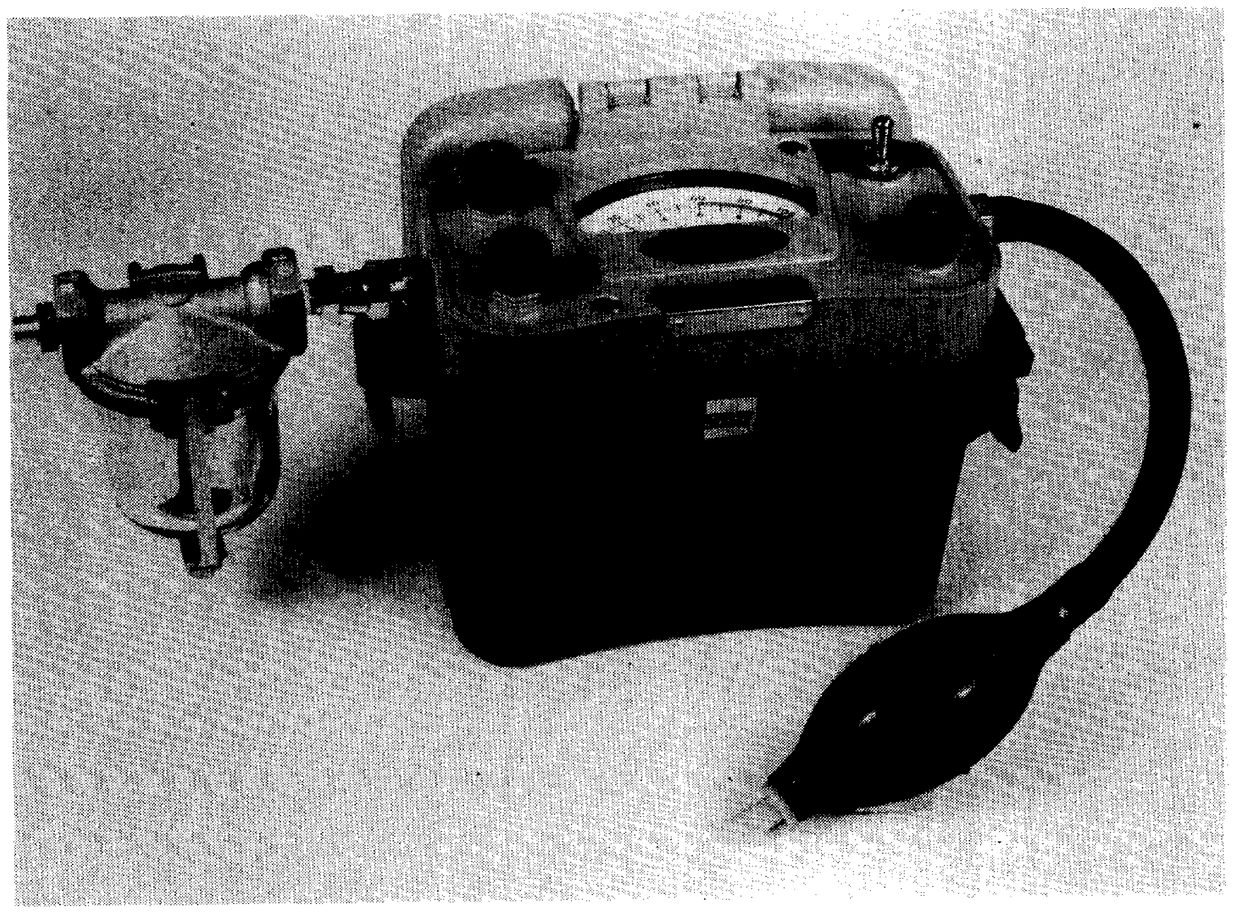

Figure II - 1 — Example of combustible gas indicator, with dual ranges, 0 to 100% LEL and 0 to 10% LEL, a dryer/trap is provided. (Photo courtesy SCOTT, Vapotester, Model D-16.)

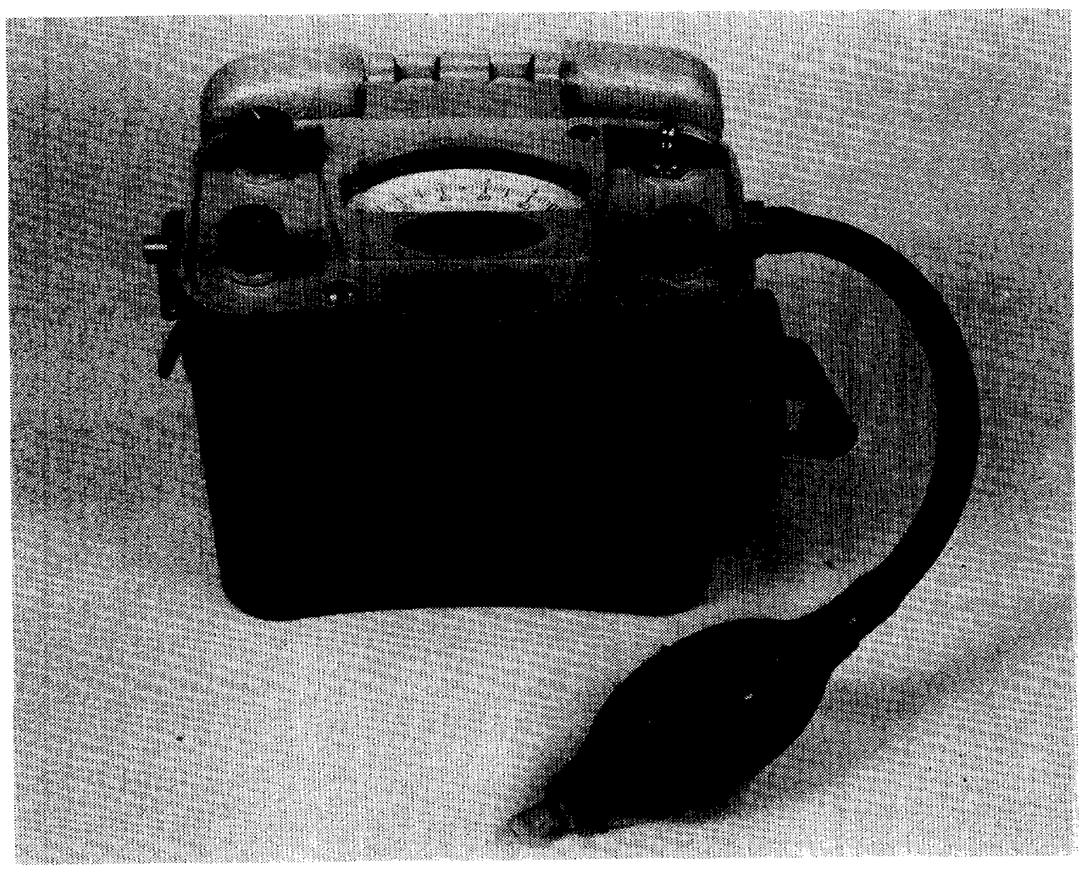

Figure II - 2 — Example combustible gas indicator, dual range 0 to 100% LEL and 0 to 10% LEL. (Photo courtesy SCOTT, Vapotester, Model D-15.)

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III. OPERATING PRINCIPLES

INTRODUCTION

A variety of instruments for measuring combustible gases and vapors are on the market today. These provide the industrial hygienist and technicians a choice of types and styles, many of which can be employed to measure the same gases. Some confusion may arise. Many vendors describe instrument parts with different terms for the same component, or the same terms for different components. It is for these reasons that this chapter will begin with a description of the major parts of these instruments to establish a "common denominator" for discussing these components. Most direct reading instruments follow the general pattern that is described, though the details or the parts may appear to vary widely from one instrument to another.

MAJOR PARTS

1. The configurations of combustible gas and vapor detectors currently available are sufficiently varied so that a schematic diagram is needed to show basic parts common to all. Such a sketch is shown in Figure III-1. Although simplified, it will provide an outline for the parts and functions to be described.

   a. *Instrument Case:* The box that holds the various components.

   b. *Sensor:* The mechanism that responds to a chemical or physical property associated with the materials being tested. An electrical signal that varies with the material concentration is generated, transmitted to the electronics section, and measured.

   c. *Electronics:* The amplifier and associated circuitry necessary for the instrument to function. It receives the signal from the sensor and displays it in a visual and meaningful manner.

   d. *Function Switches:* These are the switches and dials necessary to adjust the electronics properly, to operate the detector and to process the signal.

   e. *Readout:* The display or meter dial by which an operator can see and interpret a signal, read a concentration, etc.

   f. *Power Source:* The source of power which operates the electronics, pump, sensor, and other accessories.

   g. *Probe:* An extension which enables measurement at a desired point.

   h. *Pump:* Sample air is drawn to the sensor by a pump in most instruments. Devices with a diffusion head (sensor) do not normally require a pump.

2. This section provides some orientation for the first use and application of the combustible gas indicator. It provides information which supplements the manufacturer's instructions.

   a. Start *every* use of the instrument in the *OFF* position. Before starting *and* after finishing the use of the instrument, switch and control settings should be in position as follows:
      1) All *On-Off* switches should be in the *off* position.
      2) The *Scale Select* switch should be in the *least sensitive* position.
      3) All accessory tubing, cables, etc. should be properly connected or disconnected as appropriate.
      4) Note any possible damage marks, bent parts, etc. Repair or replace.
      5) Connect or disconnect battery charge connections as indicated.
      6) For long term shut down, follow the manufacturer's recommendations. Battery removal from instruments may be indicated. Some types of sensor cells and other parts may require special handling.

   b. As shown in Figure III-1, the probe is held in the atmosphere to be tested. The "air" is drawn by the pump through the chamber that houses the sensor. An electrical signal occurs when a combustible gas or vapor comes in contact with the sensor. That signal is transmitted to the electronics section and, in turn, the readout. Several typical sensors are described later in this chapter. It is necessary to keep the sensor clean, thus a particulate filter is placed ahead of it and in the

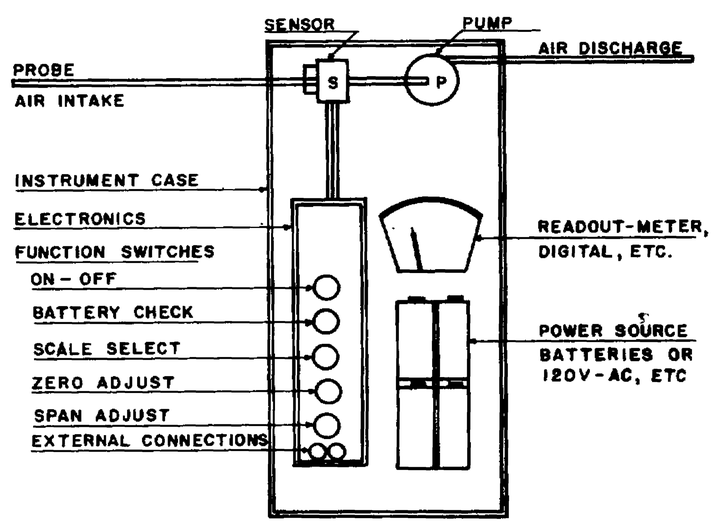

Figure III - 1 — Schematic of Direct Reading Combustible Gas Indicator.

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line. In addition to filters, metallic screens are situated in-line ahead of and behind the sensor. These are flashback arrestors and are not filters in the normal sense. Flashback arrestors cool the hot gases generated as a result of combustion occuring in the sensor to prevent ignition outside of the case of the gases being sampled.

Several options exist for the types of pumps used in the instruments. Some are electrically powered, while others employ a hand operated aspirator (squeeze bulb).

One option for the sensor involves placing the sensor in a "diffusion head" or envelope at the end of the probe. This type does not require a pump.

c. The "battery check" function switch provides an indication of the battery voltage. Typically it is displayed on the meter scale. When energized, the meter needle passes the mark "battery OK" if there is adequate power to operate the device. When there is no display scale on the instrument, follow the manufacturer's instructions. Where the detector uses 120 volts AC power and is permanently installed, Class I, Division I electrical fittings and other features are required. Installation details are beyond the scope of this manual.

d. The "scale select" switch functions as indicated on the label. It should be left on the least sensitive scale while the instrument is off, and during start up. Upon obtaining the instrument, first familiarize yourself with the instrument to understand whether it reads % LEL, % gas concentration, or ppm. Also check which gas was used for cailbration. See Chapter VII.

e. "Zero" and "span" adjustments require some explanation, especially since some other terms may be used to describe these two controls. Their proper setting is important since they affect the readout values for a given concentration of gas. The electronics can be said to read like a "rubber ruler" which has to be stretched to the proper length to read the scale correctly. Though the ruler may read precisely, the values are a function of its setting.

The "zero" setting is adjusted to read zero in pure air without any contaminants. Some instruments have this value fixed so that there are no external controls for it. When the logarithmic scale is used for the readout, some reference value is used for this setting since the scale does not extend to "zero". One or 10 ppm may often be chosen by the designer of the instrument.

Once the zero setting is made, the "span" (sensitivity, band spread, gain, etc.) is set. To do so, air or suitable gas with an accurately known concentration of contaminating gas is passed through the instrument. The span or instrument reading is then adjusted to give the "known" or "correct" value.

When the zero and span settings are made, the instrument should be ready for use. Appropriately timed retests of both settings are necessary to assure accurate readings that are not affected by the instrument drift. These settings are often checked before and after a series of runs. Additional verification is done as needed.

f. External connections provide for various accessories. Examples include recorders, earphones, etc. Most field instruments can be operated with a minimum of such devices.

3. With the outline just presented, one has a base on which to add further controls and accessories such as filters, several sensitivity scales, and dilution mechanisms, to list only a few. The manufacturer's manuals provide further examples and instructions upon their use.

SENSOR SYSTEMS

1. *Overview:* The contemporary industrial hygienist has an unparalleled selection of instrumentation for use and application. This permits a broad definition of combustible gases and listing of available devices to detect them. This variety enables one to select the most appropriate instrument for a given field situation. For example, some devices will function at high temperatures, others not. Some should be able to measure the very interferent that may foul some sensors. Some combustible gases are not even detected by some instruments. Measurement of methane and hydrogen are included among the examples.

Since an increasing number of indicators are being designed, any prepared list will rapidly become obsolete. However a classification of the general principles by which the sensors function is presented. It forms an outline which can be expanded as needed. It also provides a check list of types available for selection.

Several fine sources list devices and manufacturers according to the types of devices offered. Many technical periodicals provide annual equipment lists for this very purpose. These are not referenced here.

The reference section of this manual contains several publications that list manufacturers. The "Best's Safety Directory" is one that is updated annually. "Air Sampling Instruments" contains a substantial description of the instrument capabilities.

2. *Hot Wire*: The hot wire principle for detection of combustible gases is the earliest to be applied in electrically operated instrumentation. It continues as a proven method and is the method of choice for some applications. For example it can be made to function well at relatively high temperatures.

In some instruments the hot filaments have been modified by the addition of a catalyst that covers the hot

VAB.0001024190

wire. This changes the operating characteristics but the operating functions remain very similar. The description of the hot wire device will therefore be combined with the catalytic combustion type in the next section.

3. *Catalytic Combustion*

a. The use of a catalyst to modify the action of the sensor of the hot wire combustible gas indicator has been a successful innovation since the numbers produced have increased. Catalytic combustion has therefore become established as an operating principle and a means to classify these by type. However the measurement is much the same for both. Therefore the hot wire and catalytic devices will both be described in this one section.

b. The classical combustible gas indicator literally measures the contaminant by combustion. Air containing the contaminating gases flows over the heated filament, igniting the gases since the material is heated above the ignition temperature of the gas. As successively higher concentrations of gas are passed over the heated wire, higher temperatures are developed in the sensor chamber. The temperature simply rises with the addition of more fuel. The resistance of the filaments decreases as their temperature rises. This change in resistance is measured electrically while the contaminated vapor passes through the sensing chamber.

c. For these discussions, the main difference between the "bare" hot wire and the catalytic device is that the catalyst causes the reaction to proceed at a lower temperature. Calibration characteristics are therefore significantly changed. Other details are also involved, such as a possible reduction in the battery drain. Other more fundamental differences can be designed into the catalysts. Certain reactions can be promoted relative to others. Carbon monoxide measurement provides one such example. The material "hopcalite" facilitates the reaction of carbon monoxide with oxygen to produce carbon dioxide and heat. The heat quantity is then measured as in the combustible gas indicators described. Consequently, some classifications would group "heat of combustion detectors" together. This manual excludes such modifications where they do not apply directly to the combustible gas.

d. Since the hot wire and catalytic sensors measure the "combustibility" of a gas, they have direct application for fire service application. The fraction of the lower explosive limit shown on the readout is essentially independent of the gas or vapor being measured. Variations in the ignition temperature, heat of combustion, specific heat, etc. have only secondary effects on the reading. One overriding caution is related to methane. This hydrocarbon has a relatively high ignition temperature. Therefore the temperature of the sensor must exceed this minimum or the instrument will not respond. When measuring with a low temperature sensor equipped instrument, an atmosphere may exceed the LEL for methane and not register on the instrument, thus allowing one to be in an explosive atmosphere unknowingly. The user should check this characteristic.

e. When the contaminant concentration is in the explosive range, there is an open flame in the sensor chamber. The flame could travel upstream through the sample tube to the source of explosive gas. The result should be an explosion! The flame propagation rate of combustible gases is much more rapid than the sample inflow velocity. This would assure backflashing, if no other means of control were imposed. Therefore the "flashback arrestor" is installed. The most common example of a flashback arrestor is the grid or screen on the top of large sized laboratory gas burners. The gas flame burns on top of this barrier. If even a small portion of this grid is removed, the flame travels to the base of the burner and remains there. Then the air-gas mixture can not be controlled, and the device is not workable. In practice, the amount of combustible gas source may be much greater than it is at the base of the burner and provide more energy than a small "puff". Refer to section 11 of Field Operations in Chapter V for procedures to verify the functioning of the flashback arrestor. This section also describes examples where the arrestor was found to have been installed on only one side of the chamber. This omission would have initiated an explosion, had the instrument been immersed in an explosive volume instead of being adjacent to a test atmosphere. A similar hazard exists when the flashback arrestor is not functional.

4. *Diffusion vs Flow Through*

a. These two terms refer primarily to the configuration of the sensor and chamber. The usual arrangement is for the test gas to "flow through" the sensing chamber. It is drawn through a tube, into the instrument case, and past the sensor by some type of pump.

b. One option found on a few instruments is to hold the sensor itself in the atmosphere to be tested. The signal is then conducted to the instrument proper on a cable. There is no tube and pump arrangement. When this arrangement is used, the sensor and end of the probe must be designed to meet some of the following characteristics.

1) The cover must protect the sensor against mechanical abuses.

2) The cover must function as a flashback arrestor.

3) The test atmosphere must contact the sensor predictably and reproducibly. Principles of diffusion are usually applied to the design, hence the title "diffusion".

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c. The advantage of the diffusion head is that the sensor may be placed remotely from the instrument. When the proper electronics and cable are used, a rapid readout of the levels is possible and without the delay of pumping the gases to the instrument.

5. *Solid State*

a. The work being carried out in the field of solid state electronics is bearing fruit in the area of detectors for combustible gases and other organic compounds. These sensors react with a gas on the surface of the sensor bead, producing a change in conductivity of the bead. This change is measured electronically. In this respect, they differ fundamentally from catalytic detectors which measure a temperature change of the catalytic bead.

1) One of this family of detectors is known as the Taguchi (TGS) sensor. It is a semiconductor of the N type sintered tin oxide (SnO_2). When a gas with reducing properties reaches the surface, it is adsorbed. The response is due to the electrical properties of the oxidation-reduction chemical reactions on the sensor surface. The result is a significant drop in electrical resistance, with a corresponding increase in conductivity. This change is measured by a sensitive and appropriate amplifier. The output is then read as a function of the electronic concentration of the reducing gas that is present.

2) Since the charged ions are detected during the reaction that is electrically induced, some sensors can be operated in nearly the *absence* of oxygen.[21] The manufacturer's information also indicates that a wide range of compounds exhibit reducing properties. These include the usual range of hydrocarbons, halogenated hydrocarbons, alcohols, ethers, ketones, and esters. Nitro- and amine-compounds are detected. Several inorganic gases with reducing properties including ammonia, carbon monoxide, hydrogen, hydrogen cyanide, and hydrogen sulfide can also be detected. As calibration curves cannot be furnished for all of these compounds at all oxygen levels, it is necessary for the user to check the instrument performance in specific and unusual situations.

b. The function of the TGS sensor, a thermistor, requires some reaction with the gases that are sensed. This requires the sensor to be heated to a surface temperature of, for example, 82°C (180°F) and a higher internal temperature of 300°C to 400°C (572°F to 752°F) as variously reported by the manufacturers. (Reference 21) At these temperatures, several reactions can proceed. These are listed together with operating notes as follows:

1) Direct burning: As the term implies, the direct burning process is similar to that of the catalytic sensors. It requires oxygen to proceed and heats the sensor. The response is, as mentioned, to increase rather than decrease the conductivity. As combustion is involved, a flashback arrestor is required to isolate the hot sensor from the explosive atmosphere when high concentrations are measured.

2) Oxidation: This reaction is similar to burning, but has been limited here to that occurring at temperatures below the ignition temperatures. This process is also exothermic.

3) Reduction: This term is applied to the reduction of the semiconductor material to the metallic state. Such a change also reduces resistance since the metals are more conductive than their oxides.

4) Absorption: The physical absorption of the contaminants by the TGS bead results in some release of heat and therefore some instrument response.

5) Adsorption: This molecular process is parallel to absorption.

6) Thermal effects: The high thermal conductivity of some hydrocarbon gases tends to cool the sensor, an effect operating counter to the heat releasing processes. This is normally negligible, but can be observed. This action can typically show up during a search for gas leaks as first a gradual rise in response until a momentary dip is observed where a sudden surge of the combustible gas is met. For survey type work the transient observed can be evidence for the source of the leak, and the change in instrument sensitivity does not affect the evaluation.

c. The composite input of the reactions toward the sensor response is complex. For this reason, plus applications of electronic circuitry, the TGS sensor has been most frequently applied to survey and screening types of instruments.

d. Because the charge transfer mechanism is used for detection, this type of sensor is relatively sensitive. Response to propane was reported at 1000 ppm, less than a twentieth of its LEL of 22 000 ppm (2.2%). Carbon monoxide is detectable at the TLV level of 50 ppm. For reference, the LEL of carbon monoxide is 12.5%, a level reached only in the process equipment, not in the workroom atmosphere. This sensor is also sensitive to hydrogen sulfide in the TLV range. This combination of sensitivities makes it possible to use it as a multiple sensor for the gases that are typically found in sewage treatment processes and related manholes. Some competitive pocket sized models to warn workers have already been developed. (References: 1 and 21, NFPA 325M; 7, Enmet)

e. Gross contamination has occurred where this type of sensor had been overloaded during use. No specific

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poisons have been listed for this type of sensor. Until such information becomes available, one should be especially cautious where compounds known to be poisons for the catalyst type of sensor are known to be present. When damaged, it is probable that the sensor should be replaced. Under some conditions, it may be treated and recalibrated.

6. *Flame Ionization*

a. The flame ionization detector passes the test gas through a flame fueled with hydrogen gas. Appropriate electrodes and electronics are used to measure the electrical conductivity of the flame. The current involved varies with the quantity and structure of the carbon compounds present.

b. The flame burning in "pure air" essentially does not conduct electricity. This provides a baseline or "zero" for the instrument setting. When organic compounds are introduced into the flame, ionized carbon fragments form. Their conductivity is amplified and levels read out through the electronic system. These kinds of indicators have been highly developed for laboratory applications.

c. The flame ionization detector does *not* respond significantly to water, carbon dioxide, carbon monoxide, or the inert gases such as argon. This is fortunate since essentially all field atmospheres are contaminated with several of these gases. Background levels of carbon dioxide, for example, typically exceed 300 ppm, even in areas that are sparsely populated.

d. In addition to concentration, the sensitivity of the flame ionization detector varies with the atomic structure. When atmospheres containing a single contaminant are monitored, the device can be calibrated precisely. If a mixture is present, the reading is a composite and the meter is used as a general indicator, as with most combustible gas indicators. The more sophisticated field models of flame ionization detectors are equipped with a column to separate the individual components of the sample stream. Such devices can be used to identify individual constituents both qualitatively and quantitatively.

e. Though the sensitivity of the hydrogen flame varies between compounds, it will also respond to halogenated compounds. Though the sensitivity may be low as compared to response to methane, some "non-combustibles" may be measured. These include: trichloroethylene, chloroform, 1,1,1-trichloroethane, vinyl chloride, and others. Some materials including carbon tetrachloride and freons provide an even lower level of response.

f. When compounds are to be tested, one needs to know the capability of the instrument for that material. An inquiry of the manufacturer, review of literature and a continuing calibration/verification program are required.

g. Some models of flame ionization detectors are made with a logarithmic readout. This arrangement permits the entire range from 1 ppm to 10 000 ppm (near the LEL) on one scale. This arrangement is appropriate for area surveying. It also provides a realistic scale of concentrations.

Where a logarithmic readout is used, it has the following characteristics when compared to the linear readout.

1) A single meter setting is used while mapping a wide range of concentrations.

2) Using ideal conditions, the range of the instrument is somewhat wider than that indicated on the scale. On the high side the limit is the LEL, at which concentration the flame is extinguished by a "mini" explosion within the chamber. The low side is limited by background materials in the air and hydrogen fuel gas. These give measureable readings, typically in a few parts per million.

3) There is no problem with the non-linearity of the scale at low concentrations. On a device where the sensor provides an output current that is logarithmic, this characteristic has to be converted to the linear scale for conventional readouts. In this arrangement, the lower 10% (e.g. 5% to 20%) necessarily becomes non-linear. The combination of the hydrogen flame with the logarithmic readout remains constant throughout the scale.

4) The presence of air contaminants in the typical workroom is well described by a logarithmic-normal statistical distribution. This is compatible with the "log" readout. (Reference 18)

5) Some individuals have had more experience with the arithmetic readout and are therefore able to use it more efficiently for their applications.

6) The zero can be set on the arithmetic scale at the background level, thereby making it unnecessary to continue to subtract this value from each field reading.

7. *Photo Ionization*

a. Organic compounds may be ionized when they are subjected to ultraviolet light. The resulting conductivity of the gases in the UV light field can be measured. Hence the term "photo ionization".

b. Several gases that are normally present in air do not ionize in the detector sensor and are therefore not measured. These include: oxygen, nitrogen, argon, water vapor and carbon dioxide. The principle can therefore be applied in the design of field instruments. Neither carbon monoxide nor methane are detected by field instruments available in 1979.

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c. In addition to the lack of sensitivity to methane, the application of the photo ionization instrument differs from flame ionization in several details. One is that the photo based instrument is highly sensitive to benzene. A detection limit of 0.2 ppm is claimed by one manufacturer. This capability should be considered where aromatic compounds are involved.

d. A second consideration is the absence of a flame as an ionizing source. This makes flashback arrestors unnecessary. One must, however, consider the design of the electronic parts when the instrument might be taken into an explosive atmosphere. The risk of rupturing the UV lamp should also be considered.

e. The principle of photo ionization is applicable over wide ranges of hydrocarbon concentrations. Therefore some application of separation columns and logarithmic readouts appears to be feasible. The manufacturer should be consulted with regard to the sensitivity of this instrument to other compounds in addition to hydrocarbons. Alcohols, aldehydes, ketones, ethers, and halogenated compounds are only a few types that are of interest to industrial hygienists.

8. *Infra Red*

a. Infra red absorption analysis is a laboratory technique that has been adapted to field applications. New and relatively rugged devices have the capability of analyzing many gas mixtures for both the amount and type of material present. Essentially all of the commonly used combustible gases can be measured in concentrations from parts per million (or fractions of ppm) to percent levels, including explosive levels. One caution is repeated, that is to check with the manufacturer regarding the explosive risks. These include drawing the explosive atmosphere into the sample chamber. Consider also the risk of immersing a given model into a gas field where the concentration exceeds the explosive level.

b. The selection and application of IR analyzers should be done by industrial hygienists and chemists that are familiar with their functions. These devices are capable of sophisticated work.

c. Some few gases have color that is visible to the naked eye. Chlorine, bromine, iodine and nitrogen dioxide (tetraoxide) are the most common. In principle these exhibit color because some of the light that passes through them is absorbed. This light is typically absorbed at a relatively narrow range of wavelengths. The IR analyzers apply the same principle. The practical region lies well beyond the visible spectrum and involves long wavelengths. The separation of these wavelengths is usually shown as a graph. The absorption is shown as a series of peaks. The device is sensitive enough to measure these individual variations. It is most often used where individual compounds are to be studied, rather than as a device to measure a total or composite of all combustibles or hydrocarbons.

9. *Other*

a. Ultraviolet, Direct

1) Several organic compounds strongly absorb light in the ultraviolet region of the spectrum. This principle can be used for their detection. In practice only one group of field instruments applies this approach, and these are designed primarily for the detection of mercury vapor. Their response to organic compounds is usually recognized as being an interference to the detection of mercury. They can, however be used directly as organic vapor detectors, but this application is limited to the compounds to which the device is sensitive. These specific responses should be known in such applications.

2) The principle of "atomic absorption" is applied. A mercury vapor lamp source emits light at primarily a wavelength of 2537 Å (Angstroms, 253.7 nanometers). This light is typically absorbed in the sensor chamber by mercury vapor. The fraction absorbed is normally read out as mg/M^3 (milligrams per cubic meter of mercury). The application to combustible gases occurs since several organic compounds absorb at the 2537 Å wavelength. Calibration curves are necessary if practical use is to be made of these devices, since the gases would be reported in ppm.

3) The sensitivity for organic compounds is not very high for the usual single path instrument. Some of the compounds detectable are: benzene and related materials, alcohols, acetals, ketones, pyridine, etc. Mercury vapor detectors may not be designed for explosive atmospheres, a feature that must be checked before use.

b. Detector Tubes: Detector tubes provide a relatively sensitive and specific response to a wide variety of combustible compounds. Because of their single use characteristic, they are not used for an extended and continuous survey. They do, however, provide valuable verification of combustible gas indicator readings and identification of components. They would normally be used to provide auxiliary information in specific problem situations.

c. Miner's Lamp: The miner's lamp is still in use and is therefore a bona-fide combustible gas indicator. It is perhaps the first one used formally. The lamps are not currently used by industrial hygienists, with negligible exceptions. However, those familiar with the use of the lamps describe many detail variations in the characteristics of the flame that identify a variety of problem situations. If one would have an occasion to

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use such a flame, several variations would become apparent. The presence of halogenated hydrocarbons would, for example, cause the flame to burn green.

d. Laboratory Instruments: A sample can be taken to the laboratory for a number of sophisticated tests. Conversely some of the principles applied in the laboratory have not yet been adapted to field use. They provide a reservoir of techniques by which future specific problems can be evaluated.

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IV. FIELD CONSIDERATIONS

INTRODUCTION

A proper perspective is required of the instrument user so that a combustible gas indicator can be used effectively to obtain meaningful results. A "HAZARD LADDER" has been developed (Figure IV - 1) to enable the user to understand instrument response. Examples are provided and the reader should supplement these with field examples from his own experience.

All materials detected by a combustible gas indicator are in the gas or vapor phase. Particulate matter is excluded from the discussion. A particulate filter is placed in the instrument flow path to effectively remove all dust and fumes from the sensor. Thus the sensor responds only to combustible gases and vapors. The effect of small particulate, typically less than one micrometer in diameter, that may pass the filters, can be neglected. This exclusion of particulates also means that one can be in an atmosphere that is explosive due to dust and not know this from the readings on a combustible gas indicator. This manual does not review the techniques that are used for the evaluation of dusts. There are no field, direct reading instruments currently on the market which measure the combustibility or explosive properties of solid particulate matter. Even the approach to evaluate such conditions differs markedly from that of gases.

DEFINITIONS

1. The *Hazard Ladder* shown in Figure IV - 1 illustrates the relationship between explosion limits and Threshold Limit Values (TLVs). The concentrations of a gas or vapor in air mixtures are expressed on a logarithmic scale in terms of parts per million (ppm) and percent (%). Both scales relate the volume of contaminant to a volume of air.

2. The *letter codes*, A, B, C and D are "Hazard Potentials" which relate to ventilation of open surface tanks. See specifically OSHA 1910.94 (d) Tables G-12 and G-14, and ANSI Standards Z 9.1, 2, 3, 4; References no. 14 and 16. The application of these factors is not discussed in this manual, though some field experiences do touch upon the area.

3. The Ladder *scales* express identical concentrations. Both start at the top with a pure gas or vapor represented as 1 000 000 ppm or 100% (parts per hundred). As one moves downward on the scale, the contaminant is diluted with air. Each step indicates that the contaminant concentration is one-tenth of the concentration of the step above. The two scales are:
   a. *Parts per Million:* The ppm scale is the parts of vapor or gas per million parts of contaminated air by volume at 25°C and 760 millimeters pressure. (References 3, 8)
   b. *Percent:* The percent scale is the parts of vapor or gas per one hundred parts of contaminated air by volume at 25°C and 760 mm Hg. Temperature and pressure reference values have been chosen by the authors of this literature to be close to normal working conditions. Therefore corrections can be neglected for current discussion and most applied work. Where extreme variations of temperature and pressure are encountered, see Chapters V, Usage and VII, Calibration.
   c. The relationship between the two scales may be seen from the following example: At 1.0% the concentration is 10 000 ppm. Expressed as a ratio it becomes

$$1.0\% = \frac{1.0000}{100.0000} = \frac{10\,000}{1\,000\,000} \quad \text{or}$$

1 part per hundred parts =
10 000 parts per million parts.

4. *Explosive Levels:* Lower and Upper Explosive Levels (LEL and UEL) of representative solvents are listed. These are the lower and upper concentrations between

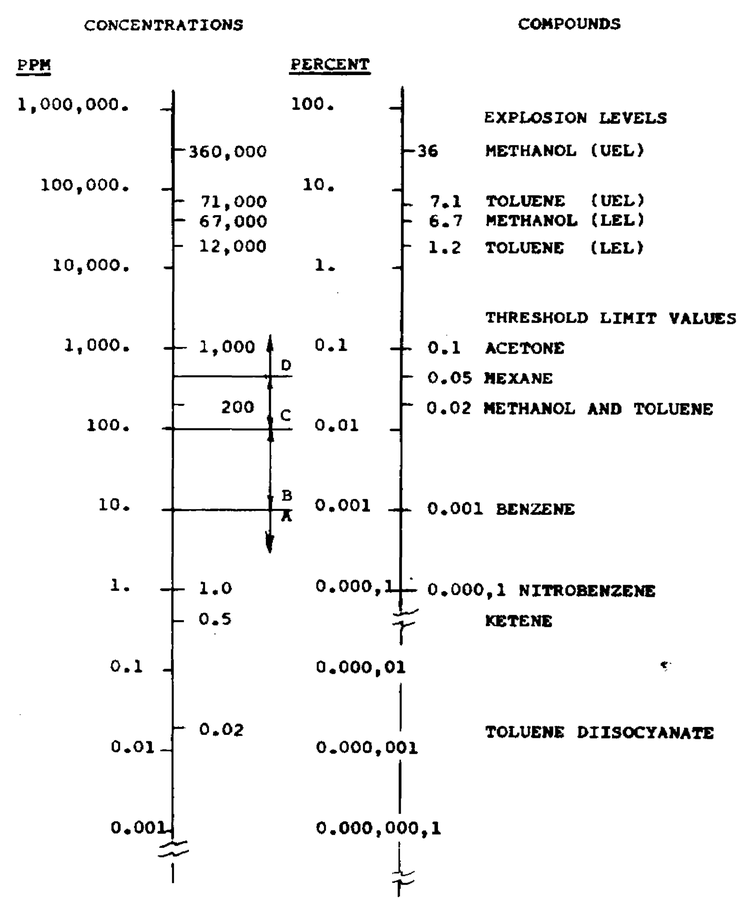

Figure IV - 1 — Hazard Ladder. Threshold limit values and explosion limits for selected gases and vapors.

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which the vapor mixtures will explode when an ignition source is present. The LEL scale of a combustible gas indicator would typically read 100% LEL at the concentration marked LEL if the indicator were calibrated for that material.

5. *One part per million* is frequently the lowest concentration discussed for TLVs. This is due to practical considerations. For example, lower TLVs are not measured on a combustible gas indicator, even the ones with a hydrogen flame detector. Some materials do have lower TLVs, therefore the scale is extended downward to 0.001 ppm (1.0 parts per billion). The scale is not extended to zero, since it would never reach zero.
6. The *percent* scale is extended to the bottom of the page for comparison purposes only. In practice, one rarely uses percentage for concentrations below 0.01%. The ppm scale would be preferred for these low levels.
7. Many contaminants are normally present in ambient air in the ppm, ppb (parts per billion) or lower levels. Many such contaminants are ubiquitous at low levels and cannot be avoided during measurement. However they should not present a significant interference effect in using a combustible gas indicator.
8. The *parts* may be measured in the English system as quarts (per quarts) or gallons (per gallons) for example. In the metric system liters (per liters) or mL (per mL) are typical. Because the ppm is a dimensionless ratio, the units in the numerator and denominator must be the same.

PERSPECTIVES

Once the concentration scales are illustrated, it is desirable to define their usage. This is done by placing examples on the charts. The reader should also add examples from personal needs or experiences. At least the TLV and LEL are required. A recap of the widely used solvent toluene (toluol) is made in tabular form as follows.

TOLUENE

PROPERTY	CONCENTRATIONS ppm	CONCENTRATIONS %	REFERENCE
UEL	71 000	7.1	NFPA - 325M
LEL	12 000	1.2	NFPA - 325M
TLV	100	0.01	ACGIH - TLV
TLV	200	0.02	OSHA - 1910.1000

Based on these few examples, several characteristics become apparent. These include:

a) A combustible gas meter set to measure in the flammable range will *not* indicate concentrations which may be present in the TLV range.
b) A meter set to measure in the TLV range will overshoot when flammable levels are encountered.
c) These detectors measure a composite of the combustible gases and vapors which are present. That is, this type of instrument is not specific and will respond to all combustible gases and vapors that are present. Interpretation of the concentration should be on the conservative side.

In summary, the combustible gas indicator functions as the instrument of choice when total combustibles are to be measured.

MEASUREMENT

1. Combustible gas indicators do not measure the concentration of a gas directly, but rather some property of the gas. Therefore some example conversions should be made. For the first of a series of examples, a typical indicator will be used to measure toluene (toluol). It is assumed that:
   a. The indicator has a scale labeled from "0 to 100% LEL" (or "0 to 1.0 LEL").
   b. The scale is effective from 10% to 100% LEL.
   c. The indicator is calibrated for toluene.
   d. The meter responds proportionally to toluene.
   e. If the descriptions are carried out as actual experiments, appropriate precautions are taken to control any flame that results. This includes, but is not limited to: catch trays, fire extinguishers immediately available, personal protective equipment including eye protection, a suitable location is used, etc.
2. The following laboratory procedure is described as an *explanation* and is *not* intended to be carried out.
   a. For a concentration of 1.2% toluene in the air, the meter would read 100% LEL. If such a mixture were to be ignited with a spark or flame, it would "explode" or "flash", though not "vigorously". This concentration would be reproduced in a laboratory

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on a small scale as follows. Chill a small amount of toluene (e.g. 50 mL, less than two ounces) in a 100 mL non-glass beaker in the freezer section of a refrigerator. Cover the beaker. Use a small flame, about the size of a pea (this is above the ignition temperature but does not warm the system excessively). Pass this flame horizontally over a small opening in or by the cover. If the liquid is below the temperature of the flash point, no flash should occur. If the liquid is warmed gradually and the flame is passed over the opening repeatedly, one should eventually see a flame or flash throughout the free volume above the liquid. This occurs at the temperature when enough liquid has evaporated to raise the concentration of vapor to the lower explosive limit. The temperature at which this action occurred is termed the "flash point". Since the container was covered, it would be termed a "closed cup" test. This effect is noted for toluene at 4°C (40°F). A standard laboratory procedure has been established so that all laboratories can carry out this test under closely controlled conditions. This is the Tag Closed Cup Flash Point Test that is described in the standard ASTM D-56 procedure (Reference 22).

b. If one would repeat the procedure described, but not ignite the vapors until the temperature raised several degrees above the LEL, the vapor concentration would be higher and the force of the explosion would be more vigorous.

c. The procedure could again be repeated but the flame withheld until the liquid temperature exceeds that of the upper explosive limit. For toluene this is 40°C (104°F). This time the flame would be observed at the air-vapor surface, but would not be seen to flash through the vapor volume. (Reference 1, Code 325M)

3. The reference point of 25% LEL is specified in NFPA codes as being the upper limit of concentration of a flammable gas that should be permitted in a (e.g.) paint dryer. To meet this design value, one should calculate the concentration. This can be done by ratio and proportion as shown by the following example for toluene.

$$\frac{C_t}{1.2} = \frac{25}{100}$$

Concentration of contaminant (toluene) in air / Reading or desired % of LEL

Reading or desired % of LEL / Concentration in % (toluene) in air at 100% LEL

SOLVING:

a. $C_t = \frac{1.2}{} \times \frac{25}{100}$

b. $= 0.3$ % concentration of toluene in air at 25% LEL

c. Using the relation that 10 000 ppm = 1.0%, convert the % to ppm.

C_t = 3000 ppm toluene in air at 25% of LEL

d. One convenient reference value is the "number of TLVs" that a concentration is in reference to the TLV. This follows:

$$\frac{3000}{200} = 15$$

ppm at 25% LEL of toluene / TLV for toluene in ppm, per OSHA

The concentration of toluene is 15 times the TLV at 25% of the LEL.

4. The same questions that were asked of toluene may be asked about any volatile and combustible material. Acetone is chosen as an example.

$$\frac{C_a}{2.6} = \frac{25}{100}$$

C_a = Concentration of acetone

$$C_a = \frac{2.6}{} \times \frac{25}{100}$$

$= 0.65$ % Concentration of acetone in air at 25% LEL.

$= 6500$ ppm concentration of acetone in air at 25% LEL.

$$\text{TLVs} = \frac{6500}{1000}$$

$= 6.5$ Number of times the concentration of acetone exceeds the TLV when the level is at 25% of the LEL.

5. Some combustible gas indicators do not read in direct proportion over their concentration range. For example, if two verifying mixtures were prepared, one at 12.5% LEL and one at 25% LEL, some instruments would not read the higher concentration at twice the lower. This depends upon the characteristics of the sensor and the electronics of the instrument. For information on the linearity of response of a given model, refer to:

a. Manufacturers instruction manual.

b. Description of non-linearity in Chapter VIII of this manual.

c. Test solutions of chosen contaminants in air can be prepared and response checked over the range of the meter as described in chapter VII on calibration in this manual.

LOWER LIMITS OF DETECTION

The minimum concentration of gases that can be measured while using a combustible gas indicator must be recognized

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and defined. It is further necessary to apply the concepts described in the Hazard Ladder to preserve the perspective. This approach supplements the manufacturer's specifications and instructions.

The practical application of a minimum detectable limit was illustrated by two surveys of a large paint dip tank. The first survey was carried out with a conventional combustible gas indicator. The levels were reported to be not detectable as read (zero on the scale). This instrument scale registered from 0% to 100% LEL. From this survey it was concluded that no action was indicated.

An industrial hygiene survey was made about two weeks later. On the sensitive scale, this instrument read 500 ppm combustibles, an average breathing zone level for two operators. The values were not specific, therefore they were used to identify the two operators out of several that had the highest exposure. These men were then equipped with personal dosimeters which collected the airborne gases. Subsequent laboratory analyses detected an average 300 ppm xylene; the remaining materials were petroleum distillates. Corrective action was recommended upon the basis that the xylene concentrations exceeded the TLV of 100 ppm.

In summary the first inaction was a result of a vapor concentration that was below the minimum detectable limit of the instrument used. As a result the health aspects of the process went unrecognized.

The above example also illustrates the need to apply the concept of the Hazard Ladder, Figure IV-1. The classical combustible gas indicator scale is ideal in reasonable fractions of the LEL, but the scale and mechanism are not suitable for the detection of trace, TLV levels. Therefore, some information is needed to define the lowest sensitivity of the instrument used. Nearly all of the discussions of combustible gas indicators refer to readout scales that are linear, that is all divisions are spaced equally. For example on a meter that reads 0 to 100% LEL, the spaces for 0-10, 10 to 20, . . . 90 to 100 are equal. See sections under Inherent Instrument Variability in Chapter VIII.

Where the minimum detection limits are not provided by the manufacturer, it may be approximated by preparing dilute concentrations of the contaminant in air as described in Chapter VII on calibration. This procedure is also a good excercise to verify one's laboratory techniques relative to the stated minimum limit. It is recognized that linear scales may be accurate only down to approximately 20% or 10% of the full scale reading. (Reference 5) See sections on linearity in Chapter VIII. These limitations due to characteristics of construction and measurement apply to instruments for other uses in addition to combustible gases. These limits must be recognized by both manufacturers and users.

Some new detectors have been developed which respond well in the 0 to 1000 ppm range. Using 10% of the full scale reading, 100 ppm, these new model detectors would be useful for selected materials in the TLV range. Some "solid state" types of detectors have been applied to measurements in this range.

The logarithmic arrangement used on the Hazard Ladder is available on some instruments. On such a scale, the spacing for 1-10 ppm, 10-100 ppm, 100-1000 ppm and 1000-10 000 ppm are equal (as opposed to 0-10, 10-20, . . . 90-100 spacings being equal). This type of readout provides an extremely wide range of response without having to change the range selector switch. In addition to monitoring fractions of the LEL, TLV levels, it is an effective tool to trace contaminant sources such as fuel gas leaks.

Commercially available instruments with a range of 1 ppm to 10 000 ppm usually operate with a hydrogen flame in the sensor. The background levels of combustible materials may often restrict the application of such an instrument to detecting a minimum of a few ppm. On the high side, one recognizes that the instrument has sampled an atmosphere above the LEL when the sensor flame is extinguished.

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V. USAGE

INTRODUCTION

Each possible use, and misuse, of combustible gas indicators has occurred in the field. Some examples of these usages are given. The details are limited to those required to make the point involved. By describing them, it is intended that the operator may derive enough background information to use a combustible gas indicator without experiencing the same consequences. It is hoped that the operator will be able to use the instrument objectively, correctly, and with confidence, but also with a knowledge of its shortcomings and limitations.

INSTRUMENT INTEGRITY

Examples where the integrity of the instrument affected the field study follow.

1. The instrument controls were not set in the proper operating mode when turned on and used.

   a. This self-evident mistake was observed in a construction area. A foreman had the responsibility of measuring the concentration of natural gas, primarily methane, before allowing welders to work on a section of pipeline. He started by turning the combustible gas indicator to "on", but he did not advance the control to "zero" the needle on the scale. For this particular model of indicator, it is d%ubtful that any reading, or at most a very low reading, would have occurred at 100% LEL.

   b. First, the operator should have known the proper operation of this instrument, so that he could properly discharge his responsibility.

   c. Second, even experienced operators find that a quick field check may often be desirable. This can be done with almost any flammable liquid or gas. One can simply pass the probe over the area where a 100% LEL concentration is expected and note the meter response. This action does *not* give precise readings, but it does demonstrate that the device is functioning. This is adequate to give the instrument operator and onlooker alike some measure of confidence in the indicator used, and the ability of the device to do the job. Choose the example carefully so as not to violate good practices, such as those described. Avoid leaded gasoline models of combustible gas indicators as many will lose sensitivity due to the lead. A very small bottle, e.g. 5 mL or 0.1 oz, of material is adequate. Felt tip pens and cigarette lighters (not ignited) release enough solvent vapors to activate the sensitive instruments.

2. *Apply the perspective* that is described in Chapter IV.

   a. An open surfaced paint dip tank was checked and found to be "satisfactory". This tank was an open tank measuring 6′ × 6′. It was checked for fire safety in the morning. This tank was used to hold paint for dipping large farm equipment accessories. As these were warmed in the sun, there was concern for the toxic exposure and fire risk to rise with temperature during the work day. This inadequate review was made with a combustible gas indicator that had only one scale, 0 to 100% LEL. It did *not* register any significant readings indicating contamination of the atmosphere in the vicinity of the tank.

   b. An industrial hygiene survey was subsequently carried out and similar results were obtained with a meter having a scale similar to the first one used. Additional tests were made with a more sensitive combustible gas indicator that read in the range of 0 to 1,000 ppm, as calibrated on benzene. Readings to 500 ppm were detected in the breathing zone of several workers. Samples collected at the site and subsequently analyzed in a laboratory by a gas chromatograph revealed levels of 300 ppm toluene in the area with the balance being other hydrocarbons. The toluene concentration alone was equivalent to 3 times the (ACGIH) TLV level. The lack of response below the lower limit of combustible gas indicators which are for determining explosion or fire risk will not provide information with respect to levels of health concern.

   c. A sample of liquid was also tested in the laboratory to determine its flash point. It was only 6°C (11°F) above the temperature of the tank. Materials to be dipped were large and had been warmed by storage in the sun. Thus it was likely that the fire potential and health exposure risk would increase over the work day.

3. *Sampling tubes* must be free of leaks. For some combustible gas indicators, the sampling line is connected to the meter with a friction connection, threaded or quick disconnect coupling. These may be worn or connected loosely to the meter. When long sampling lines are used, air drawn in can short circuit the probe end and enter via the coupling. The user is therefore sampling the air at the instrument instead of the desired sampling point. Some mixture of the two atmospheres is most commonly measured. This

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malfunction can be critical and even fatal to occasional workers that have mistakenly entered confined spaces, such as manholes, vessels, or excavations.

Sample lines may leak, but this is not a frequent problem. They may be pinched very easily and close off the sample flow. When this occurs, the amount of air entering through leaks increases. Therefore, connections in the sample line and the line connection to the pump must be tight.

The absence of leaks should be verified in the laboratory before going to the field. However field checks are still needed. A check to assure that there is no bypass of sampled air can be achieved by placing a finger over the end of the probe inlet while listening to the pump or watching the hand aspirator. If leakage is occurring, the pump will not labor or the bulb aspirator will fill quickly. The blockage at the tip should be detected readily. It may be desirable to carry out these checks in a relative quiet area.

4. *Intrinsic Safety*. Two types of measurement situations are illustrated, both in the text and by photographs (Figures V-1 through V-5). In many cases the instrument sample probe is inserted into the atmosphere to be tested. The second series describe the situation where the instrument is completely immersed in the questionable atmosphere. Some of the examples given under Sensor Systems in Chapter III demonstrated that some models can and do ignite certain explosive atmospheres. If ignition can occur, the instrument is *not* "intrinsically safe". If the instrument construction is such that ignition is highly improbable, the instrument may be termed "intrinsically safe". For precise technical definitions, one is refered to Underwriter's Laboratories and Bureau of Mines (MSHA) Specifications. It should be noted that an instrument approved as being intrinsically safe for one specific use may not be so for other applications. For example a combustible gas meter that is considered intrinsically safe for use in a methane atmosphere in a mine may not be (and probably is not) safe for use in hydrogen or some other industrial atmospheres.

FIELD OPERATIONS

Descriptions are given for the use of the instrument in unfavorable or at least non-ideal field conditions. This section will serve to provide background and solutions to some of these conditions. The means to handle a combustible gas indicator in some of these situations may require additional information. For this, communication with the manufacturer is suggested. Experimentation by an industrial hygienist, instrument specialist, or others may be required in some situations.

Remote sampling frequently requires that the meter be set in one environment with the samples being drawn from another. The variations between the two conditions may affect instrument functioning significantly. For example, the adjustments for zero settings and span adjustments may differ from the time that they are first made and when a measurement is made in a different environment. Variations involved in measurements made in a confined space before entering them is one good example. Manholes and vessels present such arrangements.

Practical examples of field problems follow.

1. *Temperatures* may vary widely between the environment in which the instrument is calibrated, set, zeroed and adjusted, and the environment in which it will be used. To have confidence in the resulting readings, one must knOw the magnitude of this effect, or have made arrangements to establish the calibration or settings at the same temperature conditions of use.

   a. For example, a manhole access to a sewage lift pumping station was to be checked. The workers had left this confined space with the complaint that they found it hard to breathe, and hardly were able to escape. Upon arrival the next day, the industrial hygiene team prepared to test the confined atmosphere for gases, including combustible gases. A combustible gas indicator was set to zero above ground. Here the temperature was −18°C (13°F). When the sample tube was dropped into the space, the reading was a substantial fraction of the LEL. Should workers be permitted to enter?

   b. In the above case, the primary purpose of the measurement was to evaluate the confinement atmosphere. This was done in detail with additional instrumentation. Some of the questions and details of this study follow:

      1) The temperature of the confinement was found to be 13°C (55°F). In addition this model of combustible gas indicator was *not* temperature compensated and gave a false reading.

      2) The humidity was over 80% in the confinement. This example therefore also fits the situation where the humidity differs greatly between the location of the instrument setting and that where read.

      3) Some heavy molecular weight hydrocarbons can be absorbed onto activated carbon, so that such a filter can be used to zero the device in the questionable atmosphere. This will *NOT* work for methane which is typically present in sewage contaminated atmospheres.

2. *Humidity* may differ widely between the environment in which it is calibrated and set, zeroed and adjusted, and the environment to be measured. The laboratory in which the combustible gas indicators are calibrated has a relative humidity which may be around 50%. Example of deviations follow:

   a. There are situations where the instrument is used to detect gases or vapor levels which are present in dry

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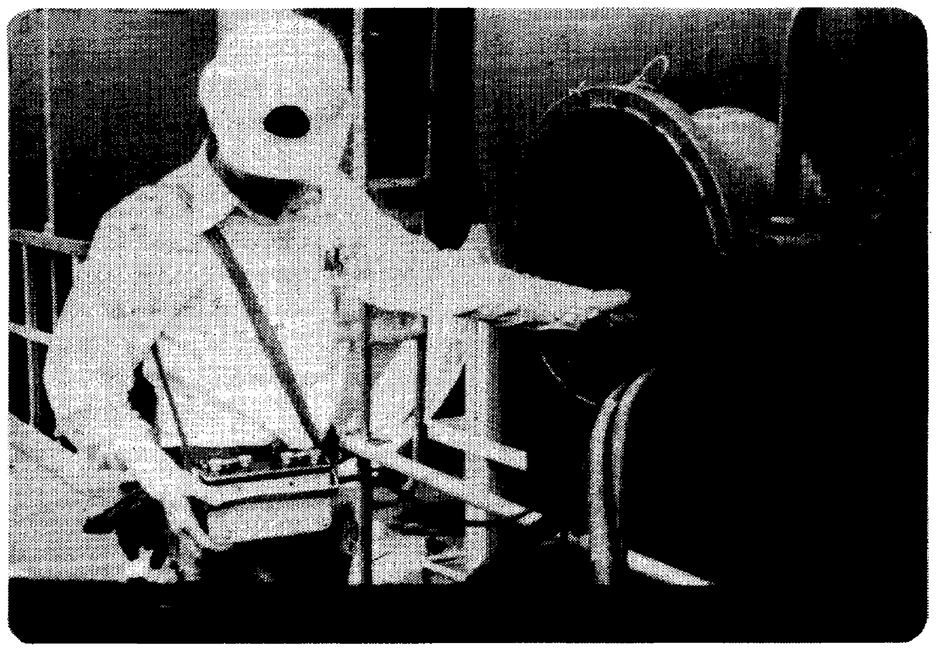
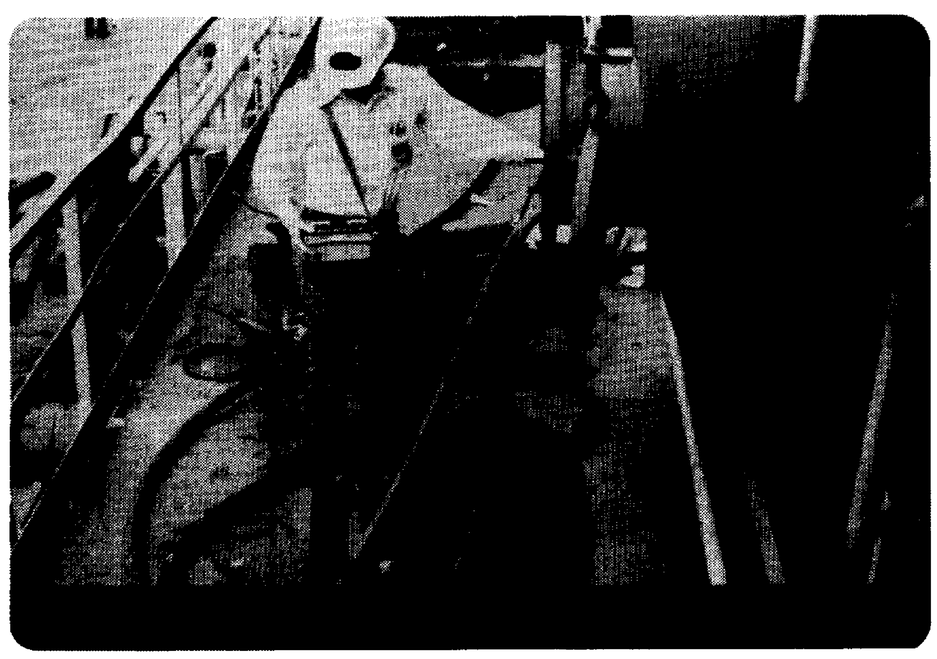
air or nitrogen. This occurs in a gas drier vessel or where dry nitrogen has been used to inert a vessel. This difference in humidity can be significant when monitoring for the presence of materials with low TLVs such as benzene, isophorone, mesityl oxide and others.

b. Situations where higher than "normal" humidity has been encountered occur frequently in wet industries such as the sewage system example given above where a level of over 80% was encountered.

c. Communications from two hygienists described their use of a combustible gas indicator as a tool in arson investigation. They searched where trace flammable liquid residues might remain after a fire had burned the area. When "high" levels, in the ppm range were found, this location was thoroughly studied. Appropriate samples were taken of both solid remains and gases for laboratory examination. Gas chromatography and other analytical procedures could then be applied. Such a search has focused the





Figures V - 1, V - 2 — The operator shown is using a combination oxygen and combustible gas indicator, in preparation for a worker to enter a pressure vessel, one type of confined space. (The instrument shown is a J&W (Bacharach) Model GPK.)

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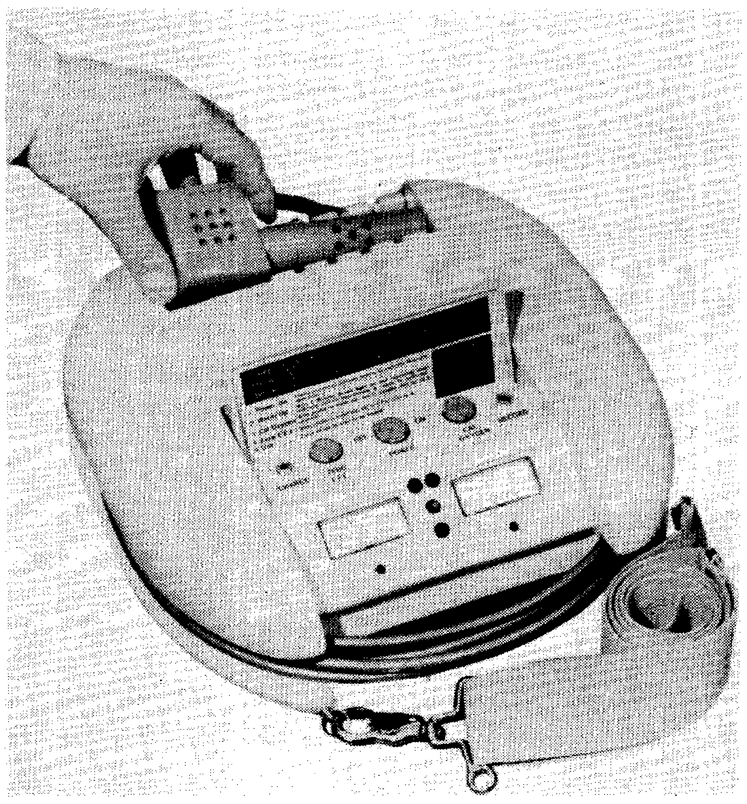

Figure V - 3 — Combination combustible gas indicator with oxygen detector. Warning lights are included. (Photo courtesy Edmont Willson.)

work on samples that are more indicative of the problem situations. Since many of these areas searched have been covered with water, the localized high humidity reduces the sensitivity of some types of indicators to where they are not useable, or perhaps misleading.

3. *Condensation* can occur in the sample tube which is used to draw the sample from a test location to the instrument. This keeps the problem material from being measured, or may reduce the measured concentration and cause faulty decisions.

   a. One specific example occurred where tetramethyl benzene (TMB) was used as a paint solvent. This solvent was selected for use in the process since it has a high boiling point (197°-205°C; 386°-401°F).* Its properties are otherwise similar to xylene, toluene and benzene. These solvents have fewer methyl groups (2, 1, 0) than the TMB (4) and, therefore, boil at lower temperatures. Two problems had to be evaluated with the TMB. One concerned the worker exposure at a "TLV level" (since no TLV had been assigned at the date of this writing, measurements should be sensitive to one or a few ppm**). The other concerned the possibly explosive level within the oven. The preliminary request had not provided the information needed to do these measurements properly. However a field demonstration was carried out where the combustible gas indicator was used in the conventional manner. Then the hose and prefilter were removed from the instrument. The sense of smell (away from the contaminated work room) confirmed that both the tube and prefilter were contaminated. The TLV levels were measured by a collection in adsorption tubes and the levels then determined in the laboratory. Oven levels eventually had to be monitored constantly with a high temperature sensor that was located within the oven and operated in that high temperature environment.

4. *Zero setting in contaminated atmospheres* is a very real problem where the instrument cannot be removed from the atmosphere being tested. The meter drift may indicate the presence of contaminants significantly higher or lower than they really are. Such locations exist within the confines of large plants and mines. Even the relatively clean ambient air, especially in cities, frequently carries a background of a few ppm of hydrocarbons from automobile exhausts and other sources. Before one applies the procedures that have been suggested as solutions, one must also be certain that other variables are not introduced in the process. Pitfalls include differences in temperature and humidity that have already been mentioned. Check for other possibilities. Some possible solutions are described as follows:

   a. Fill a gas sampling bag with an adequate supply of uncontaminated air. This bag can be carried into the area to be tested and used when needed. Several brands of sample collecting bags are now available. These have the advantage of providing the gas at the temperature at which it is used. The air can also be adjusted to the approximate humidity of the test area, if this is needed. Collect enough air to zero the instrument three or four times. Include some for a final check after all readings have been made.

   b. A small bottle of compressed air (e.g. lecture bottle size) will provide considerable air. This air is very dry when discharged; some means to humidify it may be necessary.

   c. A tube containing activated charcoal (e.g. 1″×3″) can be used to absorb hydrocarbons before they reach the sensor to provide clean air. This will *not* remove methane or carbon monoxide.

5. *Zero and adjust* the instrument at the beginning, occassionally during and after the end of a series of tests.

*Melting points vary according to the material used. These are -24° to +79°C; -11° to +175°F (Reference 19).

**Where TLVs are not assigned, a Certified Industrial Hygienist shall be consulted. In many cases, his effort may be extensive, including literature searches, consultation with physicians, NIOSH, ACGIH, legal counsel and others.

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This procedure does not appear to be self-evident to an inexperienced user of combustible gas indicators. At least this omission has been witnessed.

a. A construction foreman had been observed to have taken a combustible gas indicator, battery powered, scale 0 to 100% LEL, and start to use it with no adjustment. He simply turned it on and probed in several places to show that there was no measureable reading. In actuality, he turned the switch and dial just far enough to turn on the dial lamp. The device remained non-operative relative to measurement of the gas. He should have set zero and observed the movement of the needle. If the filament had been open on this model the device would not have operated. This particular operator would not and could not have noticed such a failure. Since the location where this action was observed was under construction and methane escaped occasionally, the welding operations could well have initiated an explosion even though the readings of combustible gases were nil.

b. During use the operator and observers can gain confidence in their instrument if they occasionally check a source of combustible gases. If the conditions are suitable, the meter should respond without overloading. Conversely, if the meter does not respond, one can conclude that something is not functioning. Usually the meter will not be responding for some reason. On occasion, one finds other reasons for such a failure. Mislabeled drums have been only one such cause.

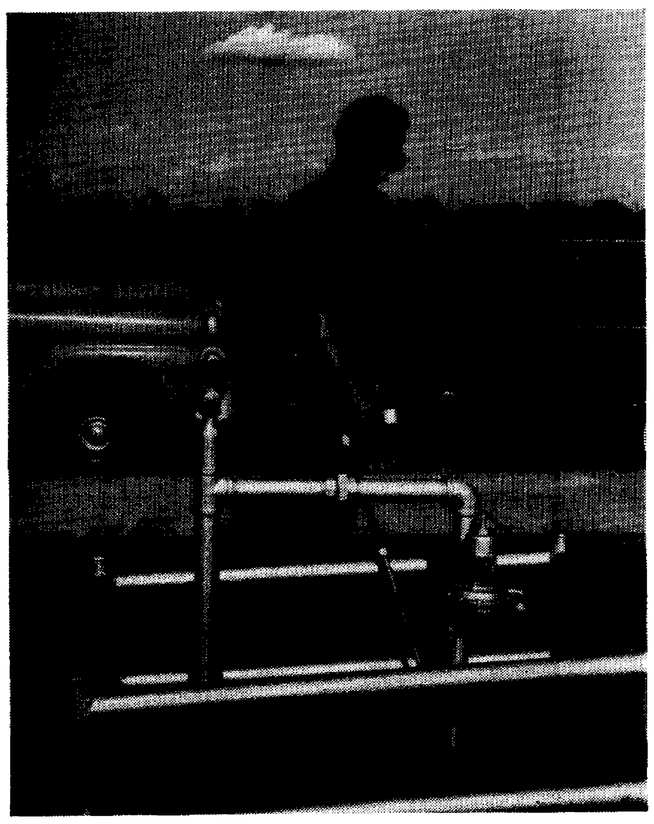

Figure V - 4 — Combustible gas indicator equipped with a flame ionization detector is being used to locate leaks in natural gas line valves and fittings. (Photo courtesy Century Systems Corp., The Organic Vapor Analyzer, Model 108 (OVA-108) Range 1 ppm to 10,000 ppm.)

6. *Liquid Contamination* has been witnessed to be a problem and so reported in one instruction manual. The sensors for the combustible gas indicator are designed to measure a wide range of gas and vapor concentrations. They are not to be immersed in any liquid, flammable or not, nor are these fluids to be drawn into the sensing chamber. If this occurs, proper cleaning is required. Replacement of the sensor is probably necessary. Recalibration and verification follows. This has undoubtedly happened as a result of an "accident". When an employee charged with the operation involving flammable liquids immersed the probe in the liquid to demonstrate the functioning of the emergency warning system, it should be apparent that a basic training session was required.

7. *Oxygen depleted atmospheres* cause misreading of the combustible gas indicator under a wide variety of conditions and at most levels for which one uses the device. Most of these examples occur in relatively confined spaces, but the exceptions should be recognized when they occur. Some examples of these situations are described as follows:

a. *Without inerting gas, Over the Upper Explosive Level.*

1) These conditions occur when the flammable liquid is so volatile that the concentration of vapors exceed the upper explosive limit. The most common example of this situation is common gasoline to fuel automobiles. This applies to every gasoline tank and container. The approximate explosive limits are 1.5% to 7.6% for automobile grade, 92 octane gasoline. Some variation exists between grades, but this is negligible for the application being discussed.

2) When one measures the vapor within the free space above the liquid, but within the confined space of the gasoline container or tank, the needle of the classical hot wire or catalytic combustible gas indicator comes to rest at a low level. It is easy to make the false assumption that there is no problem. If however, one was watching the needle of the meter, it would be seen to rise to a maximum, over the LEL and then receed to the apparently low value. The high peak is explained by the explosive level at the interface between the outside air and the high gas concentration within the confinement. This excursion of the needle readout is often the only evidence one may have to warn of a highly hazardous situation.

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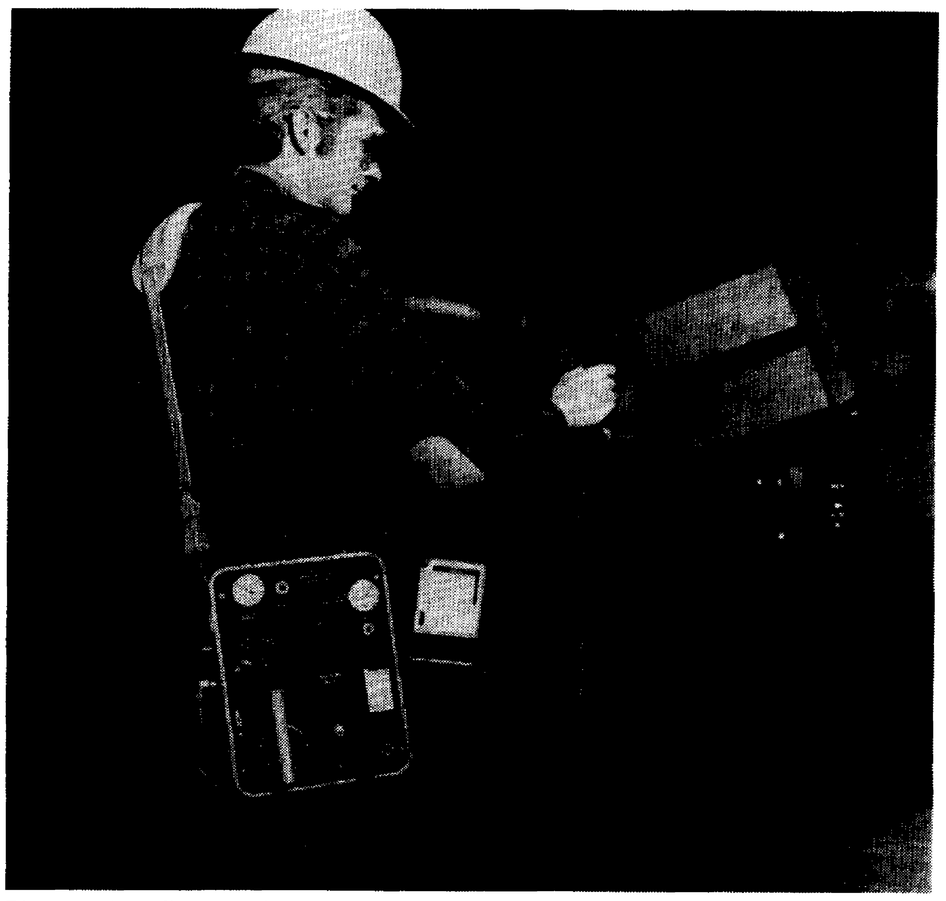

Figure V - 5 — The combustible gas indicator is being used to monitor a plant and process environment. The model shown has a flame ionization detector, and is equipped with a recorder. A gas chromatograph column permits the selection and identification of specific gas and vapor components. The logarithmic readout 1 to 10,000 ppm is visible. (Photo courtesy Century Systems Corp., The Organic Vapor Analyzer, Model 108 (OVA-180).

In addition to the toxic level and fire hazard of entering a confined space where the gas concentration is above the UEL, there is a problem of low oxygen for breathing. This was illustrated in an actual situation where methylene chloride had been spilled. The operator had supposedly checked for combustible gases with a hot wire type of meter and did not interpret the reading to indicate a dangerous situation. He entered the tank volume and asphyxiated.

This incident illustrates the need for an oxygen measurement to be made along with the measurement for combustible and toxic gases when entering confined spaces.

3) When the probe is drawing air from the confined space into the sensor chamber, the vapors have become concentrated and the oxygen displaced, so that there is too little air to register properly. If this condition is to be demonstrated, caution is advised, since the conditions are extremely hazardous.

4) Other types of sensors react differently to this set of conditions. One should be aware of the instrument response that can be expected. The flame ionization detector, for example, was reported to "blow out" the flame. When the flame extinguishes, the unit quits working in that type of instrument. One should immediately suspect concentrations above the UEL as a possible cause.

5) Other industrial and laboratory chemicals may produce a response that is similar to that described for gasoline. That is, the vapor concentration may be over the UEL in the container volume. Other materials may produce a concentration that is in the explosive range above the fluid and within the container. Such a condition illustrates the need for a flashback arrestor to be built into the openings of the container.

6) Trace compounds may cause gradual deterioration of the sensor. For example, the tetraethyl lead compound in many gasolines requires that the instrument be recalibrated and replaced

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frequently. Halide compounds found in some gasolines or solvents can also affect many sensors. Periodic verification is required to prevent false negative readings, an extreme, avoidable risk.

b. *With Inerting Gas.* The need to estimate the concentration of a combustible gas where the oxygen concentration is too low for a combustible gas indicator to function properly is a relatively common problem in many industries. One of the frequently encountered situations occurs when a vessel has been inerted, the air has been displaced with nitrogen or other inert atmosphere. The residual organic compounds continue to evaporate and may give further difficulty. To meet this situation, some manufacturers have provided an accessory which enables the combustible gas meter to detect gases or vapors even though the atmosphere tested lacks sufficient oxygen for combustion. One such device fits on the sample inlet line. It has settings available for a direct sample, dilutions of one-half, and dilutions of one fifth of the pure streams. One setting is for ambient air to check the instrument zero. With the diluter setting at 2 (or 1/2), this gives a meter reading of 500 ppm which means that the true level of the contaminant is 1,000 ppm.

1) The above example assumes that the manufacturer's indicated dilution factors are accurate. Experience indicates that the dilution factors may be different from the one-half or one-fifth (or other) values indicated by the manufacturer. Where readings are critical, the exact dilution factors should be determined and used. This can be done in the laboratory, using, for example, the bubble flow calibration procedure. (See Verification - Flow Rate in Chapter VII.)

2) Modern sophisticated instruments do make it possible to measure the concentrations of combustible gases in the absence of oxygen. These are types that function by principles other than direct combustion. Two types that give nonspecific readings include the solid state detector (e.g. Taguchi type) and the photoionization detector. Both of these respond to a wide range of concentrations. They will also respond to some compounds that are modified hydrocarbons, such as the halogenated and oxygen containing ones. For identifying the specific materials present as well as their concentration, a model operating on the infrared principle would be required.

3) Use of a traditional combustible gas indicator with a dilution attachment, or one of the alternate instruments depends upon the needs and characteristics of the situations to be measured.

8. *Oxygen Enriched Atmospheres* are encountered in several processes. These range from medical applications to steel making. One should be prepared to know the characteristics of the combustible gas indicator even if it is not to be used in the process, but where there is a chance that a release of oxygen would engulf workers using one. First, the calibration would be different in an atmosphere that was even slightly enriched. Second, the flashback arrestors may not function in the enriched atmosphere, even though they have been found to be suitable for otherwise routine use. The chance for a back-flash and ignition therefore exists. In addition, the explosive ranges of organic compounds are much broader than the values normally used, which were determined for normal atmospheric conditions.

9. *Hypobaric, Conditions of Reduced Pressure.* High altitude chambers and other facilities exist where the air pressure is reduced significantly below that found at sea level. In addition, many have gas environmental mixtures that differ from the usual components found in air. These conditions are beyond the scope of this manual. Where these instruments are used in "mile high cities" such as Denver, Colorado, and others, it is assumed that calibrations and instrument functions can be accounted for by the usual pressure corrections. Details should be checked with the manufacturer and knowledgeable industrial hygienists and technologists.

10. *Hyperbaric, High Pressure Applications.* Tunneling work and medical applications alone account for a significant amount of work done at pressures significantly higher than normal atmospheric. The excess pressure causes some changes similar to that of enriched oxygen. For example the explosive range is extended and the effectiveness of flashback arrestors is diminished. Also some gas mixtures differ widely from those found in the normal atmosphere. Therefore, it is recommended that technical assistance be obtained before work progresses. This manual does function as a check list of some of the pitfalls that occur. Even though the conditions differ, the ideas should be suggestive of comparable situations.

11. *Group A, B, C and D Atmospheres.* The flashback arrestors in the typical combustible gas indicator should ideally prevent ignition of the environment that is contaminated with gases or vapors in their explosive ranges. The traditional combustible gas indicator however, had been designed for use in methane atmospheres such as those found in mines. When the industrial hygienist took the device into the industrial plant, it worked fine on many solvents, such as toluene, petroleum naphthas and many other organic solvents. Most of the solvents and methane belong to the "Group D" gases and vapors as described in the National Electrical Code (Reference 16, ANSI C-1 (Also NFPA no. 70), Article no. 500).

Electrical fittings for use in Group A, B, and C require some modifications, or at least details that may not be required for use in Group D atmospheres. The need for different specifications must be recognized in the design

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of the combustible gas indicator if it is to be used with these gases.

a. The industrial hygienist may frequently come into contact with acetylene, a group A gas. The instrument used with acetylene should therefore not contain any copper tubing, to avoid the formation of explosive compounds known as "acetylides". See the references for further requirements of instrument construction for this application.

b. Hydrogen is frequently found in battery charging and some refinery operations. One of the contributors to this manual was requested to check hydrogen levels near a battery charging system. He refused on the grounds that he was not certain of the flashback function of the combustible gas indicator that he had available. Upon returning to the home based laboratory, he filled a plastic bag with hydrogen, wafted some air into it, and attached a long sample tube extension to the indicator. In a few moments after starting the sampler, the gas in the bag "poofed" and the remaining bag burned. The gas was ignited by the instrument, and the flame propagated upstream faster than the sample flow, in turn igniting the contents of the bag.

   Later, when a second and more sensitive combustible gas indicator was procured by the laboratory, a flashback arrestor was provided that was to be effective for hydrogen. The above test was, therefore, repeated. This time the bag did not flame, but a series of small popping explosions was heard from within the case. Since the case was sealed with a rubber gasket, but not to specifications for Class I, Division, 1, Group B electrical equipment, it is problematical as to whether the flame within the case would have set off an explosion had the device been within the explosive field. The sample tube was removed from the instrument, and the escaping gas ignited. Again the contents of the bag ignited, reconfirming that it had contained an explosive mixture.

c. Though these experiments must be done in a safe location, it is recommended that the user become familiar with the performance of the instrument before encountering problems in the field.

d. The compounds listed in the National Electrical Code are only a sampling of the materials with which a hygienist may come into contact. They are however, a representitive sampling which one with a background in this work can expand upon. The materials listed in the National Electrical Code, Chapter 5 Special Occupancies, Article 500 Hazardous Locations, Paragraph 500-2 Special Precautions, Table 500-2(c) lists the following chemicals by groups.

1) GROUP A ATMOSPHERES
   Acetylene

2) GROUP B ATMOSPHERES
   Butadiene
   Ethylene oxide
   Hydrogen
   Propylene oxide

3) GROUP C ATMOSPHERES
   Acetaldehyde
   Cyclopropane
   Diethyl ether
   Ethylene
   Isoprene
   Unsymmetrical dimethyl hydrazine
   (UMDH-1, 1-dimethyl hydrazine)

4) GROUP D ATMOSPHERES
   To provide a reference of the types of atmospheres that may contain combustible gases, the Group D materials are listed as follows:
   Acetone
   Acrylonitrile
   Ammonia
   Benzene (Benzol)
   Butane
   1-Butanol (Butyl alcohol)
   2-Butanol (Secondary butyl alcohol)
   n-Butyl acetate
   Isobutyl acetate
   Ethane
   Ethanol (Ethyl alcohol)
   Ethyl Acetate
   Ethylene dichloride
   Gasoline
   Heptanes
   Methane (Natural gas)
   Methanol (Methyl alcohol)
   3-Methyl-1-butanol (Isoamyl alcohol)
   Methyl ethyl ketone (MEK)
   Methyl isobutyl ketone (MIBK)
   2-Methyl-1-propanol (Isobutyl alcohol)
   2-Methyl-2-propanol (Tertiary butyl alcohol)
   Petroleum naphtha (Benzines - Not a USA term)
   Octanes
   Pentanes
   1-Pentanol (Amyl alcohol)
   Propane
   1-Propanol (Propyl alcohol)
   2-Propanol (Isopropyl alcohol)
   Propylene
   Styrene (Vinyl benzene)
   Toluene
   Vinyl acetate
   Vinyl chloride
   Xylenes

5) GROUP E, F, G ATMOSPHERES
   The Group E, F, and G atmospheres refer to particulate contamination and are not detected by

VAB.0001024207

the combustible gas indicator. When airborne, these materials do form explosive atmospheres.

12. Use in the presence of *halogenated hydrocarbons.*

a. A solvent degreaser containing trichloroethylene was drained and cleaned on a periodic basis. A written set of clean-out procedures was established for this degreaser. One of the procedures required that a combustible gas meter be used to measure levels of trichloroethylene inside the degreaser. When concentrations were below a predetermined value, the employee was permitted to enter the degreaser and perform the necessary clean-out operation.

This step in the clean-out procedure is highly questionable. First, the instrument was not designed, nor intended, to be used for measuring a halogenated hydrocarbon. Had the user attempted a calibration of the instrument for trichloroethylene, this fact would have been evident. Each time the trichloroethylene passed over this instrument's sensing element, breakdown products such as hydrochloric acid deteriorated and corroded the sensor. Thus, even though the instrument responded to "high" levels of trichloroethylene, it would be impossible to accurately quantify instrument readings because of constant deterioration of the sensor. In addition, this condition prevented the user from obtaining accurate results when the instrument was used as intended.

Even though the employee entered the degreaser only when the measured level of the trichloroethylene was below an arbitrary level, as instrument performance deteriorated, the actual concentration of trichloroethylene to which the employee was exposed increased each time the unit was cleaned. Thus the potential for a hazardous condition unknowingly increased with time.

b. The example above was recognized at some time after the operation was measured with the instrument described. The work should continue with an instrument of the type which will measure the trichloroethylene, or whatever halogenated gas is being used.

c. It should be remembered that the indicators for combustible gases and halogenated hydrocarbons do NOT measure the oxygen content of the vessel. Almost any hydrocarbon gases, whether they are halogenated or not, are heavier than air so that they tend to displace air. Continued monitoring is necessary to avoid having a build-up of toxic levels or decrease in oxygen availability while the cleaning progresses. Concurrent oxygen monitoring is necessary as well as other precautions such as continued ventilation, etc.

d. The presence of halogenated hydrocarbons in a welding arc produce phosgene. This material is highly toxic in levels far below the sensitivity of almost any field device used for measuring combustibles. The instrument may give a reading on the original halogenated compounds, but not record phosgene (TLV 0.1 ppm).

13. *Use with Other Compounds.* Most types of combustible gas indicators will respond to many other types of organic compounds and a few inorganics. Their reading is simply added to the total combustibles that are in the atmosphere to be measured. In some cases they may be the primary compound of interest. For others, they may be considered as interferants. Some may corrode the instrument parts, therefore they should not be used under normal conditions. Where used, all of the following types of compounds read higher or lower than the meter calibration. Check the instructions. If no factor is given, carry out your own checks and determine the factor. The following notes refer to some example compounds.

a. *Alcohols.* Most meters should respond well to the alcohols. However, the effect of water vapor should be known, since a high humidity would be expected in many situations. Some commonly used alcohols that may be encountered would include: methyl, ethyl, isopropyl, etc.

b. *Acids.* Some volatile organic acids would give a response on several types of indicators. These would tend to be highly corrosive to some detectors or the internal parts of the instrument. Acetic and propionic would be good examples. These could be expected in adhesive manufacture, sewage plant gases, and other processes.

c. *Aldehydes.* These should be found in several processes. If levels are high enough for the combustible gas indicator to read, one should be cautious, since few aldehydes have a TLV defined. Some common examples in production use include: formaldehyde, acetaldehyde, glyoxal and others. Several higher molecular weight compounds are used, but not commonly enough to list here.

d. *Ketones.* These compounds are most widely used as solvents. Acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK) are a few such examples.

e. *Esters.* These compounds are used as solvents and fragrances. Some examples include: ethyl acetate, cellosolve acetate, etc.

f. *Aromatics.* These were already mentioned by the example of toluene. Several models of indicators are calibrated for benzene or toluene. Many other materials would be candidates for measurement.

g. *Nitro compounds.* Nitromethane, nitroethane, and nitropropane are listed in the TLV tables. These should respond to detection, however, the reaction products would tend to be corrosive to instrument parts. Check the manufacturer's instructions before

VAB.0001024208

testing for the presence of nitro compounds. Frequent calibration checks would also be in order.

h. *Amines and other compounds* should be considered as the contact with the material occurs.

14. *Use with Inorganic Compounds.* Most inorganic compounds are measured by instruments other than combustible gas indicators. Several considerations are involved that make it necessary to include them in this manual.

a. Considerations for understanding instrument response to inorganic compounds include:

1) Hydrogen selenide and selenium compounds poison certain detectors and should be avoided. Arsenic and volatile heavy metals may also be poisons. Tetraethyl lead is a classical example.

2) Occasionally interfering compounds are present. The response should then be known. One contributor to this manual used the instrument in sewage works where hydrogen sulfide could be present. The instrument used was a model sensitive below the 1,000 ppm range. The reading in practice was a composite of hydrogen sulfide, methane, and other combustible gases.

3) On occasion it appears feasible to use a combustible gas indicator to make check measurements of process gases. These may be in concentrations high enough for several types of meters. Examples could include ammonia (LEL = 16% per NFPA 325M), Carbon monoxide (LEL = 12.5%), and hydrogen sulfide (LEL = 4.0%). Exposure to these gases at these levels are generally lethal very quickly, if not immediately. However many of the organic compounds are also. Therefore, they must be considered in certain problem situations.

b. Most inorganic vapors do not read, nor interfere with the instruments. However, hydrogen sulfide, hydrogen cyanide, carbon monoxide and ammonia are exceptions. When questions arise, verify the instrument and check with the manufacturer.

15. *Unusual Oxidizers.* Conditions met in industry vary as widely as the chemistry background that made production of chemicals possible. Therefore unusual applications for combustible gas indicators may be encountered. One example involves an atmosphere of chlorine. Several materials will burn in such an atmosphere; hydrogen will burn explosively. The use of some type of combustible gas indicator in such atmospheres, particularly for the control of processes, is certainly possible. Further elaboration is not provided since the committee did not have experience in such a situation, but recognized that such a problem could arise and should be listed to complete the tabulation of possible pitfalls.

16. *Use in Mixtures.* Most industrial uses for a combustible gas indicator or hydrocarbon analyzer would be in a mixture of vapors, rather than an exposure to a single pure vapor. Examples can be drawn from every industry. A few examples would include a toluene and petroleum distillate mixed solvent for enamels, an acetone solvent used near paint solvents for silk screen work, trichloroethylene vapors from a dip tank that reach a paint spray operation. Some general guidelines may be helpful for effective instrument use.

a. *Fire applications:* Many applications to limit airborne concentrations to less than LEL or 25% LEL do not require a detailed knowledge of the vapor concentration. Simply reading the composite concentration may provide a sufficient warning for control of the process or ambient gases.

b. *Gross TLV Controls:* Where the total concentration of the mixture can be held to a composite reading that is less than the TLV of the material with the lowest TLV, the composite may be satisfactory for control. Paint solvents made of toluene and petroleum distillates provide a good example. If the total reading indicates that there is less than 100 ppm even when both gases are being measured, this may be satisfactory.

c. *Separation by vapor pressures:* Where two (or a limited number of compounds) are present, an estimate can be made of the concentration of each. By Raoult's Law it can be assumed that the concentration of each vapor is present in proportion to its vapor pressure. Therefore, knowing the relative sensitivity or response of the instrument to each component of the contaminants, one can estimate their relative concentrations. This approach assumes that the two are in the same, well mixed container and other considerations that make precise application of this procedure very difficult.

d. *Analytical Separations:* Where it is necessary to know the concentrations of the separate components in a complicated mixture; it is necessary to use a hydrocarbon analyzer that has separation capability. These include field models of gas chromatographs or infrared analyzers. These devices are expensive, are complicated and require the services of an industrial hygienist familiar with their sophistication. Where needed, there is no substitute. However, once a problem situation is defined, it is often possible to carry out routine monitoring, environmental control and other functions with the simpler instruments.

VAB.0001024209

VI MAINTENANCE

INTRODUCTION

1. *General.* Maintaining the performance of combustible gas indicators is a relatively simple task. The accuracy of these instruments is vital. The techniques to assure satisfactory performance of these instruments will therefore be described.

   Even though the instrument has been factory calibrated, response should be checked upon receipt, since the device could be damaged in transit. The condition of the batteries and other parts has an effect upon the instrument response. Age and some contaminants may affect the sensor. With all of these potential problems, it is evident that periodic maintenance and calibration are necessary for one to have confidence in the reading.

2. *Record Keeping.* Record keeping of instrument maintenance and calibration is recommended for each instrument. Questions such as "When were the batteries changed last?" become important and helpful in assuring the proper functioning of the device.

   Many types of record keeping systems can be devised. These all share some common features whether they are a set of file cards, bound notebook or a computer record. These requirements include at least the following:

   a. Records must be kept up to date.
   b. The date and person doing the work must be shown.
   c. It must be possible to retrieve the information efficiently.
   d. Reference to the instrument must be unambiguous.
   e. The work done must be adequately described so that it can be traced in detail. This is especially important for calibrations.

MAINTENANCE

1. *Manufacturer's Instructions.* This manual of recommended practice *supplements* the manufacturer's instructions and is not a substitute for them. The truism "When all else fails, read the directions." is well known but does not have a place when dealing with combustible gas types of instrumentation. The instrument user should be very knowledgeable about the operating manual and manufacturer's operating instructions before using the instrument in the field. The risk involved should be most evident.

2. Although various combustible gas indicators may operate on similar principles, each has inherent differences and each should be operated as a complete system to produce appropriate response characteristics. Under certain situations it could be considered expedient by the user to interchange components between combustible gas indicators made by different manufacturers. *At no time under any circumstances should a user operate an instrument with parts other than those specified by the manufacturer.* Taking one manufacturer's probe and operating it with another's electronics may result in an improper response. Interchanging parts also negates any approval or certification regarding the safety and operations of combustible gas indicators. When replacing defective parts, such as the electronics or the sensing head with special replacement parts, the user should carefully adhere to the manufacturer's instructions and recalibration procedures.

3. *Maintenance of Components and Parts*

   a. *Batteries.* Most portable instruments operate on battery power. As a general rule the cells will operate the instrument for about eight hours or a period of one work shift. Periodic checks on the batteries are necessary for the continuing operation of the combustible gas indicator. Check the operating instructions for specific details that apply to each model used. Some check list items follow:

      1) *Dry Cells*

         a) Check with a battery tester that applies an appropriate load during the test. A multimeter or volt-ohmmeter normally is not satisfactory because of the light load that is drawn.

         b) Replace after 8 to 10 hours of continuous service. Longer life can be expected from intermittent usage.

         c) Do not store the batteries in the instrument for long periods of time. Remove the batteries from the unit if it has not been recently used, for example, three weeks.

         d) Date each battery at the time that it is received and when it is installed.

      2) *Rechargeable Cells*

         a) Keep a continuing record of the installation, charge cycles, and replacement of the cells used.

         b) Follow directions. Most instructions recommend an overnight charge after the instrument is used. For intermittant use, other procedures are indicated. Some recommend keeping the unit on continuous charge. Others may recommend only periodic recharge (eg, monthly). Some manufacturers state that their batteries should be fully discharged periodically (as often as weekly) or the life of the battery will be reduced.

   b. *Sample Tubing.* The "plumbing" of the combustible gas indicator is one of the most important parts of the working system. When one drops the sample line down into a confined space, such as a manhole which

VAB.0001024210

has a potentially explosive atmosphere, there is no excuse for one to be sampling surface air through a leak at the connection of the sample tube to the instrument case. In addition to being disconcerting, this malfunction can result in a fatal mistake. The type of instrument that uses a diffusion head instead of sample tubing, may have an analogous problem where a connection has become loose. This section only describes the checks made for the type of combustible gas meter where the sample gas to be tested is brought to the sensor by means of tubing, pump and appropriate fittings.

One quick field method to check for leaks is simply to block the incoming air to the sample tube. This can be done by holding a finger over the air intake. If the pump mechanism labors, it can be assumed that the sample is drawn through the system satisfactorily. During this test the pump is obviously subjected to a strain which may be great enough to rupture the diaphragm of the pump. Thus the test should be done with caution and discretion. During use, care should be taken so as not to kink the tubing and shut off the air. If the pump has a bypass system, such as found on certain personal sampling pumps, this approach may not work directly. If the pump is a squeeze bulb, the bulb should remain collapsed. One may also have to hold a finger over the outlet of the bulb to assure that this end does not have a faulty valve. If so, it should be replaced.

The presence of leaks can be determined in the laboratory. First, connect a manometer to the sample line at a small glass or copper tee. Next, draw a vacuum of 20 to 60 cm of water. When the system stops oscillating, read the actual level, vacuum in centimeters of water. Reading can be made in inches of water gage (the recommended scale measures in tenths of an inch). Ideally, the change should be less than one millimeter per minute from the initial reading. An alternate procedure is to calculate the volume of the tubing system and set a standard that allows less than 1% leakage per minute. Also check the leak rate against the flow rate. The leak loss should be negligible by comparison. The procedure described requires one to be familiar with the details of the instrument in use. It may be simple to carry out on instruments where the air outlet is in the form of a fitting. Other instruments may require opening the case. This is particularly necessary for the units that release air directly from the pump, a practice used to pressurize the case.

This procedure to test the integrity of the sample tubing should be done when the instrument is new, to give the user confidence in the device. It should also be repeated after every major maintenance job performed on the system, such as the replacement of a filter, sensor, or sample tubing.

For the models that use a sample line to bring combustible gas or vapor to the sensor within the instrument, the air flow may vary within rather wide tolerances. It is recommended that this flow rate be checked for conformance with manufacturer's specifications. This can be done readily with the use of the bubble flow meter. See verification section of Chapter VII.

When an extension tube is added to the usual sample line, one can readily approximate the lag time involved by its addition.

c. *Filters.* Filters are placed in the inlet sample line to keep particulates, dust and smoke out of the sensing chamber. If filters become clogged with excessive contaminants, the air flow into the instrument will decrease and it will cause a corresponding reduction in response speed and possibly sensitivity. If the response is still slow after the filter is replaced, other items such as the flashback arrestors should be checked. See the instruction manual for details.

Some instruments include absorbing columns in the system to remove water and specific interfering gases. These also need frequent servicing. Humidifier chambers, where included in the system, also require servicing.

From the above discussion, it should be evident that the filters are an integral part of the functioning system and are to be considered for regular operation.

d. *Flash Back Arrestors.* The most common flash back arrestor that provides a definition by example is the one used in chemistry laboratories. Any gas burner that has a top diameter of 2 to 3 cm has a screen or grid across that opening to prevent the gas flame from "flashing back" to the gas outlet jet in the bottom of the burner. If this grid is removed or damaged, the flame will only burn at the base (spud) and not function properly. So, with the combustible gas indicator, the sensor in many models responds to the combustion of the contaminants. This flame, under certain conditions, may burn the gas within the sampling tube all the way upstream to the gas source, and ignite the very atmosphere being tested. At the very least, it is embarrassing to have this be the cause of the very explosion that one was trying to avoid. At the worst, this can also be a most serious mistake. Proper handling is therefore critical. (See Figure III-1).

For certain models that are approved by MESA (See Chapter X, Governmental Agencies, 2, a and the instruction manual) as being "permissible", the instrument must be returned to the factory when repair to the flash back or flame arrestor is necessary. Several legal rules, responsibilities and the risk of losing the permissible rating make it mandatory to return the device. In addition, the manufacturer has the capability to properly install the arrestors as well as to verify that they are functioning properly. This function is especially important when the instrument

VAB.0001024211

is to be used in the presence of hydrogen or other Group A, B, or C gases. (NFPA group ratings).

Occasionally, the situation arises where the flash back arrestors require cleaning because of contamination. From a practical standpoint, these inexpensive parts should then be replaced. Care should be exercised in handling them. Damage so slight that it is overlooked even by careful examination, can prevent parts from functioning properly, while they give the operator a false sense of security.

If no replacement parts are available *and* an emergency indicates that cleaning must be done, some arrestors can be carefully removed from the inlet and outlet of the combustion chamber. They may then be washed in water and detergent. Flammable solvents should be avoided if possible because of the difficulty of removing the last traces of combustible fluid from the device. When replacing the arrestors, care must be taken to obtain a snug fit. The proper functioning of this part is vital in preventing the possibility of flame propagation from the chamber.

Verifying the functioning of the flashback arrestors is perhaps more important than even the calibration checks that are recommended in this manual. This work can be done for example, by immersing the entire functioning instrument into a plastic bag filled with an appropriate combustible gas mixture, between the LEL and UEL. This procedure is *not* recommended, except for laboratories that are *adequately* equipped for such operations, such as the manufacturer's and MESA. It is recommended that, in emergencies where there is doubt that the flame arrestors are working properly, an instrument *known* to be functioning properly be procured.

To illustrate the risk of igniting an explosive atmosphere, consider the following episode which was experienced by one of the authors. During a field survey a request was made to document the combustible levels of a large battery charging operation. The request was refused on the basis that the combustible gas indicator available was not designed for use in hydrogen atmospheres.

After returning to the laboratory home base, the hypothesis was tested. Hydrogen from a gas chromatograph unit was used to fill a plastic gas of approximatley 10 - 12 liters. Some air was wafted into the bag and the bag was then closed. A long sample tube was used to carry the atmosphere from the bag to the instrument in question. Shortly after the instrument was turned on, the bag flashed and the plastic started to burn. This verified both the fact that the bag contained a flammable mixture and the ability of the instrument to ignite it.

Later a new and different brand of instrument was purchased with the specification that the flashback arrestor would be effective in the presence of hydrogen. After receiving the new instrument, the experiment was repeated. This time the bag did not ignite. There were a series of popping noises from the instrument case which were small explosions ignited by the mechanism. Since this gas was released within the case which was pressurized by the sample pump, one can only guess what would have occurred if the meter itself had been in the explosive atmosphere. When the sampling tube was disconnected at the instrument, a match was used to light the gas in the sample tube. The gas in the bag again flashed, confirming the presence of the explosive test atmosphere.

e. *Sensor.* Two references are necessary to describe the maintenance needed for the sensor. The first is the manufacturer's instruction manual. This is necessary since the design and properties of each type of sensor vary widely.

   Second, refer to Chapter VII on calibration as described in this manual. Periodic verification is needed to ascertain the condition of the sensor. The effects of corrosive gases and poisons have already been described. High humidity may have a significant effect on the need to maintain a sensor that operates on catalytic principles. Though humidity may have an effect on the level of reading made, it probably has little effect on the need for the maintenance of hot wire or hydrogen flame ionization detectors.

f. *Electronics.* Erratic fluctuations of the meter needle during adjustment or testing may indicate dirty or clogged potentiometers. When the instrument is not used for some time the contacts, particularly on the potentiometers, become oxidized and must be cleaned. This can easily be accomplished by disconnecting the power supply and cycling the switches about 15 times.

   Difficulty beyond the problems with dirty contacts probably requires service by an instrument shop. Certainly there is little that can be done on site for involved electronic servicing. Very often the instrument must be returned to the manufacturer.

4. *Field Servicing.* Some malfunctions in the field can be easily corrected. In all cases refer to the manufacturer's instruction manual. Some common examples include the following conditions.

   a. The meter needle goes to the high end of the scale. This may be due to the following.

      1) The combustion well or chamber may be filled with an explosive mixture. In this case, the instrument should be flushed with fresh air. The filter may need replacement.

      2) The zero adjust may be set too high. Reset it.

      3) The connections to the detector may be loose. Secure them. The terminals on the "compensator" filament may be touching. Replace. The compensator is a filament that adjusts for variables in the sample stream.

VAB.0001024212

4) The filament may be burned out. Replace.

b. If the meter pointer remains below zero, usually to the left, the following are example problems.

1) The zero adjust may be set too low.

2) The compensator filament may be loose.

3) The terminals on the detector filament may be touching each other.

4) The compensator may be burned out.

5) One may be sampling in a contaminated atmosphere.

c. On some models, when the meter cannot be adjusted to the "check" point, zero, with the indicator turned "on" and the "selector" switch in the "check" position, the batteries must be replaced.

d. On all instruments, the adjustment of the zero setting must be done occasionally. This gradual shift of the zero reading is known as "zero drift". When the zero setting changes excessively or much faster than is characteristic for that specific instrument, some maintenance may be required. When the instrument is operating and the instrument is taken into fresh air, but the reading does not drop to zero, the inlet stream may be clogged, or the inlet filter or flash back arrestor may need replacement. In some field situations, the "fresh" air can be contaminated. This is occasionally a problem with the more sensitive instruments and in areas where the gases are widely diffused.

e. If the indicator operates sluggishly, the flow in the system is probably restricted for some reason. These include:

1) Filters of flashback arrestors may be clogged.

2) The sample extension tubing (when used) may be kinked.

3) There may be a leak in the sampling system.

4) The sample pump may need adjustment. The valves, for example may be worn and not seat firmly. This diminishes the air flow.

5) An obstruction may cover the air discharge.

f. An erratic reading meter may be caused by dirty potentiometer contacts, loose connections etc.

VAB.0001024213

VII CALIBRATION

INTRODUCTION

1. *General.* This chapter is an extension of the one on maintenance. It describes the techniques that verify that the maintenance has been done well and that the instrument is not out of adjustment.

   The need for a chapter on calibration is best related in the history of the device. For example some of the oldest models were used in mines. As they functioned primarily to measure methane, they were called "methanometers". In this setting they were more specific and quantitative than anything previously available. In addition, they had to be used where a factor of safety had to be applied, therefore their accuracy was adequate if the measurement was within 10% to 15%, in the concentration range of 0.5% to 4% of methane in air, 10% to 100% LEL. (Reference 15).

   With the passing of time, the methanometers or combustible gas indicators were adopted for measuring gases outside of mines. These applications would typically include gasoline vapors and eventually solvents such as benzene. This trend toward wider usage included refinements in the instrumentation, including greater sensitivity to measure lower concentrations. These refinements also brought the need for greater precision. Certainly the variation of 10% to 15% at 10 to 100 ppm is a more stringent constraint than a similar variation of 10% to 15% in the percent concentration range.

   The broader application for the combustible gas indicator has been recognized by manufacturers. This is evident by the fact that these instruments are available with calibration that is based on any one of several gases. These include: methane, pentane, hexane, benzene and others. Manufacturers also recognize the broader applications in the field. There they provide conversion or sensitivity factors for a series of common solvents. These may include toluene, xylene, acetone, esters, ether and other solvent vapors.

   Additional information required by industrial hygienists includes:

   a. The need to verify the response of the instrument to measure the gases or vapors for which it was calibrated.

   b. Confirmation of the sensitivity factor may be required, even where provided.

   c. Determination of the sensitivity factor may be required for compounds where it is not provided.

   d. Interfering compounds need to be checked for instrument response.

   e. Some models of instruments respond to compounds with low flammability. This includes halogenated hydrocarbons such as trichloroethylene, methyl chloroform, methylene chloride, and others. This response may need to be quantified. However, when the corrosive gases that result from detection degrade the sensors used, this test should be avoided. An instrument that can operate under these conditions may have to be selected.

   Calibration is the term often applied when verification would be more appropriate. The meanings of these terms overlap and some clarification is required. The main difference lies in the degree of effort applied to the work.

   Calibration requires that the complete range of the instrument be tested for sensitivity and conformity with the readout scale. It implies testing with high precision, generally in a laboratory. It may include the adjustment and trimming of the internal electronics and mechanics to provide the appropriate response.

   Verification is the procedure for ascertaining that the instrument is functioning properly and provides the proper readout. Most of the work described in this manual can readily be done at a level of precision that is acceptable for verification. It would usually require some refinement if applied to a calibration procedure. When one or two readings are verified, one normally proceeds on the basis that the instrument functions well over its entire range.

   Conversion or sensitivity factors can be determined by calibration or well done verification techniques. This may be necessary where the manufacturer does not provide such factors for the material to be measured.

   Though it cannot be called verification, there is a time in the field where one does have to demonstrate that the device will respond to the material that is being measured. This can be done by checking a known source.

   For example, if one draws a vapor from above a flammable liquid and the meter needle or readout indicates a substantial reading, the instrument user and observer recognize that the device is active. This brief action can instill confidence that the device is functioning, or give an immediate signal that it is not.

2. *Record Keeping.* Good records are necessary for at least two reasons. One is technical. Quantitative information requires that the measured facts are recorded and not simply remembered. In addition the number of facts involved are great enough to require systematic documentation. Second, it may be necessary at any time to demonstrate that a given set of data is valid. Records assist in meeting such challenges – from inside as well as outside of the organization.

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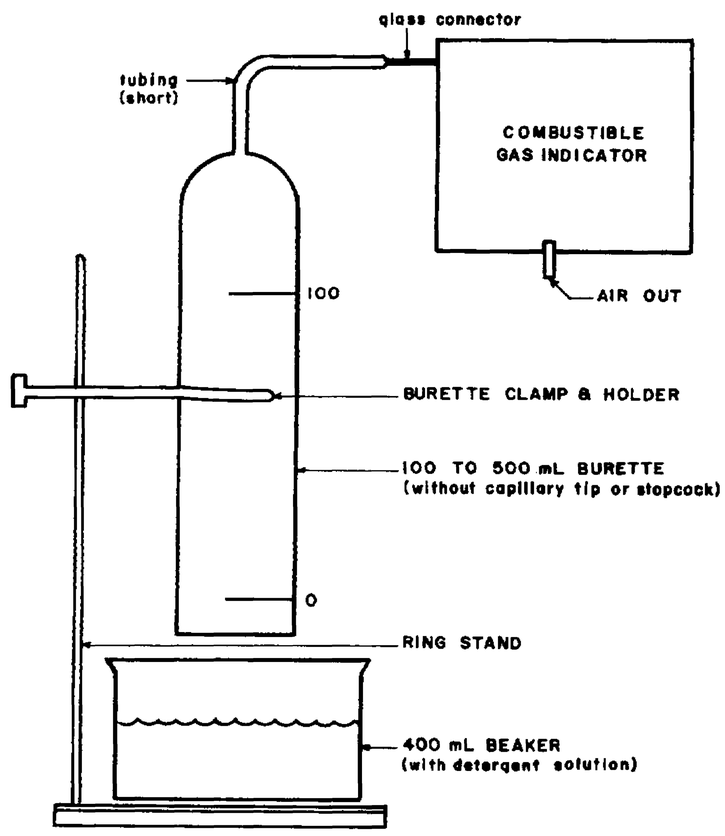

Figure VII - 1 — Bubble flow meter.

Each organization has its own system of record keeping, therefore only one comment need be made. Even though much of the formal data is on systematic records, the detail of taking the raw data should be made in bound notebooks. This is good laboratory and field procedure. Taking notes on scraps of paper is slipshod and has no place in good industrial hygiene practice. Some work will have to be done on forms, such as graph paper. These pages, properly labeled, cross referenced, dated and signed can be filed in a formal file. One option is to tape and staple representative sections into the log book.

VERIFICATION

1. *General.* A series of techniques and examples are presented so that one can verify the operation of a combustible gas indicator or device to measure the concentration of several organic vapors. However the number of examples is necessarily limited when compared to the numbers encountered in practice. Therefore when a different material is to be handled, the examples described can be used as a guide for selecting a suitable procedure. To adapt the procedure, one must go to the literature and find the necessary chemical and physical data. The boiling points and vapor pressures are needed so that one will be certain that the material will be airborne at the concentrations desired. Information on the reactivity of the vapor is necessary so that the material to be measured is not lost by, for example, reaction with the surface of the container used to confine the vapors. Toluene is such an example. This material is so readily absorbed by rubber that a rubber lined vessel would lower the airborne concentration significantly, especially at low concentrations in the TLV range.

2. *Leak Test.* The first in a series of verifying tests is to confirm that the sample is drawn into the inlet tube properly. Refer to the description of this procedure in the maintenance section of Chapter VI.

3. *Flow Rate.* The flow rate of sample air passing through the instrument may vary within rather wide limits. The value specified by the manufacturer should be known to assure that the instrument is functioning properly. The user also needs some measure of the length of time it will take a sample to reach the instrument sensor while one is using the extended sample tube. If an excessive time is taken, other problems become suspect. Leaks in sample tubing and faulty adjustments in the pump are two problems that may have developed.

   One of the requirements to measure the flow rate of these types of instruments is to do so without applying an appreciable flow resistance on the system. The bubble flowmeter described has had wide acceptance for this purpose. It is simple, direct and, if done properly, will give good results. Some precautions and limits include:

   a. The fittings should have minimum restriction. Do not, for example, use burettes with glass stopcocks in them.

   b. Any number of bubble solutions are suitable for use. A 0.5% soap solution in distilled water, warmed slightly to disperse the soap, may make a satisfactory solution. Commercially prepared solutions are available. These include the children's toy bubble solutions.

   c. All glassware must be clean with respect to the bubble solution used. This is necessary to keep the bubble free of distortion and drag.

   d. Use the bubble meter for only short periods of time. With long periods of use, the humidity and aerosol droplets may wet the filters that preceed the sensor and cause excessive flow resistance. The bubble flow meter is applied as follows (Reference Figure VII-1):

      1) Connect the pump and start to draw air through the system.

      2) *Briefly* raise the detergent solution to the bottom of the burette. This forms the bubble that indicates the air flow. When starting the test, several bubbles may have to be started so that the tube wall wets and the bubble can travel the calibrated length of the burette.

VAB.0001024215

3) Time the travel of the bubble between the zero position and the top calibrated mark. A stop watch is usually adequate and desirable.
4) Calculate the ratio of milliliters of air flowing per minute of time. This value should be recorded.
5) The ambient temperature and barometric pressure should be recorded as a matter of good practice. Corrections are normally not made for temperature, pressure or humidity in typical field work.

4. *Span Gas*

a. Introduction. Known mixtures of a combustible gas or vapor in air are used to set the sensitivity, range or "span" of the instrument response. For this reason they are known as span gases. A wide variety of such mixtures are now available. Some have the concentration known and confirmed by analysis to a high level of precision. These gases are easily used in a wide variety of instrumentation from field devices, such as combustible gas indicators, to sophisticated laboratory gas chromatographs.

The gas-air mixture (known) is furnished in a compressed gas cylinder, lecture bottle, or aerosol can. From this high pressure source it is released into a reservoir, often a plastic bag. The gas from the source is not directly connected to the instrument, so that the pressure from the container does not affect the instrument readings, or even rupture the device. In addition, the instrument samples from the reservoir in the same manner as when air is sampled.

The span gas technique is limited to materials that are gases and will remain in the gas phase during the manipulations needed for the calibration or verification procedures. Combustible gases that can be procured for such a procedure include methane, propane, ethylene, carbon monoxide and others. The field indicators can readily be checked at various locations and at a wide range of conditions that may be met on site.

b. Equipment (See Figures VII-2 and -3)

1) Combustible gas indicator
2) Appropriate plastic bag

Figure VII - 2 — Combustible gas indicator being verified by the Span Gas - Balloon Method. (Photo courtesy MSA, Explosion and Gas, No. 861, Hart.)

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Figure VII - 3 — Example of Span Gas Cylinder with pressure reducing and flow rate control valve. These are available in a variety of sizes with other gasses. (Photo courtesy MSA, Propane in Air is shown, No. 862, Hart.)

3) Appropriate tubing and connections
4) Span gas cylinder with pressure reducer and fittings

c. Procedure
1) Flush and fill the bag with span gas
2) Connect the bag to the indicator
3) Draw span gas through the combustible gas indicator
4) Compare the instrument readings to the span gas concentration. Adjust the instrument as required.

d. Discussion. The plastic bags can be made of any of a wide variety of materials. When the tests are to be carried out at the LEL range, down to the 1000 ppm (0.1% gas in air) range, most plastic bags including polyethylene garbage bags, balloons and others have been used successfully. If the procedure requires lower concentrations, in the 1000 to 100 ppm range, the inert sampling bags of tedlar, aluminum foil and other materials that are now available, are recommended. With careful techniques, concentrations as low as approximately 10 ppm can be calibrated with these bags.

As previously mentioned, the span gas usually is furnished in a pressurized container. The use of proper fittings is necessary. Protective glasses should be worn, as in any laboratory procedures.

The span gas concentrations that are described are assumed to be used directly from the compressed gas source. Laboratory techniques are available which can be used to extend the range of concentrations being tested. These also make it possible to run a calibration test series from a single gas source that would normally be used as a single verification point.

These would include metering techniques where measured amounts of air or contaminating gases would be added. These are discussed in some of the references that have been cited.

A combustible gas indicator that has been zeroed is connected to the plastic bag containing the test mixture by means of a tube and connector. The gas is withdrawn carefully so that the limp plastic does not restrict the flow. One advantage of the use of a bag over the rigid container is that the bag collapses. There is no problem with air progressively diluting the mixture being sampled. The resistance due to bag collapse is small and can be ignored.

The gas in the bag can be mixed easily by kneading the bag very gently.

Note the time that it takes the gas to first give a response or a reading of 10% of the concentration. Note also the time that it takes for the meter to give a near maximum reading, specifically 90% of the eventual equilibrium value. These two times, response time and rise time are not the ones quoted by the

VAB.0001024217

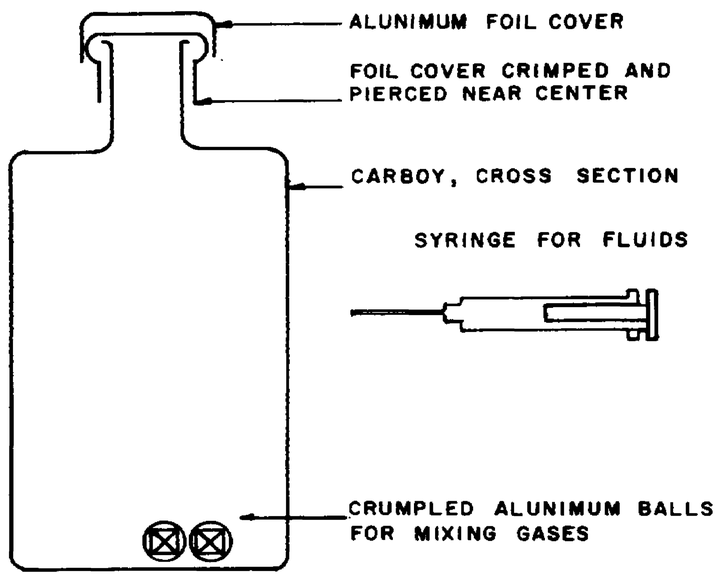

Figure VII, B-5,1 — Batch calibration, carboy method.

manufacturer. These include the additional time to transport the gases through the entire tubing and system. They are excellent values to keep in mind for field work since they measure the delays involved in actual sampling.

When the span gas from a reliable source has the concentrations and tolerances certified, one can assume that the gas concentration is correct. The instrument is adjusted to the stated value. The meter should then read correctly. With some instruments, a correction factor is applied to the scale reading. Where used, this must be taken into account.

When two different batches of span gas are checked and the values do not agree, a third batch of calibrating gas should be used. If the comparison does not resolve the problem, the solution is beyond the scope of this manual. It may be necessary to seek the assistance of a qualified laboratory, such as the ones that are certified by the American Industrial Hygiene Association. One such interesting example related to us concerned discrepancies in the concentration of carbon monoxide in air. The anomaly was finally resolved when it was demonstrated that the gas reacted with the steel walls of the compressed gas cylinders. This effect occurred slowly over a period of several months. One result of this study has been to use special aluminum cylinders for this mixture.

5. *Batch Calibration.* Detection of volatile solvent vapors comprises a large portion of the work for which a combustible gas indicator is used. Many compounds fall into this category. This is complicated by the wide range of TLVs and explosive levels involved, as well as their vapor pressures or tendency to evaporate.

The wide variety of solvents involved also make it difficult for the manufacturer to provide calibrations for all of these compounds. Finally there are occasions where more than one solvent is present. The need for verification of the instrument response to the materials being tested is essential. A simple, direct, inexpensive method known as batch calibration is thus very useful for this purpose. This is a very workable system for many compounds. Some substances include toluene, octane, ethyl ether, acetone and others. In general this method is applicable for materials which are liquids at room temperature, have a vapor pressure high enough to evaporate and produce the desired concentration, and are easily measured.

An example follows:

a. *Acetone* will be selected as the material for a practical example of the batch calibration method. This material is widely used in industry, is readily available and can be readily measured with a combustible gas indicator.

b. A batch calibration at *25% of the lower explosive limit (LEL)* will be selected. This level is a practical concentration that can be safely prepared in a rigid wall container. Literature references recommend 25% as a maximum concentration that can be safely handled. (References 1, 17, 23).

   If a more concentrated solution than a 25% LEL mixture of acetone in air is to be made, a variation of this procedure using a plastic bag is available. 100% of the LEL for acetone is 2.6% acetone vapor in air (Reference 1, NFPA Code 325M). 25% of this value is *0.65%* acetone in air.

c. The *container* should be chosen at this point. Usually a 20 liter (L), (5 gallon) narrow neck carboy is ideal. It is large enough so that the liquid volume required to make the concentration can be measured accurately and easily, and will provide enough volume so that the meter can be run for a long enough time to determine the response. One can sample approximately one tenth of the volume of the container before the mixture is diluted appreciably. If the instrument being checked samples at a rate of one liter per minute, this mixture would be useable for two minutes before the concentration has been reduced excessively.

d. The nominal size of a carboy is an approximation of the volume contained. For purposes of calibration, the volume of the container will have to be determined precisely, to within two decimal places. As the gaseous mixture will fill the container to the lip of the opening, this is the level which will have to be measured. Usually the most convenient procedure is to fill the carboy with room temperature water, measured from a large laboratory graduated cylinder. Alternately,

VAB.0001024218

one may weigh the amount of water that is contained and convert it to volume. For purposes of illustration, the precise volume of the carboy was 20.17 liters (L).

e. The carboy should be clean and dry. That is, oily materials that may absorb the vapor or gas which is added, must be removed. No moisture should remain on the walls of the container. The humidity in room air is usually recorded, but ignored in the calculations made for calibration. Extremes of humidity, especially high humidity, may have some effects on the sensor. Where this may become a problem, consult the instruction manual for the instrument being used. Some verification checks may be in order.

f. For illustration, a calibration mixture using 25% LEL acetone will be selected. At 100% LEL, the concentration of acetone is 2.6% acetone in air by volume, according to the NFPA 325M. Therefore 25% of this LEL equals 0.65% acetone in air. For this example a carboy whose volume is 20.17 L of air will be used. The liquid volume of acetone needed is then calculated by the formula given in Equations (2.a.3) of the Calculations section of this chapter and as shown below.

$$V_L = \frac{0.65}{0.8} \; \frac{20.17}{100} \; \frac{34.0}{24.45} = 0.228 \text{ mL}$$

g. Supplies needed for the calibration point include the following:
   1) Acetone. Reagent grade is preferred.
   2) Carboy. The volume is to be known precisely.
   3) Micropipet. Choose the appropriate size with which to dispense the calculated amount of liquid.
   4) Aluminum Foil. Prepare four squares approximately 10 cm on a side. Two are used to cover the carboy, two are loosely crumpled and provide a means to agitate the air - vapor mixture. (See Figure VII-4)
   5) Glass rod or tube. This item is optional. If used, add a small piece of absorbent paper.
   6) Combustible gas indicator. This unit to be tested should have been prechecked.
   7) Log book. The items needed to properly record the calibration, time, etc. should be on hand.

h. The steps in the procedure are:
   1) Clean and dry the carboy.
   2) Crumple two of the aluminum pieces and place these into the carboy.
   3) Place the tube with absorbing paper into the carboy, if used.
   4) Cover the bottle with the two remaining pieces of foil. By hand, crimp the first one firmly around the container lip.
   5) Measure the acetone using the proper pipette technique. Do the next step quickly so that no appreciable amount evaporates.
   6) Add the liquid through a hole in the first layer of foil. Allow the liquid to drop onto the absorbent paper and/or the bottom of the carboy. Touch the tip of the pipette to the neck of the carboy to leave the last droplet in the bottle. Cover the carboy and foil opening with the second layer of foil.
   7) Thoroughly mix the acetone in air solution by picking up the bottle and shaking it. The foil balls should be made to rotate as they move up and down. This provides both vertical and horizontal mixing. The mixing should continue until all of the liquid has evaporated.
   8) With the instrument operating, insert the air intake tube or probe into the center of the carboy. Record the time required to reach 90% of the concentration and the maximum instrument reading.
   9) Compare the maximum reading with the calculated concentration specifically for the gas or vapor used. The two should agree to within 10%. If the work has been done with good techniques, 5% agreement can be obtained. If the comparison is not satisfactory, review and correct the procedure. Then repeat starting with step one.
   10) The time required to reach 90% of the reading can be compared to instrument specifications. It does however include the delays due to the length of the sampling tubing. If this delay time is known, when extension tubes are used in certain field situations, one has a guide as to when a reading may become meaningful. It also can provide a clue as to possible leaks in the system if the delay is excessive.

i. The example procedure has been applied successfully to many volatile liquid substances. One can readily adapt variations to fit the individual situation. Some notes follow:

   1) (a) Alternate containers can be used. Among the best are plastic sampling bags which may be purchased commercially. These are made of teflon, tedlar or other non-absorbent material. If properly chosen, they are inert to the solvent. They can also be obtained in a wide range of sizes. One major difference in their use is that air must be metered into them, since the container does not have a fixed volume.

      (b) Non-rigid containers *must* be used when concentrations above 25% LEL are to be prepared. Controlled, safe and preferably remote procedures are required. These levels are above those permitted for routine operations by the NFPA and others because of fire and explosion risks. When it is considered necessary to verify instrument responses at these high levels, it is emphasized that only flexible, thin wall containers be used. The ubiquitous polyethylene plastic garbage bag is

VAB.0001024219

ideal. These are quite inert to many solvents and the slight tendency to absorb traces of solvent on its surfaces can be tolerated at the high concentrations called for at 25% LEL.

2) Some sample bags and containers have narrow openings which make it difficult to insert materials. One can prepare small "boats" of aluminum foil for the liquids. In some cases the liquid may be deposited directly onto the bag material.

3) The proper choice of materials is important, not only for the sample container, but for its cover, sample tubing, etc. Some materials, for example gum rubber, will absorb significant amounts of toluene and other aromatic solvents.

4) Pipettes are available in the microliter through the milliliter sizes. Choose the one that permits measurement to closer than 5%, preferably to within 2% of the calculated volume. Gas syringes are also available for the direct addition of a gas as well as a liquid.

5) The addition of the contaminant to the test volume has been recognized as one of the operations to be done with care. The precision of the calibration is dependent upon this operation.

6) The final part of the test procedure is simply to insert the probe of the combustible gas meter into the test volume and measure the concentration. Where a rigid walled container is used, draw only 10% of the container volume for the test. If mixing is continued during the sampling, the sample concentration will have dropped to about 95% of the original level. If a higher precision is required, several containers can be connected in series, a procedure that is described in the literature. (See References 9 and 10)

   When a plastic bag is used for sampling, the bag collapses while the air-contaminant mixture is withdrawn. There is therefore no problem due to dilution.

7) When one does remote sampling while using a long sampling line, the time delay should be known for safe and prudent operation. For example 20 feet of extension tubing can increase the response time substantially beyond that given by the manufacturer's specifications which were made using the probe provided.

8) Instruments that have a "diffusion head" which "senses" the gas levels at the end of the probe instead of drawing the atmosphere into the instrument are handled in the same manner as those that conduct the sample to the sensor within the instrument. It is sometimes difficult to place the sensor into the test atmosphere. A wide mouth bottle is usually needed. The probe can be left in the test atmosphere for a considerable time with little dilution effect on the test concentration. A "rule of thumb" would be to leave the probe only as long as required to get a maximum reading on the instrument.

9) This procedure tests the instrument response against the calculated concentration. When the number response does not match the calculated value within about 10%, the entire procedure should be reviewed and the test repeated. There is no short cut.

10) It should be recognized that the meter response to materials other than the one for which the instrument was calibrated by the manufacturer will not read out the concentration directly. Factors must be applied to the meter reading to obtain the "true" concentration. A meter calibrated on hexane will only provide direct meter readings for that material. If this instrument is used to measure atmospheres containing acetone, methane, ethyl chloride or other materials, the reading must be multiplied by a factor to obtain the concentration of that material.

    The calibration method described can be used for materials other than those for which the instrument was calibrated at the factory. It then provides a check on the factor. Some instruments have a potentiometer control which adjusts the readings. This may be used in place of factors if the instrument is to be used in such atmospheres for extended periods of time. It is more common to have this adjustment fixed and not accessible.

6. *Dynamic Systems.* Dynamic systems have been developed. These are often used where higher levels of precision are required, lower concentrations are needed, or wall effects are significant. They can be applied to combustible gases, volatile liquids and other airborne materials. Please consult other sources for these techniques.

CALCULATIONS

1. *Introduction*

   a. The example of the preparation of test atmospheres and their variations that were described involved the measurement of a volatile liquid, and it can be applied to gases as well. The concentrations involved range from combustible or flammable levels down to parts per million. With the infinite number of combinations possible it is necessary to calculate the amount of contaminant involved for the desired combination. This section describes these calculations. Reference will also be made to relevant sources of information.

   b. The calculations for the amount of contaminant to be added to a test mixture are such that one can proceed

VAB.0001024220

directly to section 2 and apply the formulas as they are written. The assumptions and conditions that are made and have to be met to provide such simplicity are briefly described for background. They will also be valuable to review when one checks the discrepancy between the test measurement and the calculated value. These are itemized as follows:

1) *Standard Temperature* is assumed to be room temperature. The value chosen is 25°C (77°F). At this temperature the volume of one "mole" of a compound is 24.45 liters. So long as the work is done within about 5°C, (25 ± 5°C, 77 ± 9°F) the temperature corrections are negligible. The temperature chosen is often used for ventilation work (References 2 and 10). The work can therefore be done without applying temperature corrections and also relates to other literature. It should be noted that this definition of standard temperature is different than 0°C, the one used in classical chemistry.

2) *Standard Pressure* is assumed to be the ambient pressure. The reference value is 760 mm mercury, the standard value for most gas calculations. For the precision required, the difference in ambient pressure for most days and at altitudes less than 300 meters (1,000 feet) has a negligible effect and can be used without a need for correction. It is good practice to record the barometric pressure for the period during which the calibration is being done. If this information is procured from weather services, be sure and record whether the reading is an absolute reading or whether the value was corrected to sea level. If a correction is incorporated, the value of the correction and altitude to which such a correction is made, should also be corrected. Corrections are required in many mountainous areas, e.g. Denver.

3) *Gases Mix Proportionally by Volume.* This principle is applied to the calculations for both gases and vapors as a simple ratio and proportion. It is a direct use of the "Gas Laws". The following physical phenomena are involved and are listed for background.

(a) Avogadro's law states that equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.

(b) Dalton's law states that the total pressure exerted by a gas is equal to the sum of the partial pressures which would be exerted by each gas alone.

(c) Boyle's law relates that the volume of a gas varies inversely with pressure at a constant temperature. As the usual work done is essentially one pressure, atmospheric, any corrections cancel out. That is, the ratios of the two pressures involved is one (760/760 = 1.000).

(d) Charles' law states that the volume of a gas varies inversely with the absolute temperature at a constant pressure. Since the calibrations and work are normally made at (nearly) a single temperature, corrections reduce to a ratio of one.

(e) It should be recognized that precise work or work under extreme conditions may require corrections based on one or more of the above laws.

(f) Field work may be done under conditions vastly different from that at which the calibration was made. It may be assumed for most cases that the laboratory calibration will hold reasonably well. Reference should be made to the manufacturer's instructions for effects of temperature and pressure on instrument response. The procedures described can also be used to verify the effects of any variables that may be encountered.

c. Several terms are used in the calculations and in the preparation of test solutions which require definition. The following are provided to clarify their meaning.

1) Density or Specific Gravity.
The density of water is stated in grams per milliliter (g/mL) or in grams per cubic centimeter (g/cc). With either label the value is 1.00 to two decimal places. Specific gravity is the ratio of the density of a material to that of water. For example the specific gravity of acetone is 0.79, i.e. a given volume weighs 0.79 times as much as the same volume of water. Therefore one cubic centimeter (cc or mL) of acetone weighs 0.79 gram (g). Also:

$$\text{Volume in mL (or cc)} = \frac{\text{Weight in g (calculated)}}{\text{Density in g/cc or Specific Gravity}}$$

2) Microliter = milligram (μL = mg) for water.
The terms mL, cc, and g are assumed to be equivalent measures of volume and weight (mass) for liquid water. Many measurements that are needed for the described calibrations are small fractions of a mL or g. The common unit used is one-thousandth (milli) of these amounts. For such small volumes the term "cc" is not used and will be omitted from further discussion. Micro (μ) indicates millionth. The relationships between the volume and weight of water (1.00 g/mL) are as follows:

1.00 liter (L) = 1,000 gram (g)
0.001 L = 1.0 milliliter (mL) = 1.00 g
0.001 mL = 1.0 milli mL* = 1.0 microliter (μL)
1.00 μL = 1.00 mg

*This term is for illustration, is correct, but not used.

3) 24.45 L (liter) is the gram molecular volume.
The molecular weight of the gas or vapor at the reference temperature of 25°C occupies 24.45 L.

VAB.0001024221

This value is used in all of the example calculations as 25°C is essentially room temperature. It is also the reference temperature used in the "Industrial Ventilation, Manual of Recommended Practice" (Reference 23). If another reference temperature was used, for example 20°C, one should recalculate the molecular volume. At 20°C it becomes 24.04 L.

2. *Equations*

a. The following three formulas relate the amount of *liquid* which must be used to obtain given gas or vapor concentrations. These are as follows:

1) For concentrations given in mg/M^3.

Volume of test liquid in μL
Concentration of vapor (gas) given in mg/M^3
Volume of the test container in liters

$$V_L = \frac{C_g}{d} \cdot \frac{V_{tc}}{10^3}$$

Conversion factor, cubic meters = 10^3 liters
density of test liquid in g/mL (or Sp Gr)

2) For concentrations given in *ppm*.

Volume of test liquid in μL
Concentration of vapor or gas given in ppm
Volume of test container in liters
Molecular Weight of the test compound

$$V_L = \frac{C_g}{d} \cdot \frac{V_{tc}}{10^3} \cdot \frac{MW}{24.45}$$

Molecular Volume of vapor in L
Conversion factor to give test liquid in mL, vapor concentration in ppm
density of test liquid in g/mL (or Sp Gr)

3) For concentrations given in *percent (%)*.

Volume of test liquid in mL
Concentration of vapor or gas given in %
Volume of test container in L
Molecular Weight of the test compound

$$V_L = \frac{C_g}{d} \cdot \frac{V_{tc}}{10^2} \cdot \frac{MW}{24.45}$$

Molecular Volume of vapor in L
Conversion factor to give test liquid in mL, vapor concentration in %
density of test liquid in g/mL (or Sp Gr)

b. The following formulas relate the volume of a *gas* used to give a chosen *gas* level.

1) For concentrations given in *ppm*.

Volume of test gas in mL
Concentration of gas given in ppm
Volume of test container in L
Conversion factor (1/1,000)

$$V_g = C_g \cdot V_{tc} \cdot 10^{-3}$$

2) For concentrations given in *percent (%)*.

Volume of test gas in mL
Concentration of gas given in %
Volume of test container in L
Conversion factor

$$V_g = C_g \cdot V_{tc} \cdot 10$$

3. *Tables.* Selected gases and vapors with which an industrial hygienist may have to work have been listed in the table in this section. It provides the base for further examples. As the materials that may be contacted are extensive, the table also provides a guide to some of the sources from which data may be obtained for compounds that are not listed. See the footnotes to the table and the references in the appendix of this manual.

VAB.0001024222

SELECTED INFORMATION FOR BATCH CALIBRATION

	(1) Chemical Name	(2) Density Sp Gr *D	(3) Mole. Weight (g) *D	(4) Threshold *E Limit Value ppm	mg/M³	(5) Microliters of Liquid - to Give TLV in 10 Liters	(6) Lower *F Explosive Limit %	(7) Milliliters of Liquid - to Give 25% LEL in 10 Liters	(8) NFPA Group
1	Benzene *B	0.879	78.11	10	32	0.363	1.3	0.118	D
2	Toluene *B	0.867	92.13	100	375	4.346	1.2	0.130	D
3	Xylene *B	0.868	106.16	100	435	5.002	1.05	0.131	D
4	Styrene	0.907	104.14	100	420	4.696	1.1	0.130	D
5	Ethyl Benzene	0.867	106.16	100	435	5.008	1.0	0.125	D
6	Hexane	0.660	86.17	100	360	5.45	1.1	0.147	D
7	Heptane	0.684	100.20	400	1600	23.40	1.05	0.157	D
8	Methylene Chloride	1.336	84.94	200	700	5.24	15.5	1.007	-
9	Trichloro-ethylene	1.466	131.40	100	535	3.666	12.5	1.146	-
10	1,1,1 Trichloro-ethane	1.256	133.42	350	1900	15.21	12.0	1.303	-
11	Methanol *A	0.793	32.04	200	260	3.305	6.7	0.277	D
12	Isopropanol *A	0.785	60.09	400	980	12.52	2.0	0.157	D
13	Ethyl Acetate *A	0.901	88.10	400	1400	16.00	2.2	0.220	D
14	Methyl Cellosolve Acetate *A	1.007	130.05	25	120	1.321	1.7	0.225	D
15	Ethyl Ether *A	0.713	74.12	400	1200	17.01	1.9	0.202	C
16	Acetone *A	0.792	58.08	1000	2400	29.99	2.6	0.195	D
17	Methyl Ethyl Ketone *A	0.805	73.072	200	590	7.425	1.8	0.167	D
18	Nitropropane *B	0.99	89.064	25	90	0.920	2.6	0.239	*H

*A Anhydrous form of the chemical is used. The water solution for the chemical would change the result.

*B Synonyms for the chemical are listed using the number of the line.

B-1 Benzol

B-2 Toluol

B-3 Xylol (Pronounced Zylol) (o, m, p, and mixed forms are considered equivalent and their properties are averaged.)

B-10 Chlorethane, Methyl chloroform

B-11 Methyl alcohol

B-12 Isopropyl alcohol

B-14 Ethylene glycol monomethyl ether acetate

B-15 Ether

B-17 MEK, 2-Butanone

B-18 1 or 2 Nitropropane are considered equivalent.

*C Chemical groups listed include:

GROUP	LINES
Aromatic	1-5
Aliphatic (Straight chain hydrocarbons) (Constituents of gasoline, etc.)	6, 7
Halogenated Hydrocarbons (Chlorinated examples listed)	8-10
Alcohols	11, 12
Ester	13
Ether	14, 15
Ketone	16, 17
Nitro aliphatic	18

*D Specific Gravity and Molecular weights were procured from the Handbook of Chemistry and Physics (Reference 19). Other handbooks list the same information.

*E Threshold Limit Values (TLVs) were quoted from the Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1978, as published by the American Conference of Governmental Industrial Hygienists. Except where TLVs were updated, OSHA 1910.1000 Subpart Z, Tables Z-1, Z-2 used the 1968 and 1970 edition of these TLVs. Check the values in the latest table available, as these values are changed occasionally. Time weighted averages were listed (References 2, 14). Compounds that are listed and have a skin or ceiling notation include: Skin: Toluene, Styrene, Methanol, Methyl cellosolve acetate.

*F The National Fire Codes (NFPA) for LFLs, Article 325M Properties of Flammable Liquids, Gases, and Solids. (Reference 1)

*G National Electrical Code, Article 500 Hazardous Locations, Table 500 - 2(C) Chemicals by Groups. Reference is also NFPA No. 70, ANSI C1. (Reference 1)

*H The National Fire Codes (NFPA), Article 491M, Manual of Hazardous Reactions. (Reference 1)

VAB.0001024223

4. *Mixtures*

The example provided for instrument calibration has been made for a single contaminant diluted with air. This condition is necessarily an ideal for laboratory verification. It is also a condition found in some field situations. On the job, mixtures are found more often than pure contaminants. When these mixtures are encountered, one must recognize them, get enough information to define the situation and then measure the concentration by a method that is consistant with the purpose of the measurement.

Field Operations in Chapter V, Usage, includes several descriptions of field situations that concern mixtures. These should be consulted.

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VIII MEASUREMENT PROPERTIES

INTRODUCTION

The variations that are inherent in every measurement, are herein specifically applied to the evaluation of combustible gases. Some variations that are characteristic of direct reading meters, and particularly combustible gas indicators and hydrocarbon detectors, are expanded further. It is necessary to define several terms and concepts to provide a common ground for discussions on the uses of these instruments. For further in depth applications, the user is urged to consult References 12 and 17 and other texts on statistics, especially those applied to laboratories and the use of instruments.

Most discussions about variations revolve around variability and *"errors"*. These concepts completely exclude *"mistakes"*. This definition is adopted from statistical practices and is applied throughout this Manual. For example, some mistakes include reading a numeral 3 (three) as an 8 (eight). Another is using a meter that is not in calibration. Another is sampling an enclosed space, such as a manhole, through a tube, whereby the air entering the sensor is leaking through a connection on the instrument, but outside of the critical volume. Certainly this list provides only a few suggestions.

The term "error" applies specifically to the variability of a system or set of readings. Every series of measurements made on a system will reflect or be affected by this variability. In turn, variability can itself be measured. The "standard deviation" is one of the quantitative estimates used for such a measurement. Many of the important types and sources of variation will be discussed in this chapter.

ACCURACY, BIAS AND PRECISION

1. INTRODUCTION
   a. Some chosen terms from the language of statistics can be used to generalize about measurements made by direct reading instruments. Although the ideas are expressed by the terms used, they are best defined when they are described for a series of repeat readings that are made on a condition that is stable and does not change between measurements. One such example would be a series of measurements made on the concentration of a combustible gas in an infinitely large test chamber. For this illustration, one can also assume that the same operator is using the same instrument for these repeated tests (References 12 and 17).

2. MEASUREMENTS
   a. Refer to Figure VIII - 1 for a graphical presentation of selected statistical terms. By design, the circle represents the "bullseye" of a target, or by analogy the "true" value of the concentration of the contaminating gas or vapor being tested. The "X" represents a "hit" or measurement. The terms that apply are further defined as follows (Reference 17).

      1) *BIAS:* Bias is a constant error which causes results to be shifted from the "true" value. The terms "determinate error", "assignable error", or "systematic error" are synonyms. This is shown in the sketch by the relative closeness of a given point or points to the center of the bullseye, the true value.

      2) *PRECISION:* Precision is the degree of agreement among results obtained. It is usually obtained by repeated "checks" made on a single sample under a given, controlled set of conditions. From this data, the distribution of these results is often described by the calculation of its "standard deviation". The precision is independent of the bias, or magnitude of displacement from the true value for the entire series of measurement. In Figure VIII - 1, precision is represented by the closeness of the grouping of hits.

      3) *ACCURACY:* Accuracy relates to the amount of a compound or element measured by the instrument compared to the ("true") amount actually present. Accuracy is therefore a combination of bias and precision, both terms being needed for quantitative work.

   b. Figure VIII - 2 describes the same terms as were shown in Figure VIII - 1, but the sketches show the instrument response curves. Cases are parallel in both diagrams. In Figure VIII - 2, the instrument is measuring the same concentration repeatedly. As the concentration is shown on the horizontal scale and the response on the vertical scale, all points are shown in a vertical line. When a small number of replicate measurements (e.g. 4) are made on a single concentration, the distribution of results is often approximated by the spread (difference between the highest and lowest value) instead of calculating the standard deviation. This approach is shown to be feasible on Figure VIII - 2.

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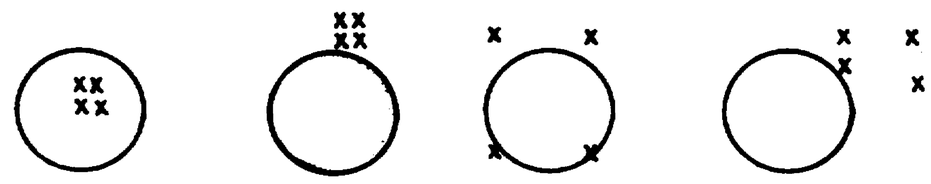
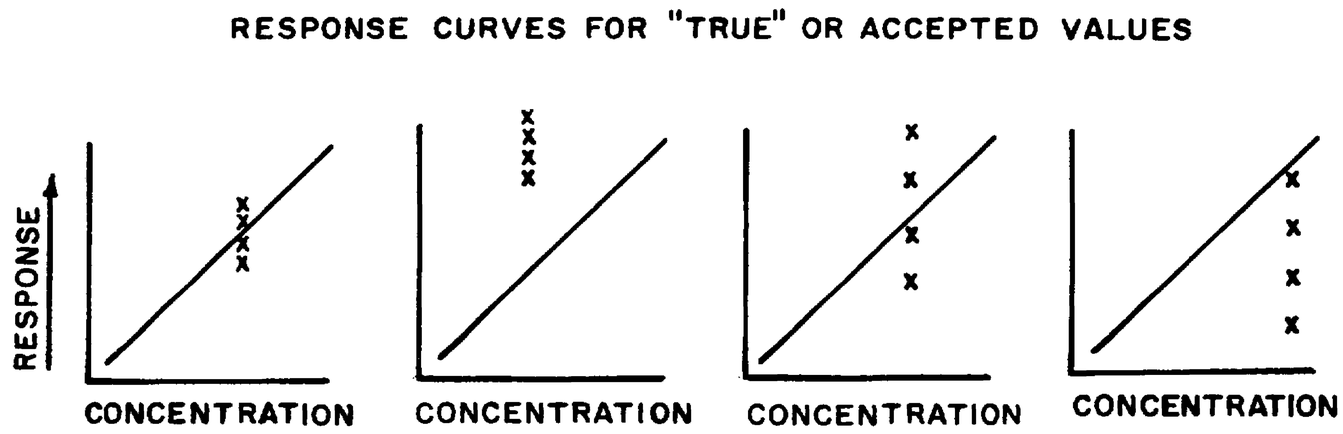


CASE	A	B	C	D
BIAS	NO	YES	NO	YES
PRECISE	YES	YES	NO	NO
ACCURACY	YES	NO	NO	NO

Figure VIII - 1 — Bullseye Analogy; accuracy, bias and precision by groups.



CASE	A	B	C	D
BIAS	NO	YES	NO	YES
PRECISE	YES	YES	NO	NO
ACCURACY	YES	NO	NO	NO

Figure VIII - 2 — Bullseye analogy applied to graphs; accuracy, bias and precision on calibration curves.

INHERENT INSTRUMENT VARIABILITY

1. Two example response curves are shown in Figures VIII - 3 and 4. For each figure, the horizontal scale, the absisa, shows the concentration of contaminating gases in parts per million (or percent). In practice, the scale could have any measurement units. The vertical scale, the ordinate, indicates the instrument response for each of three gases.
2. In Figure VIII - 3, the instrument is much more sensitive to material "A" than "B". It also shows that if a given response curve is assumed, that a mistake of 50% in the concentration of a gas can readily be made. For example, if an instrument was calibrated on curve "A" for toluene, but a situation called for estimating the concentration of methane which (for discussion) followed curve "B", a gross underestimate would be made if the proper calibration curve were not used.
3. Figure VIII - 4 shows that the response or sensitivity of a given instrument may change over the measurement range shown, an example of non-linearity. This feature is typically a function of the sensor, but may be due to other reasons. Whatever the reason, the instrument may be useable if the curve is known and the response is reproducible. One specific example was given of an instrument calibrated on methane that would read isopropyl alcohol correctly at 17% LEL, but approximately 35% low at 65% LEL. This is a very significant difference for fire considerations.
4. "Noise level" is the amount of the signal variation that is not due to variations of the concentration being measured. This property is often masked in the models of combustible gas indicators for which one sets a control onto the "zero" mark. Noise level is nevertheless an inherent property of each instrument.

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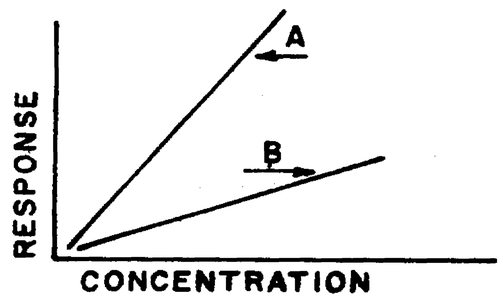

Figure VIII - 3 — Sensitivity.

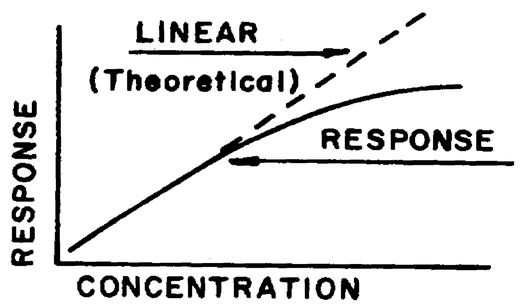

Figure VIII - 4 — Linearity.

5. By definition, *sensitivity* is the minimum concentration which produces a signal twice the noise level. It is this minimum concentration that must be recognized in combustible gas indicators for safe usage. When an instrument is zeroed on contaminant free air, and then presented with a very slightly contaminated atmosphere, it will be found that a certain minimum concentration is needed to produce a significant and reproducible reading. If the lower limit of detection is above the TLV of a vapor or gas, there may not be a response even though the TLV is exceeded. One can approximate these limits by the use of the calibrating techniques described in Chapter VII. Precise methods are available to define sensitivity by the use of electronics and mathematics. This Manual does not explore such procedures in detail. The term "minimum detectable change" may also be applied to sensitivity as described here. There are some technical differences, since the minimum detectable change can be applied at any response level.

6. In addition to the instrument errors, three other areas of error, or variability should be discussed. These are:
   a. Operator error. The mechanics and precision with which each operator handles and reads a given instrument will provide some variation. To repeat, this variation excludes mistakes such as misreading the meter, failing to set the "zero" or the "voltage adjustment" (gain).
   b. Instrument errors, including calibration errors must be considered since the instruments are either set or verified by the use of span gas.
   c. Environmental and sampling errors include the variation of the concentration of the gas within a given volume. This manual has considered this aspect only for the calibration gas situation. The variables of sampling a work atmosphere require an additional study which is beyond the scope of this text. These are considerations that are also beyond the items described in Chapter V on usage.

TIME RELATED SEQUENCE

1. When a gas is measured at more than one concentration, a noticable time passes while the readout needle indicates a change from one level to another. The characteristics involved are shown graphically in Figure VIII - 5. The stepped curve (top) labelled "A" shows a theoretical series of three concentrations which are to be sampled.

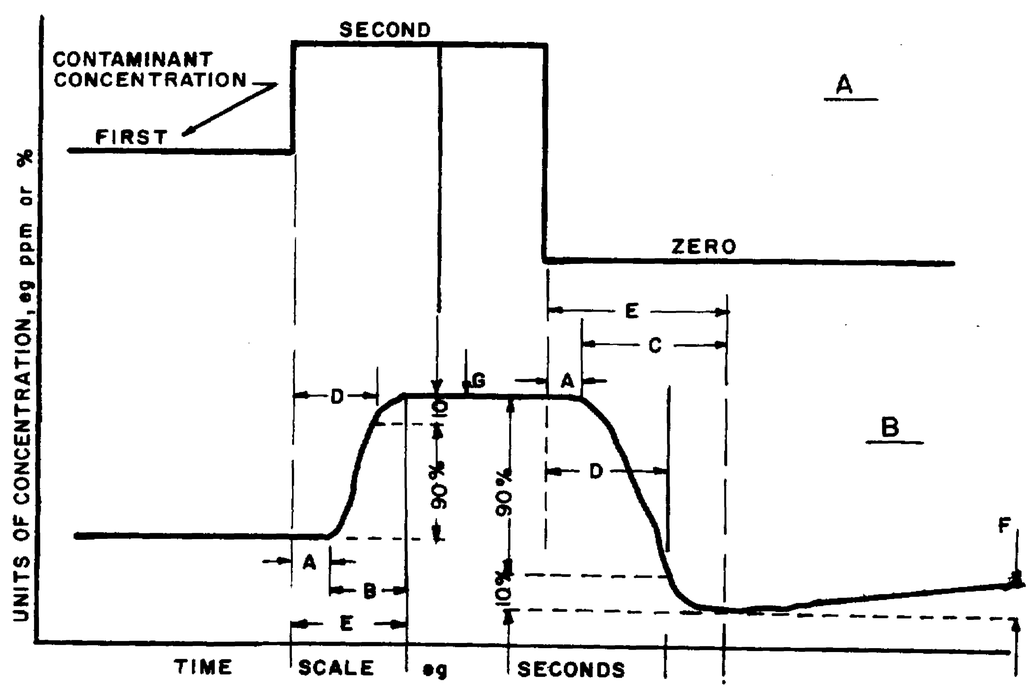

Figure VIII - 5 — Performance parameters.

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For this theoretical consideration, no appreciable time elapses between two adjacent levels. Time has been displayed on the absissa or base line. Concentration is on the ordinate, or vertical scale.

2. The lower graph, "B", shows the meter response when it is exposed to the concentrations shown in curve "A".
3. Items coded on the graph are as follows:

(A) *LAG TIME* — The time interval between a step change in input and the first observable corresponding change in response.

(B) *RISE TIME* — The time interval between initial response and 90 percent (or 95% where specified) of final response after a step increase in input concentration.

(C) *FALL TIME* — The time interval between initial response and 90 percent (or 95%) of final response after a step decrease in input concentration.

(D) *RESPONSE TIME* - 90%, Also RECOVERY TIME - 90% (OR 95%). This is a total of the lag time and rise or fall time to 90%, or 95%. This is an important instrument performance parameter. It is specified under standardized test conditions. It should be checked in the field since unusual conditions may be imposed upon instrument operation. Sample tube extensions, and/or low operating temperatures which diminish battery output can prolong the apparent response time.

(E) *FINAL RESPONSE TIME* — This term is a total of the lag time plus the rise (or fall) time for the instrument to reach equilibrium or a peak (or minimum) reading after a step change in concentration.

(F) *ZERO DRIFT* — The change in the continuous monitoring system output over a stated period of time of normal continuous operation when the contaminant concentration at the time of measurement is zero.

(G) *PLATEAU* — The equilibrium or peak reading read on the instrument after a step change in concentration.

(H) *SPAN DRIFT* — (Not illustrated) The change in the measurement of a given test concentration over a stated period of time of normal continuous operation.

CONCLUSION

All of the criteria that have been discussed may be important for any intended use. The user should evaluate the items covered and apply each to the specific mode and location of use. One can then make a knowledgeable appraisal of the minimum acceptable effects for each application.

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IX SUMMARY OF LIMITATIONS

INTRODUCTION

Combustible gas indicators and hydrocarbon detectors provide the means whereby personnel concerned with health and safety activities can easily determine the presence of and evaluate the concentration of combustible gases or vapors in the work place. The simplicity in use of these instruments has created a great market for them. In turn, much effort is being devoted by the manufacturers to make the instruments more desirable. Improvements in weight, portability, sensitivity, reliability and intrinsic safety are among these features that the prospective user is interested in. These types of instruments have a number of limitations that must be understood in order to assure that it can be relied upon in actual field use.

SUMMARY

This chapter attempts to summarize the limitations that the user should recognize and consider while using a combustible gas indicator. These items follow.

1. A combustible gas indicator is a quantitative instrument, not a qualitative one. That is, it can detect the presence and concentration of a combustible gas or vapor or a composite of the gases present. It cannot differentiate between various substances. If calibrated for a single gas or vapor, it can be relied upon for accurate determinations of that substance in the environment, provided there are no other combustible or interfering gases or vapors present in that environment. Some sophisticated models of hydrocarbon detectors have the capability to make such separations, but this procedure is complicated and requires instrument handling well beyond that required of the typical combustible gas indicator.

2. A traditional combustible gas indicator should not be used for, or in the presence of halogenated hydrocarbon gases or vapors. The thermal decomposition products generated by these substances will corrode the sensor and alter its sensitivity and integrity. If these conditions are known to exist, an appropriate model should be found for such use, but the selection is very limited.

3. A combustible gas indicator or hydrocarbon detector must be selected for the purposes intended. If it is to evaluate health exposure to toxic gases or vapors which are combustible, the sensitivity of the instrument must be greater than if the instrument is to be used for the determination of potential fire hazard levels.

4. All combustible gas indicators and most hydrocarbon detectors must be equipped with flame (flash-back) arrestors. When properly designed and installed, they isolate the sensing chamber from the combustible gases both upstream and downstream from the sensor. The type of flame arrestor determines the type of gases or vapors that may be measured safely. For example, an instrument that is used to evaluate an environment with methyl ethyl ketone would probably not be safe in an environment containing hydrogen gas.

5. Not all combustible gas indicators are intrinsically safe! That is, the instrument is not constructed so as to allow it to be brought into a mine, petroleum refinery, a petrochemical plant, or other locations where the combustible gas envelops the indicator. *Use only certified intrinsically safe instruments in fire hazardous environments.*

6. The sensitivity and accuracy of combustible gas indicators are affected by a wide range of conditions. These include the presence of dust, high humidity and extremes of temperature. For these reasons the sampling probe or sampling line on most models should be equipped with a dust filter and a drying agent. The instrument should not be used in extremely hot or cold environments without a knowledge of the effect of temperature extremes on the instrument response.

7. Do *not* interchange parts between two instruments of different manufacturers. If parts of two identical instruments (model and manufacturer) are interchanged, the instrument must be recalibrated before it is used.

8. Any instrument that requires repair work that replaces the flame arrestor or that breaches the intrinsic safety of the device, should be sent to the manufacturer for testing and recertification of its safe use for the purpose intended.

9. A combustible gas indicator or hydrocarbon indicator should be tested with a known gas or vapor concentration, e.g. with span gas, before each use to verify its state of operation. The instrument should be tested in a condition similar to that expected in the field. For example, if a long sampling line is needed in the field, the same length of line should be used during the calibration check.

10. All instruments exhibit "zero drift". That is, the indicator drifts from "true zero" as the instrument is used. For this reason it is important to check and reset the "zero" reading in a clean environment on a frequent basis. If the instrument is taken into a mine or other environment where vapors are always present, a sample of "clean air" should be carried with the instrument to facilitate frequent zeroing adjustments.

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X APPROVAL AND CERTIFICATION

INTRODUCTION

Organizations that test instruments for their performance to design specifications are briefly described. Each has an area or selection of instruments tested. In addition, each group tests the devices for certain uses. These constraints and requirements must be kept in mind for the use of an instrument. The example that a methanometer may not be suitable for use in a hydrogen contaminated atmosphere has already been given. Industrial hygienists have a wider range of application for some of these instruments than were anticipated when the devices were designed. The user must understand the specifications and conditions involved.

The organizations listed write specifications for the purposes that they serve. These are simply referenced in this text. Should one require specific information, contact the sponsoring group. Many performance, test and design specifications are beyond the scope of this manual. One important example is the Tag closed cup flash point test, ASTM D-56 (Reference 22). Such sources must be traced and located when the information is needed.

GOVERNMENTAL AGENCIES

1. NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH (NIOSH): The "Evaluation of Portable Direct Reading Combustible Gas Meters" was published in 1974 (Reference 5). This study formed a part of the basis for specifications for the instruments reviewed. It has been developed into a certification program. Complete quality assurance plans and testing procedures are required of the instrument manufacturers.

2. MINING SAFETY AND HEALTH ADMINISTRATION* (MSHA); MINING ENFORCEMENT AND SAFETY ADMINISTRATION* (MESA): *During the writing of this Manual, the name of the organization known as MESA had been changed to MSHA. Both names are listed here for reference. This organization is continuing the testing that was originally done by the United States Bureau of Mines. All equipment that is tested pertains to mining and is to be taken underground. Some of the areas that are included follow:

   a. Schedule 2G, Part 12.68. This approval means that the equipment cannot ignite a *methane* in air mixture. MSHA (MESA) also has approval schedules for the performance of methane sampling devices.

   b. Under Schedule 32A, Part 27, approvals are issued for machine mounted methane monitors which must be able to shut the machine off in less than two percent methane, for 500 consecutive times, while in wind, face velocities of 61 to 305 meters per minute (200 to 1,000 feet per minute).

   c. Under schedule 8C, part 22, hand held combustible gas indicators are approved. Basically these instruments must read to within 60% at 0.25% methane (0.10% to 0.40% methane) and to within 7.5% at 4.0% methane (3.7% to 4.3% methane). These tolerances are to be held over the temperature range of 4.5°C to 21°C (40°F to 70°F). The 100% LEL is 5.0% methane in air per NFPA 325M.

   d. Under title 30, part 29, portable continuous duty methane alarms are approved. These must operate a warning light which flashes when the methane concentration is between 0.8% and 1.2% methane (16% to 24% LEL). If the device also gives a quantitative measurement, these must read to within 60% at 0.25% methane (0.1% to 0.4% methane) and to within 7.5% at 4.0% methane (3.7% to 4.3% methane). These tolerances are to be held over the temperature range of 10°C to 21°C (50°F to 70°F).

3. ENVIRONMENTAL PROTECTION AGENCY (EPA): The EPA does not have an approval program for combustible gas indicators in the combustible range. They are primarily concerned with continuous monitors in the ppm range. Their functions include methane, hydrocarbons and others.

4. UNITED STATES NAVY (USN): The USN has an internal approval program on the performance of combustible gas indicators and other instruments.

5. UNITED STATES COAST GUARD (USCG): The USCG approves combustible gas indicators and other instruments on an installation by installation basis. Their approval consists of a review of the manuals, drawings and construction of the instrument. This review does not denote approval of the instrument for any other locations or situations.

ORGANIZATIONS

1. FACTORY MUTUAL RESEARCH CORPORATION (FM): FM issues approvals for fixed and portable combustible gas indicators under Classes 6310 and 6330. The fixed units must provide an electrical switching operation at less than 50% LEL and operate in Class I, Division 1, Group A, B, C, or D atmospheres.

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2. INSTRUMENT SOCIETY OF AMERICA (ISA): Subcommittee SP.13 of ISA has prepared standards for fixed, stationary, and portable combustible gas monitors. Specifications are included for electrical safety (shock), location (Class I, Division 1 atmospheres), and operational accuracy. The ISA organization plans to submit the standard to the American Society for Testing Materials (ASTM). It is unlikely that ISA will actually do any of the testing or approval of instruments.

3. UNDERWRITER'S LABORATORIES (UL): UL tests and approves laboratory instruments for shock and fire hazard under UL 1262 at the current time. They do not test for performance.

VAB.0001024231

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    International Sensor Technology, 3201 South Halladay Street, Santa Anna, California 92705.
    Figaro Engineering, Inc., 3303 Harbor Boulevard, Suite D-8, Costa Mesa, California 92626.
    Note: Relatively complete lists of manufacturers of all other types of combustible gas indicators, hydrocarbon detectors and related devices can be found in references numbered 3 and 4.
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VAB.0001024232

XII INDEX

Accuracy VIII, 2
Acetone IV, 4
VII, 5
Acids V, 13, b
Alcohols V, 13, a
Aldehydes V, 13, c
Amines V, 13, h
Aromatic Compounds V, 13, f
Batch Calibration VII, 5
VII, 3
Batteries VI, 3
Bias VIII, 2
Bubble Flow Meter VII, 3
Calibration VII.
VII, 3
VIII.
Carbon Monoxide V, 14, a
Chlorine V, 15
Combustible Gas Indicators (Definition) II, 1
Concentration IV.
Condensation V, 3
Contaminants IX, 6
Diffusion Head III, 2
Dynamic Systems VII, 6
Electronics VI, 3, f
Environmental Protection Agency X, 3
Error VIII, 3
VIII, 6
Explosive Levels IV.
Explosive Limits (Definition) II, 3
Factory Mutual Research Corp. X, 1
Fall Time VIII.
Field Servicing VI, 4
Filters VI, 3, c
Flammability (Definition) II, 2
Flash Back Arrestors VI, 3, d
IX, 4
Flash Point IV, 2
V, 2, c
Flow Rate VII, 3
Fume (Definition) II, 6
Gases (Definition) II, 5
Gas Laws VII, 1
Gram Molecular Weight VII, 1
Halogenated Hydrocarbons V, 12
IX, 2
Hazard Ladder IV.
High Atmospheric Pressure V, 10
History II.
Humidity V, 2
Hypobaric Conditions V, 9
V, 10
Inorganic Compounds V, 14
Instrument Schematic III.
Instrument Society of America X, 2
Interchangeability VI.
IX, 7
Intrinsic Safety V, 4
IX, 5
Ketones V, 13, d
Lag Time VIII.
Leaks V, 3
Leak Test VII, 2
Linearity IV, 5
Liquid Contamination V, 6
Logarithmic Scale IV.
Low Atmospheric Pressure V, 9
Lower Explosive Limit II, 3
IV, 1
VII.
Maintenance IX, 8
Measurement IV.
Milligrams per Cubic Meter VII, 2
Mine Enforcement and Safety Administration X, 2
Mine Safety and Health Administration X, 2
Mistakes VIII, 2
Mixtures V, 16
VII, 4, a
Minimum Detectable Limit IV.
National Fire Protection Association; Group A, B, C, D V, 14
National Institute for Occupational Safety and Health X, 1
Nitro Compounds V, 13, g
Noise Level VIII, 4
Oxidizers V, 15
Oxygen Depleted Atmospheres V, 7
Oxygen Enriched Atmospheres V, 8

VAB.0001024233

Parts Per Million IV, 2
IV, 4
VII, 2
Percent IV, 2
IV, 5
VII, 2
Precision VIII, 2
Record Keeping VI, 2
VII, 2
Response Time VIII.
Rise Time VIII.
Sample Tubing VI, 3, b
Scope I.
Sensitivity VIII, 5
Sensor III, 1, b
VI, 3, e

SENSORS
Catalytic Combustion III, 3
Detector Tubes III, 9
Diffusion III, 4
Flame Ionization III, 6
Flow Through III, 4
Hot Wire III, 2
Infra Red III, 8
Miner's Lamps II, 1
Photo Ionization III, 7
Solid State III, 5
Ultra Violet III, 9
Sensor Poisons V, 14
Span VIII, 3
Span Adjustment III, 2
Span Gas VII, 4
Standard Pressure VII, 1
Standard Temperature VII, 1
Tag Flash Point IV, 2
Temperature V, 1
Threshold Limit Values II, 4
Time Related Response VIII.
Toluene IV.
Tubing VI, 3
Underwriter's Laboratories X, 3
United States Coast Guard X, 5
United States Navy X, 5
Unusual Oxidizers V, 15
Upper Explosive Limit V, 7
Vapors (Definition) II, 5
Verification V.
V.
VII.
IX, 9
Zero Adjust III, 2
Zero Drift VIII, 3
IX, 10
Zero Setting V, 4

VAB.0001024234