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HYDROGEN LEAK AND FIRE DETECTION

A SURVEY

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

HYDROGEN LEAK AND FIRE DETECTION

A SURVEY

By

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Technology Utilization Division

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Foreword

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The effort described in this report was performed during the period March 1, 1963 to August 31, 1968. This report on the detection of hydrogen fires and leaks contains a critical review of the applicable literature, a discussion of the experiences and needs of typical producers and users of hydrogen, an evaluation of the present state of the art of detecting hydrogen fires and leaks, and recommendations for further development of equipment and basic research.

RONALD J. PHILIPS, Director
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Introduction

Hydrogen, in both liquid and gaseous forms, has many industrial uses. Its extreme flammability, however, makes handling and storing hydrogen hazardous to personnel and equipment. A hydrogen flame is nearly invisible in normal lighting, and, the development of sound safety procedures is of continuing importance. During recent years much progress has been made, however, in reducing the hazards encountered in using hydrogen and in accelerating progress in hydrogen fire and hydrogen leak detection. Improved devices and methods have been developed and reported by numerous Government agencies, industrial users, detector manufacturers, and research organizations.

Because hydrogen is both plentiful and useful, its expenditure and diversified use has increased rapidly in recent years. Only a few decades ago gaseous hydrogen was used mainly in laboratory experiments, to fill balloons, to "harden" fats and oils, and to produce intensely bright theatrical spotlights. Liquid hydrogen was little more than a laboratory curiosity. Today, however, hydrogen is used in petroleum processing, hydrogenation processes, welding and brazing, cooling such equipment as electric generators and nuclear reactors, and production of ammonia and other chemicals. Hydrogen is also used in the laboratory now for cryogenic research, and in bubble chambers and targets for nuclear physics investigations. The growth of space technology has led to extensive production and use of liquid hydrogen as a rocket propellant. In addition to these uses hydrogen may be employed in such processes as the rapid charging of storage batteries and electrochemical machining.

In all these applications the hazards attendant to handling and storage are an ever-present problem. Hydrogen accidents continue, with damage ranging from no injuries and slight losses to several deaths and totally destroyed facilities. Hydrogen is highly prone to leakage and, when mixed with air, it readily forms a potentially explosive and easily ignited mixture. The near-invisibility of hydrogen fires burning at leak sites sometimes results in injury to personnel through unexpected contact with the flames or nearby

heated objects. The Hindenberg dirigible disaster in 1937 was a dramatic example of the violence and destructiveness of a hydrogen mishap.

Means of detecting hydrogen gas before flammable or detonable mixtures accumulate, and promptly locating hydrogen fires, are needed so that appropriate action may be taken before damage is done. Since detection, in general, is based on sensing one or more of a number of physical properties of both hydrogen gas and hydrogen fires, it is necessary to have a variety of sensors and detection methods. A fairly broad selection of detectors is now commercially available, and more are being developed.

For this survey, several sources of information were used. Pertinent literature was reviewed, and users and producers of hydrogen were interviewed in person or by telephone about hydrogen fire and hydrogen leak detection practices. Visits were made to a diversified group of facilities in which hydrogen was used or handled. Finally, fire and leak detector manufacturers were asked for information regarding their products.

The following industrial plants, NASA installations, and research laboratories were visited: Bureau of Mines, Explosive Research Center, Pittsburgh, Pa.; Langley Research Center, Hampton, Va.; Lewis Research Center, Cleveland, Ohio; North American Rockwell Corporation, Rocketdyne Division, Canoga Park, Calif.; North American Rockwell Corporation, Space Division, S-11 Santa Susana Operations, Santa Susana, Calif.; Standard Oil Company of California, Richmond Refinery, Richmond, Calif.; Proctor and Gamble Company, Port Ivory Plant, Staten Island, N.Y.; Union Carbide Corporation, Linde Division, Liquid Hydrogen Plant, Sacramento, Calif.; Dow Chemical Company, Midland, Mich.; John F. Kennedy Space Center; Princeton—Pennsylvania Accelerator, Princeton, N.J.; and Charles Pfizer Company, Groton, Conn.

Other hydrogen users who were contacted by telephone included: Westinghouse Astronuclear Laboratories, Pittsburgh, Pa.; Shell Oil Company, Martinez Refinery, Martinez, Calif.; Allied Chemical Company, Morristown, N.J.; Humble Oil and Refining Company, Esso Bayway Refinery, Linden, N.J.; Bell Aerosystems, Buffalo, N.Y., and Hercules Powder Company, Salt Lake City, Utah.

The properties of hydrogen and hydrogen flame will be reviewed as background information for the discussion of detection techniques. Some of the hydrogen properties given also indicate both the usefulness and hazards associated with hydrogen. This review

of properties will be followed by an examination of methods and devices for detecting hydrogen and findings of recent research. A similar examination of hydrogen fire detection will then be made. In addition to references from the text, a bibliography of related documents useful in the study of hydrogen safety and detection, is included.

Properties of Hydrogen

Knowledge of the essential properties of hydrogen is required to understand the principles involved in the devices discussed later in this survey. The most important properties fall into three categories: (1) the physical and chemical properties of liquid and gaseous hydrogen, (2) hydrogen combustion properties, and (3) the physical properties of hydrogen fires.

LIQUID AND GASEOUS HYDROGEN

Liquid hydrogen is a transparent colorless liquid. Since it is usually in contact with, or near, materials that are at temperatures above its boiling point, gaseous hydrogen is present whenever a liquid leak occurs. Hydrogen gas is colorless, odorless, non-toxic, and noncorrosive.

The physical and chemical properties of hydrogen have been described in numerous textbooks, handbooks on hydrogen (refs. 1, 2), an earlier NASA Technology Utilization Survey (ref. 3), and several hydrogen safety manuals (refs. 4, 5). An excellent summary of the physical and chemical properties of hydrogen that are pertinent to the nature of the hazards of hydrogen leaks and fires is given in the appendix of the Bureau of Mines technical report on hydrogen safety (ref. 4).

Nature of the Leak Problem

Liquid hydrogen is an extremely low-temperature fluid. (Only liquid helium has a lower boiling point.) Its low temperature causes thermal contraction of confining materials, thereby creating incipient leaks and, at times, catastrophic failure of confining equipment. The parts most liable to develop leaks are the flanges, connections, or joints of transfer lines through which liquid hydrogen flows intermittently, resulting in numerous temperature cycles from ambient down to 20° K (normal boiling point of hydrogen). Even when lines are precooled with liquid nitrogen (boiling point, 77° K), the thermal shock is relatively large.

The small size of the hydrogen molecule permits it to leak through air-tight seals and escape from systems that appear leak-

free when tested with more conventional fluids. The viscosity of liquid hydrogen also contributes significantly to the leak problem. At its boiling point, the viscosity of hydrogen is lower than that of most cryogenic liquids. Because leakage is inversely proportional to viscosity, leakage of liquid hydrogen will be roughly 12 times that of liquid nitrogen and 14 times that of liquid oxygen. Gaseous hydrogen also is particularly subject to leakage, being about twice that of nitrogen or oxygen.

Because of the low molecular weight of hydrogen gas, it has a very high diffusion coefficient (ref. 6). As a result, hydrogen in an open area diffuses to nonexplosive mixtures very rapidly; a spill of 500 gallons of liquid hydrogen in an unconfined area will diffuse to a nonexplosive mixture in about one minute. This rapid diffusion, however, makes leak detection difficult, since a concentration of gas will not build up at the leak exit. The problem is compounded further by the buoyancy of hydrogen gas. When its temperature is that of the ambient air, its density is only $\frac{1}{14}$ that of the air density. Thus, the properties of diffusivity and buoyancy make it very difficult to locate the exact site of a leak.

Properties Used in Hydrogen Leak Detection

Although hydrogen will react violently with strong oxidizers, such as oxygen, it is not hypergolic with oxygen (i.e., usually an ignition source is required). As a result, flammable mixtures of hydrogen and air can exist in the absence of an ignition source.

Hydrogen gas can be combusted catalytically on a heated filament at temperatures below the ignition temperature of hydrogen and air. At present, this is the most common property of hydrogen used in commercial hydrogen leak detectors. The thermal conductivity of hydrogen gas is the highest of all known gases. Very small amounts of hydrogen in air will cause a significant increase in the thermal conductivity of the gas mixture.

Palladium has long been known to be an absorber of large volumes of hydrogen. At 80° C and 1 atmosphere of pressure, palladium absorbs up to 900 times its own volume with the evolution of considerable heat. When the palladium is in the form of a thin film, the electrical conductance of this film is a function of the partial pressure of the hydrogen concentration. These two properties of hydrogen with palladium have been studied recently under separate NASA-supported programs in the development of specific sensors for hydrogen.

The difference in the refractive index of hydrogen from that of air has been the basis for another hydrogen leak detector. At 0° C and 760 mm of pressure, the refractive index of air is 1.0002926,

while that of hydrogen is 1.000132. An optical interferometer has been used to detect small changes in refractive index. Other investigations based upon the electrochemical consumption of hydrogen and the fuel cell principle have been made recently.

Because of the continuing growth of hydrogen usage in both aerospace and nonaerospace industries, it seems likely that efforts to find accurate, specific, sensitive, and more reliable hydrogen leak detection devices will continue.

HYDROGEN COMBUSTION PROPERTIES

The principal reason for considering hydrogen a hazardous material is its flammability and detonability in air over a wide range of conditions. Hydrogen combustion has been the subject of much study. Lewis and Von Elbe's basic text (ref. 7) presents a thorough summary of combustion phenomena, including some data on hydrogen combustion. References 7 and 8 are valuable compilations which concentrate on hydrogen combustion properties. References 4, 9, and 10 contain summaries of properties relating to the combustion hazards of hydrogen in air.

A mixture of hydrogen and air may be ignited in several ways, and the resulting flame may propagate in various ways. The conditions affecting the ignition characteristics include: contents of the gas mixture, temperature, pressure, geometry of the surrounding walls, ignition energy and, in some cases, gas velocity. Such conditions determine whether there will be no ignition, a stationary flame at a source of hydrogen gas, a deflagration through a volume of gas, or a detonation. Ignition sources may be a hot solid body, a flame or other hot gas, an explosive charge, or an electric spark.

Combustion can propagate through a hydrogen air mixture either as a deflagration, a deflagration which grows to a detonation, or as a detonation from the start of ignition. (A deflagration is a flame propagating at subsonic velocity, whereas a detonation produces a shock wave propagating at supersonic velocities.) In a confined space, a deflagration can raise the pressure by about a factor of 7—enough to cause some structural damage. A detonation can cause a very rapid rise in pressure by as much as 20 times the initial pressure (ref. 4). Either of these processes may be accompanied by a sound (sometimes very loud), and the term "explosion" is applied to both processes. "Flammable" applies to a mixture in which any type of combustion can propagate.

Flammability Limits

Hydrogen has a wide range of flammable mixtures with air, being exceeded only by acetylene and hydrazine (ref. 11). The

usually recognized upper and lower flammability limits for hydrogen in air saturated with water vapor at ambient temperature and pressure are 74 and 4 percent hydrogen by volume. The 4-percent hydrogen concentration point is called the lower explosion limit (LEL).

Flammability limits are affected by pressure, temperature, and the presence of inert diluents. As the pressure is raised above atmospheric, the range of flammable mixtures narrows up to about 5 atmospheres, then gradually widens as the pressure is raised (ref. 8). As the pressure is lowered, the limits of flammability narrow (refs. 12, 13). Raising the temperature of the gas widens the flammability limits (ref. 12).

The addition of inert gases to hydrogen-air mixtures narrows the flammable range in a manner dependent upon the inert gas. Compared to the effects with hydrocarbons, nitrogen and carbon dioxide are less effective in reducing the flammability of hydrogen in air. For instance, the fuel-lean limit is hardly affected by addition of up to 60 percent CO₂ by volume (ref. 8). Enrichment by oxygen raises the fuel-rich limit. The rich limit of hydrogen in pure oxygen is about 96 volume percent (ref. 12).

Flame Speed

Flame velocities in hydrogen-air mixtures are given in reference 8. The maximum velocity is about 300 cm/sec, compared to about 40 cm/sec for methane and propane.

Ignition Energy

The energy required to ignite a mixture near the stoichiometric ratio is quite low, but increases as the flammability limits are approached. The minimum ignition energy required increases as the pressure is lowered (ref. 8). This energy is about one tenth that required to enflame most hydrocarbons. An electrostatic discharge which can hardly be seen or felt can ignite a hydrogen-air mixture (ref. 9). The ease with which hydrogen ignites with air contributes to the burning of accidental leaks of hydrogen. Although no ignition source may be apparent, hydrogen leaks and unflared hydrogen vent stacks often ignite. It is assumed that a small discharge of static electricity is usually responsible, but this has not been conclusively proved (ref. 14). The autoignition temperature is quite high, about 1075°F, compared to 400° to 666° F for most hydrocarbons.

Detonation Limits

The range of detonable mixtures of hydrogen in air is 18 to 59

percent hydrogen by volume. Therefore, not all flammable mixtures are detonable. The occurrence of a detonation wave is dependent upon conditions of confinement, and is especially likely when the mixture is near-stoichiometric, the ignition source is strong, there are confining walls, and the flame path is long. Even partial confinement of hydrogen, for example, by four walls, can allow initiation of detonation (ref. 4). These reactions can be quite violent and destructive, and numerous examples of the damage that can be done are given in the literature (refs. 10, 15, 16). Detonation velocities are shown in reference 8.

Quenching Distance

When the dimensions of a passage or enclosure containing the gas mixture become small, the heat transfer and/or active particle loss can become great enough to prevent propagation of a flame. When a gas mixture has a certain temperature, pressure, and composition, a resulting flame cannot pass through openings smaller than some minimum size, which is called the quenching distance. This distance depends on the geometry of the passage, but apparently not on the nature of the surface. Most laboratory measurements of quenching distance are for flames propagating between parallel plates. The dependence of quenching distance on hydrogen concentration and pressure is illustrated in reference 8. By comparison, at atmospheric pressure, the minimum quenching distance for hydrogen in air is 0.06 cm, and for propane in air it is 0.2 cm. The quenching distance also decreases with increasing temperature.

These results are applicable to flame arrestors or flame traps to stop a flame from passing from one place to another. It is of great importance to have adequate flame arrestors in electrical equipment operated around a flammable hydrogen-air mixture. This has been a problem with some leak detectors having flame traps that were acceptable for hydrocarbons but not for hydrogen; they can serve as ignition sources, an obviously dangerous situation. In practice, workable flame arrestors must have openings even smaller than the minimum quenching distance, because there may be a large pressure gradient driving the flame and hot gas toward the arrestor. Fine mesh screens often are used to arrest hydrocarbon-air flames, but the problem is more difficult with hydrogen. Sintered metal, particularly bronze, has been found fairly effective as a flame stopper without greatly impeding the flow of gas (ref. 4). Whether any screen or porous metal practical for leak detectors can fully stop a detonation is in doubt. The considerations of quenching also apply to explosion-proof electrical equipment (in-

cluding fire detectors), which must be mechanically strong and have close-fitting covers so as not to allow combustion to propagate from inside the equipment to the outside (ref. 9).

PROPERTIES OF HYDROGEN FIRES

Hydrogen fires and explosions have certain physical properties by which they may be detected. They have fewer observable characteristics than fires involving hydrocarbons, however, and this limits the choice of sensors for hydrogen fire detection.

Flame Temperature

Hydrogen burns in air with a flame that is comparable in temperature to that of most hydrocarbons. For a premixed flame of 43 percent hydrogen in air, the temperature is 3680° F, compared with 3400° F for methane, 3500° F for propane, and 4215° F for acetylene. A diffusion flame, such as that occurring at the site of a hydrogen leak, burns at about 3000° F (ref. 4). These comparative figures indicate that overheat fire detectors should work as well for hydrogen fires as for ordinary fires.

Smoke and Ionization

Pure hydrogen flames burn without smoke. The ionization of hydrogen-air flames is several orders of magnitude lower than that of organic flames, which typically have 10^7 to 10^9 ions cm^3 (ref. 17). Hydrogen flame ionization is so low, in fact, that it is extremely difficult to measure, and can be ruled out, at present, as a detectable flame property.

Noise

Stationary flames on open burners produce some acoustic noise. Except for large-scale combustion, such as in jet engines, there has been little study of this phenomenon. The sound from both premixed and diffusion flames increases rapidly as the gas flow increases enough to cause turbulence, and the noise of a burning mixture is greater than from a jet of an unignited gas (ref. 17).

Optical Radiation

The total electromagnetic radiation emitted from hydrogen-air flames is lower than from many organic flames by a factor of about 10. Values of emissivity (ratio of emitted radiation to that of a perfect radiator, or blackbody, at the same temperature) have been given variously as 0.01 to 0.1. These variations probably result from different measurement conditions, variations in the

atmospheric absorption of the radiation, and different estimates of flame size and temperature (ref. 9). In any case, the total heat radiated by hydrogen fires to personnel and structures is significantly less than is radiated from other, more familiar fires.

For purposes of fire detection, a more important consideration than total radiation is the spectral distribution of the radiation; that is, the amount of radiation emitted in the various wavelength regions of the electromagnetic spectrum. The optical radiation from pure hydrogen-air flames comes almost entirely from two kinds of molecules, OH and H₂O. These molecules emit ultraviolet and infrared radiation, but neither emits appreciable visible light. The visible light from hydrogen flames comes most from impurities, particularly sodium. Pure hydrogen flames usually can be seen if the surroundings are quite dark; but even with moderate illumination they can be seen only by variations in the transmitted light or "heat wave." Even when the flame location is known, or when it contains some impurities, hydrogen fires often cannot be seen.

OH Radical Radiation.—The hydroxyl radical, OH, is a short-lived intermediate product in the combustion process. Its principal emission is in the ultraviolet. OH emission is in the form of bands, that is, collections of spectral lines. There are seven principal OH bands with heads at wavelengths of 3428, 3124, 3064, 2875, 2811, 2677, and 2608 Å (1 Å=10⁻¹⁰ m). The most intense bands are at 3064 and 2811 Å, and are shaded toward the red. In hydrogen flames, this radiation appears to arise mainly from thermal excitation, and is much weaker than OH radiation from the reaction zones of hydrocarbon flames. This radiation comes principally from the reaction zone, and disappears almost immediately when the flame is extinguished, although the hot gases still remain. The appearance of these OH bands on the film of a spectrograph is discussed in reference 18. A low-resolution spectral scan of relative intensity vs wavelength is discussed in reference 19. Very little data are available on the weak radiation from hydrogen-air flames between 2000 and 2600 Å (ref. 20). Information on spectral distribution is useful for fire detection because it shows the distribution of radiated energy. If the ultraviolet emission is to be detected, this spectrum can serve as a guide to the necessary spectral response of the sensor or sensor-filter combination.

A quantitative measurement of the power radiated from hydrogen flames in the ultraviolet is necessary to specify the size of the flame that can be detected and the requisite sensitivity of the detector. For fire detection, the radiant intensity (that is, the

power radiated into a unit solid angle) is a convenient quantity. The power incident upon a detector or its collecting optics can be calculated for a given size of fire at a given distance, if the radiant intensity is known. Measurements of ultraviolet radiant intensity from hydrogen-air diffusion over the spectral range of 2200 to 4000 Å have been reported in reference 19. Results for three burner sizes and a range of hydrogen flowrates have been determined. There is no accepted standard size of fire or detection distances used to specify the response of fire detectors.

The ultraviolet emission from hydrogen-air diffusion flames also has been studied as a function of ambient pressure (ref. 19). It has been determined that the ultraviolet radiant intensity increases as the pressure is lowered. At about 60 mm Hg, it is over three times its value at atmospheric pressure. The radiant intensity then drops rapidly from 60 to about 15 mm Hg.

H₂O radiation.—Water is the final combustion product of hydrogen and air. Almost all its radiation is emitted in the infrared region of the spectrum, with some very faint bands in the deep red part of the visible region. The H₂O bands of interest in fire detection occur at about 1.4, 1.9, and 2.7 microns (1 micron = 10⁻⁶ m). Other H₂O radiation bands are located at about 0.65, 0.72, 0.8, 0.9, 1.1, and 6.3 microns. The bands are fairly wide and generally do not have well defined heads as do the OH bands, so these wavelengths are only approximate. The intensity increases with wavelength up to 2.7-micron band, which is by far the strongest band in the water spectrum. The bands extending into the far infrared are weaker and, at present, are inconvenient to detect (detector considerations). Some of these bands are shown in ref. 21. (It should be remarked here that cooler water vapor in the atmosphere also absorbs part of the radiation in these bands. This will be discussed in the chapter on hydrogen fire detection.)

The radiant intensity of a hydrogen-air flame in the 2.2- to 2.7-micron range is shown as a function of ambient pressure in reference 19. The level of infrared emission is fairly constant from atmospheric pressure down to about 100 mm Hg, then decreases steadily as the pressure is lowered further.

Time-varying radiation. Another important characteristic of optical emission from flames is the time-varying component. The light output from flames at atmospheric pressure is not steady, but is modulated at a set of frequencies determined by various flame parameters. This time-varying component, analyzed for frequency, is discussed in reference 13. These plots of signal amplitude vs frequency are variously called ac spectra, modulation spec-

tra, or flicker spectra. The data were obtained by analyzing the tape-recorded output from an ultraviolet-sensitive radiometer viewing the various flames. No significant difference in the frequency content of infrared and ultraviolet modulation spectra has been observed. This time-varying component of flame emission can be used as a basis of discriminating flame light from the light emitted by nonvarying sources. However, expected output levels of this ac component are not well known for various conditions that might be encountered. There is both a lack of experimental data and little understanding of flicker phenomena and the functional dependence of frequency and amplitude upon various factors such as rate of flow, burner size, gas composition, and ambient pressure. Another way in which radiation depends upon time is displayed by hydrogen-air explosions. As a flame is ignited in a gas mixture, its emitted radiation increases rapidly with time.

Hydrogen Leak Detection

The properties by which hydrogen may be detected include some that make this lightest of all gases unique—catalytic combustibility, exothermic absorption by certain materials, thermal conductivity, reducing properties, and refractive index.

Detectors specifically designed for hydrogen rely on one or more of the properties of hydrogen to effect a change in some physical or chemical system which, in turn, can be used to signal the presence of hydrogen. Specificity can come from the property being unique to hydrogen, or the property being so significantly different from that of air and other gases that small amounts of hydrogen can cause a large change, thus making the detection device for practical purposes relatively specific. Detectors for gas leaks in general are frequently used for hydrogen. Although they are not always specific, they will be discussed as an important means of detecting hydrogen. Ten or more different principles of hydrogen detection will be reviewed. A general review of all methods of leak detection by J. W. Marr (ref. 6) may be referred to for additional information.

PRINCIPLES OF DETECTION

Combustibility of Gas

The combustibility of a gas may disclose its presence in air or oxygen-containing gas mixtures, and many detectors are based on this property. Either a hot wire, a catalytic heated thermistor surface, or some other heat source forms one leg of a Wheatstone bridge arrangement. The bridge is balanced usually with both a sensing leg and a reference leg heated, but with only the sensing leg exposed to the sample gas. Combustion of a gas at the surface of the sensing element causes the temperature to rise above that of the reference leg and results in an alternation of the resistance of the sensing element and an imbalance in the bridge. This imbalance is used to signal the presence of a combustible gas, usually quantitatively.

Catalytic surfaces on platinum hot wires, on thermistors, or other temperature sensing devices allow the combustion to occur at temperatures lower than the ordinary ignition temperatures of

the gases detected. There is a flame arrestor around most of these catalytic combustion devices to prevent the heated sensing element from igniting hydrogen in the air surrounding the detector. These flame arrestors are generally sintered metal cylinders made of such materials as bronze and steel, which apparently act as heat sinks. Flames are quenched not only by excessive heat loss, but also when the diameter of the openings of the arrestor is less than the quenching distance for the particular fuel/oxidizer combination. The quenching distance for stoichiometric hydrogen-air mixtures at 1 atmosphere and room temperature is 0.057 cm (ref. 7). Both producers and users of liquid and gaseous hydrogen now use leak detectors based on the principle of catalytic combustion.

Bubble Testing

Leaks of any gas caused by a ruptured line, a poorly sealed flange, or a faulty valve seat can be located regardless of the identity of the gas by several methods. A simple method involves the application of some liquid that forms bubbles when it flows over a gas leak site. Leaks as small as 1×10^{-4} atmosphere cc/sec are said to be detectable by the bubble method, and the indication is instantaneous. This principle of detection applies bubble blowing by the gas leak in a liquid that contains substances to adjust the solution viscosity and surface tension so that bubbles are easily visible and durable. In the testing procedure, a liquid is placed in contact with the outside of the system wherever a leak is suspected or liable to occur. Because of the pressure differential between the inside of the system and its surroundings, leakage can be detected by observing bubbles formed at the point of leakage.

Sonic-Ultrasonic Testing

Several instruments "listen" in the sonic-ultrasonic range for high frequency whistles of gas issuing from orifices. The use of sensitive directional microphones with high amplification to detect leaks was developed first by NASA in an effort to pinpoint leaks from space suits. It has been reported that ultrasonic leak detectors can detect a 5-mil-diameter hole in a system pressurized at 1 psi at a distance of 5 feet or a 3-mil-diameter hole in a 25-psi system at a distance of 25 feet (ref. 23). Typical detection distances as a function of orifice size for different pressure levels are shown in figure 1. In some of the more sensitive instruments, a cigarette glow sounds like a forest fire and even an eye blink can be heard. Lack of discrimination between sonic and ultrasonic sounds in some devices, however, makes this type of leak detector unsuitable where background noise levels are normally high and

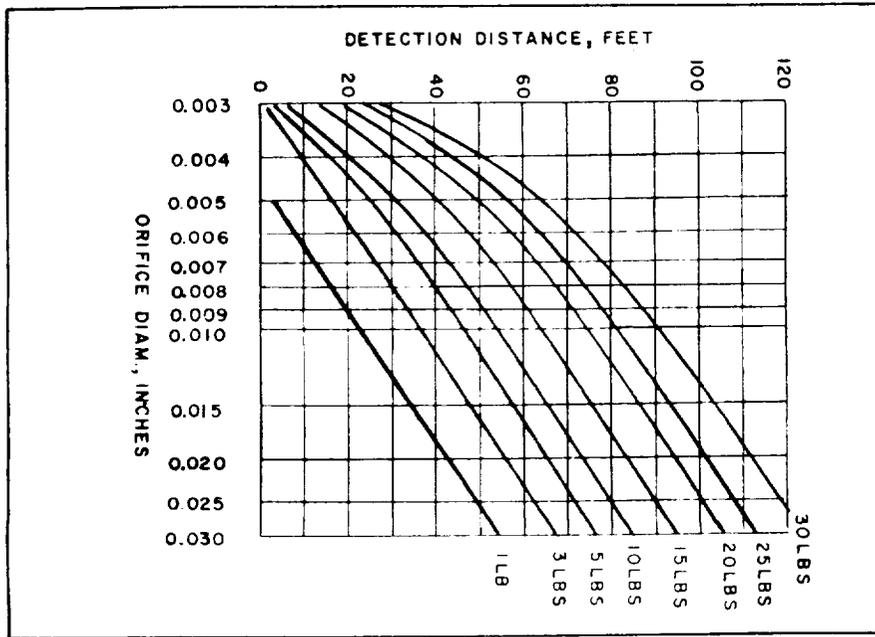


FIGURE 1.—Detection distances vs orifice size (ref. 24).

varied, e.g., amid oil refinery roar, thus restricting its use to conditions of low-level noise background. Under some other conditions, too, it is impractical to detect a leak by the sonic energy generated; a hole in a pressurized line may become so large for example, that the gas is not accelerated sufficiently to produce a signal in the 36 to 44 kHz range. A labyrinth leak path, in which the gas escapes through a devious, multiturn path through insulation, would also tend to lower the acceleration of the gas to below a detectable level of sound. Because the threshold level of a detectable leak volume/rate is related to such numerous parameters as hole diameter and pressure, only a rule of thumb value, like 0.01 cc/sec, can be quoted with real meaning.

Thermal Conductivity

Thermal-conductivity detectors are based upon the principle that a heated thermistor or filament pair forming legs of a Wheatstone bridge will be cooled by a gas sample according to the thermal conductivity of the gas. Two identical hot wire cells mounted in the analyzer form adjacent branches of a Wheatstone bridge.

Each cell consists of a resistor mounted in a chamber containing a gas. The sampling chamber contains the gas to be analyzed and the comparison chamber, the reference gas. If the atmosphere does not contain contaminating gas, the equilibrium temperature of both resistors is the same because the heating current is the same. When the sampling gas differs, however, the heat loss differs. This tends to change the equilibrium temperature of the sampling chamber in proportion to the inverse of the thermal conductivity. This, in turn, changes the resistance of the heating element, which results in an output signal from the Wheatstone bridge circuit. Because of the large difference between the thermal conductivities of air and hydrogen, the sensitivity for hydrogen in air is better than 0.1 percent. A detector based on thermal conductivity has the advantage of giving linear readings from 0 to 100 percent concentrations. Commercial leak detectors based upon thermal conductivity are available from a number of companies, but their use has been limited.

Gas Density

Gas-density measuring instruments monitor the specific gravity, relative to air, of a gas or mixture of gases. These instruments are often used to monitor industrial processes where the gas to be analyzed is known and calibration for composition over a fairly well defined range can be accomplished. Portable models for detecting leaks also are available. These devices operate on a mechanical principle involving two hollow cylindrical chambers in each of which there is a motor-driven impeller and an impulse wheel. One impeller draws in a continuous sample of the gas to be tested and spins it at high speed against the vanes of the impulse wheel, creating a torque proportional to the density of the gas. The other impeller draws in a continuous sample of ambient air, spinning it at the same speed in an opposite direction to the test gas, creating on its impulse wheel a torque proportional to the density of the air. The difference between the opposing torques is a measure of the specific gravity of the test gas and of its composition.

Palladium Absorption

Properties that are unique to hydrogen have been used in detectors that specifically indicate its presence. One such property is the exothermic absorption of hydrogen molecules by palladium metal which, in the presence of oxygen, is immediately followed by the even more exothermic formation of water as shown in the reaction:

		<i>H cal mol⁻¹</i>
4 Pd + H ₂	2 Pd ₂ H	— 9 605
2 Pd ₂ H + 1/2 O ₂	H ₂ O + 4 Pd	—48 195
H ₂ + 1/2 O ₂	H ₂ O	—57 800

The heat from this reaction can be used to indicate the presence of hydrogen by using palladium or a similarly catalytic material in conjunction with the Wheatstone bridge arrangement used in the catalytic-combustion. Catalyst-coated thermistors or other temperature-sensing devices that respond only to hydrogen take advantage of the unique hydrogen absorption characteristic of palladium or perhaps a few of the transition metals.

An unusual detection device based on this principle is a tape developed by Rocketdyne (ref. 25) that uses the heat from the palladium-hydrogen and hydride-oxygen reactions to change the color of a thermochromic paint. In this device, a finely divided palladium black is placed between two layers of material. One layer of material is porous enough to admit gas molecules by diffusion, but fine enough to retain the palladium black; the other layer is painted with a commercial nonporous chromic paint. Hydrogen passing into the packet reacts with the palladium, creates heat, and changes the color of the paint. Because the reaction is catalytic in nature, such an arrangement must be prevented from overheating in the presence of large quantities of hydrogen to prevent the packet from becoming an ignition source that will ignite or detonate high concentration of hydrogen in air. This is accomplished by mixing a reaction-quenching material with the palladium that is stable at ordinary temperatures but which reacts with the palladium black to deactivate it at a temperature high enough to allow the paint to change color. The tape is not yet available commercially, but test specimens may be obtained.

A hydrogen leak detector developed by the Bendix Corporation relies on a temperature-controlled element composed of a thin film of palladium metal. The electrical conductance of this thin film is a function of the partial pressure of the hydrogen concentration in the sample gas. Because this device does not rely on the combustion of hydrogen and oxygen, it should work satisfactorily in a nitrogen atmosphere. This detector is not yet commercially available.

Electrochemical Oxidation

In another device, electrochemical oxidation is used to measure the partial pressure of hydrogen in gaseous mixtures. This device consists of a pair of electrodes (platinum anode and silver-silver

chloride cathode) enclosed within a single plastic housing. An electrolyte gel surrounding the electrodes is held in place by a gas-permeable membrane that fits firmly against the anode. As hydrogen passes through the membrane, it is electrolytically oxidized at the anode, and a current flows between the electrodes. This current develops an input voltage to an amplifier in the device. Because the sensor is not dependent on the presence of oxygen in the gaseous mixture for the electrolytic reaction, it may be used to monitor hydrogen in various other gases, e.g., nitrogen and helium. A polarographic hydrogen device is manufactured by Beckman Instruments, Inc., Space Engineering Department (ref. 26).

Optical Interferometry

The basis for another hydrogen detector is optical interferometry. In such a detector, response is by visual observation of an optical fringe shaft. Fringe displacement is brought about by a change in the refractive index of the gas between two light beams. There is a slight difference between the refractive indices of air and hydrogen and the response is essentially linear from 0 to 100 percent. Serious deviations in accuracy can be anticipated, however, if other gases are present. A portable optical interferometer is manufactured by Riken Kieke Fine Instrument Company, Tokyo, Japan.

Miscellaneous Principles

A principle commonly used for the detection of leaks is the observation of a change in color of a chemical compound when in contact with the gas sample. Scott Aviation Corporation manufactures a Scott-Draeger multi-gas detector based on this principle. It can be used to detect more than 85 different gases and vapors. The complete detector has two parts: the gas detector pump and the special detector tube on which a calibrated scale is printed. The presence of the hazardous gas is indicated by a stain or color change of the chemicals within the tube. The color change progressively increases in length as the concentration of the gas increases. Scott also manufactures a tube for measuring hydrogen gas with a range of from 0.5-to 3-volume percentage.

The principle of the fuel cell is another basis on which a phototype detector has been designed. In this detector, the hydrogen concentration is measured by a fuel cell hydrogen-oxygen reaction. The device is reported to be highly specific and sensitive to hydrogen.

Also being developed is a detector based on a principle that

makes it possible to measure the amount of radioactive krypton-85 released from metal oxides that react with hydrogen. This development, supported in part by the U. S. Air Force, will be discussed in a succeeding section.

DETECTION LIMITS, INTERFERENCES, AND SAFETY

Perhaps the most important factors in selecting a leak detection system are sensitivity and selectivity (ref. 27). The former indicates ability to detect either a range of concentration or a minimum leak rate. Selectivity, on the other hand, concerns the ability to detect a particular vapor or gas in the presence of one or more other gases. For hydrogen leak detection, however, J. A. Grumer, et al. (ref. 4) state that although the requirements differ from one type of detector to another, all devices should satisfy certain conditions: specificity (selectivity), reproducibility and accuracy, response and recovery time, reaction to environmental conditions, linearity, and safety.

Detection Limits

Although hydrogen itself is not considered a toxic compound, it presents a serious fire and explosion hazard in the presence of air. Thus, the common hydrogen detectors are designed to provide for detecting the presence of free hydrogen gas in areas where there is a possibility of a hazardous accumulation. Because the lower flammability limit for hydrogen in air at 1 atmosphere pressure is 4 percent by volume, commercial hydrogen detectors are designed to signal when the hydrogen concentration approaches this lower limit. Consequently, the units of measurement are expressed in percent lower explosion limit (LEL). More recently, manufacturers have started using the term lower flammability limit (LFL), which is probably a more correct term.

For locating leaks, especially in such hazardous areas as special test cells, rocket engine test stands, and certain chemical production areas, remote sensing is necessary. Therefore, an additional detection limit is that of distance. Also, some detection techniques by their very nature are limited, i.e., the application of a bubble-forming liquid at a suspected site. Others are limited by the length of lead wire from the sensor to the control and readout cabinet. For portable detectors the detection distance is a function of the sensitivity of the particular physical property being measured.

The detection limits of the various types of detectors previously discussed as shown in table 1. The limits are given in three units: leak rate, percent, and distance. The values are average values obtained from various literature sources (refs. 6, 23, 24, 28), from

TABLE 1.—Sensitivity limits of hydrogen detectors

Principle	Minimum Detection Limits, average values						Distance, feet
	In air			In nitrogen			
	atm-cc/sec	percent hydrogen	percent L.E.L.	atm-cc/sec	percent hydrogen		
Catalytic combustion	8.0	0.02	0.5	80	0.2 ⁽¹⁾	2000 ⁽²⁾	
Bubble testing	1×10^{-4}	(3)	(3)	1×10^{-4}	(3)	(3)	
Sonic-ultrasonic	1×10^{-2}	(3)	(3)	1×10^{-2}	(3)	100 ⁽⁴⁾	
Thermal conductivity	1×10^{-3}	5×10^{-4}	0.01	1×10^{-3}	5×10^{-4}	—	
Gas density	1×10^{-2}	5×10^{-3}	0.1	1×10^{-2}	5×10^{-3}	(3)	
Hydrogen tapes	0.25	1.5	35	—	—	(5)	
Scott-Draeger tubes	—	0.5	13	No information		(3)	
Electrochemical	—	0.05	1.2	—	0.05	1000 ⁽²⁾	
Optical interferometer	—	0.2	5	—	0.2	(3)	

⁽¹⁾ Only one commercial catalytic instrument has been claimed to detect hydrogen in nitrogen.

⁽²⁾ The sensing head is remote from readout.

⁽³⁾ Not applicable.

⁽⁴⁾ For pressure differential of 25 psi with orifice of 0.20 inch.

⁽⁵⁾ Tape can be placed on suspected leak site and visually checked periodically.

circulars of manufacturers, from discussions with technical representatives of manufacturers, and from experimenters who have performed laboratory evaluation of detectors. These values should be used as guidelines only, because they do not take into account manufacturer's quality, and recent advances in the state of the art that are only now becoming available.

It can be seen that all of the detectors that can be used for remote continuous monitoring and, which can actuate either visual and audio alarms or cutoff switches, have detection limits at 0.05 percent or below. This is well below the lower flammability limit (1.2 percent LEL); consequently detectors based on any of these principles have sufficient sensitivity for monitoring purposes. For other applications, this table can serve as a general guide in selecting detecting equipment.

Interferences

The terms "interferences" and "specificity" are related, because specificity depends upon the absence of interferences by other gases. Interferences can be divided into two categories: those that cause a signal when hydrogen is not present, and those that prevent a signal in the presence of hydrogen. When the former occurs and if the signal is significant, the instrument is considered non-specific. Of the 12 principles of leak detection discussed, two of these (bubble testing and sonic-ultrasonic testing) are completely nonspecific. The applications where they are used, however, generally preclude the necessity for specificity.

The principles of catalytic combustion, thermal conductivity, gas density, and optical interferometric phenomena are all affected to some degree by interferences. As mentioned, the catalytic combustion detector will respond to hydrocarbons. Because of the difference in catalytic ignition temperature of hydrogen and hydrocarbons, however, a detector designed and calibrated for hydrogen possesses a reasonable degree of specificity. For example, the sensitivity to methane has been reported to be one-thirtieth that of hydrogen for a particular instrument. Thus, a 3 percent methane-air mixture results in a signal output equivalent to only 0.1 percent hydrogen in air. Some companies are investigating the use of different types of catalysts that are specific to hydrogen only; and prototype models based on this principle are being produced. A number of gases tend to poison the platinum catalysts, especially if the detector is off and the filaments are cold, and subsequent actuation of the detector will result in reduced sensitivity or no response at all. Sensors that are reported to resist poisoning are now commercially available. The thermal-conductivity detectors

are interfered with primarily by helium, because it is the only other gas whose thermal conductivity approaches that of hydrogen. Other common gases have thermal conductivities similar to air and only large percentages would be equivalent to 1 percent hydrogen in air.

The electrochemical detector is reported to be specific for hydrogen. An additional factor that would decrease the effect of interferences is the diffusion-limited membrane used in this detector. This controls sensitivity and, because hydrogen diffuses very rapidly, sensitivity to hydrogen should be much greater than that of other reducible gases. It is not known whether the Scott-Draeger color-change tube possesses specificity. However, a few simple tests with other gases should determine whether such gases as carbon monoxide, methane, or other hydrocarbons interfere.

Safety

Hydrogen-air mixtures, which have a wide flammability range (4 to 74 percent), can be ignited by sparks with as little energy as 0.019 millijoule, and can propagate through channels as small as 0.06 cm (0.025 in.). Accordingly, a leak detection instrument must not itself be a source of ignition. Some of the principles used for leak detection inherently are ignition sources, e.g., the heated sensing filaments in the combustion detectors. The detector, therefore, must have a built-in method for eliminating the ignition source. Detector principles that are igniting sources and the methods used for eliminating the hazard are shown in table 2. Detectors should be approved for use in hydrogen-air mixtures only after appropriate testing in-house or by an agency such as Underwriters Labora-

TABLE 2.—*Ignition hazards of hydrogen detectors*

Principle	Ignition hazard	Method of elimination
Catalytic combustion	Yes	Flame arrestor
Bubble testing	No	--
Sonic testers	No	--
Thermal conductivity	Yes	Flame arrestor
Gas density	No	--
	(mechanical type)	
Hydrogen tapes	Yes	Quenching material
Optical interferometer	No	--
Electrochemical	No	--
Scott-Draeger tubes	No information	--

ories determines that methods for eliminating igniting sources are satisfactory.

Several companies advertise a broad line of leak detectors and specifically design or calibrate the devices for hydrogen detection. Some carry at least six different models: portable, battery-powered, single sensor detectors to remote-sensing, multi-sensor, multi-channel, and stationary detection systems. Many companies do not list sensitivity limits, but only the range of the readout scale.

APPLICATION OF HYDROGEN LEAK DETECTORS

Selection of a hydrogen detector or a hydrogen detection system is guided by the particular application. Among the various producers and users of hydrogen contacted for this survey, almost every type of instrument principle discussed in the preceding sections had been used at one time or another as part of a leak-detection program. As a guideline in the selection of the specific leak-detection equipment, several situations will be described and the preferable systems recommended.

System Build-Up and Checkout

Bubble-testing detectors are the most common ones used during a facility build-up and checkout. Very frequently, a newly completed system is first checked with high-pressure helium and, if no leaks are found, the system is then pressurized with hydrogen and leak checked again. If the hydrogen operation is indoors and access to the area is limited, sonic detectors may be suitable. For outdoor operations, portable detectors, including either combustion meters or thermal conductivity detectors, are frequently used in addition to bubble testing.

Leakage Monitoring During Facility Operations

Throughout facility operations, continuous monitoring of the atmosphere by a remote sensing technique at a number of possible leak sites is usually required. For example, in static test firing of the J-2 rocket engine, which uses liquid hydrogen as the fuel, the test stand is usually closed to operating personnel during propellant loading, countdown, firing, and de-tanking operations after firing. When the propellant is being loaded, leaks not present at ambient temperatures sometimes develop when the tanks, valves, and plumbing are subjected to cryogenic temperatures. Leaks also may develop in the facility complex, and during the engine firings severe vibrations may cause additional leaks.

For leakage monitoring, the catalytic combustion detector with multiple-remote-sensing heads, which sample by diffusion and

convection, is recommended. These fixed detectors normally monitor continuously the accumulation of hydrogen; and at a predetermined hydrogen level, they automatically warn by audio or visual signals or activate safety control circuits. Any other system designed to perform this same operation, whether it is based upon thermal conductivity, optical interferometry, or electrochemical oxidation, would be satisfactory.

Very frequently, repeated tests of the same equipment are carried out over extended periods of time. For example, a research J-2 rocket engine may be fired once to twice daily for a period of 4 to 6 weeks with only minor hardware changes, and over this period of time a number of flanges and connections may develop leaks. Because the test stand is outdoors, very small leaks (50 scim or less) will not be detected by area sensor heads. The use of an inexpensive hydrogen sensitive tape, which is resistant to such environmental conditions as wind, humidity, and rain, would be a valuable adjunct to the area monitoring system. Tape can be placed at suspected leak sites and examined visually after each test. In this way a small leak can be detected before it becomes a serious flammability hazard.

Repairs and Modifications

Although the hazard associated with repairs and modifications is not really a leak problem, hydrogen-detection equipment must be used to safeguard the operating personnel. All equipment under repair must be fully purged with an inert gas (e.g., nitrogen or helium) prior to entering the system. Hydrogen-detection equipment should be used to ascertain the absence of hydrogen before air is admitted to the system. For this purpose, a detector which operates in the absence of air and, which is linear over the entire range (9 to 100 percent) of hydrogen-inert gas concentrations, is recommended; a detector based on the principle of thermal conductivity is most often used. After completion of repairs, procedures to restart should be the same as for initial start.

Research and Development in Leak Detection

New uses of hydrogen have sometimes posed new problems in hydrogen detection. For example, the firing of hydrogen-fueled rocket engines in vacuum chambers simulating altitudes up to 100 000 ft has created a need for hydrogen detectors that operate in inert atmospheres or in a vacuum. Detectors with low temperature limits also are needed for liquid hydrogen systems. These needs have stimulated considerable experimental work.

The great bulk of research and development has been sponsored by NASA or the Space Nuclear Propulsion Office (SNPO). This work has progressed along two lines: evaluation and improvement of present detector systems, and development of detectors based upon new principles. A complete review of all of the work recently done is beyond the scope of this survey, but some of the more important government-supported efforts will be briefly reviewed.

EVALUATION OF HYDROGEN DETECTORS

By far, the broadest experimental program in hydrogen safety has been carried on continuously for the last 5 years by the Explosives Research Center, Bureau of Mines, Pittsburgh, Pa., and supported by SNPO, Cleveland, Ohio. A substantial portion of this work has been the evaluation of some 15 commercial or prototype hydrogen detectors. Results can be found in the "Annual Reports on Hydrogen Safety" by the Explosives Research Center, Bureau of Mines, published in 1965, 1966, and 1967. The hydrogen-detection work was published in December 1967 (ref. 29). Although manufacturers and model numbers are not available in the reports, performance and limitations of a cross section of the presently available commercial detectors are sufficiently significant to warrant mentioning. The report also offers some guidelines as to how to perform a meaningful evaluation of detectors. The following factors were tested:

1. Linearity of response
2. Response and recovery time

3. Minimum detectable hydrogen concentration
4. Zero drift
5. Ignition hazard
6. Sensitivity to combustibles other than hydrogen
7. Effect of wind
8. Effect of temperature and humidity changes.

The test methods are described in Appendix A. Conclusions for this work were included in a hydrogen-handling manual (ref. 4) published in June 1967. Although it may be somewhat overly critical of the available detectors, the section of the manual presenting these conclusions is extremely useful to anyone contemplating a hydrogen-leak detection system. An extract from this Bureau of Mines manual follows.

DETECTION OF HYDROGEN LEAKS

Well-placed, reliable hydrogen detectors are imperative for a safe installation. They determine the concentration of hydrogen in the surrounding air and may be used to activate emergency ventilation fans and other equipment. The number and distribution of sampling points in a detection system should be based on the possible rate of leakage, the ventilation and the size of the room. The location of the detection head is critical. It must be placed where it will sample combustible mixtures and, since hydrogen rises rapidly, it should be located at an elevated point. However, a single sampling point does not insure adequate sensing since a stream of combustible mixture may not flow by the sampling point. Adequate protection often requires a number of well-placed detectors.

Commercially available detectors vary from small, battery-operated portable instruments to large, multi-unit permanent installations. Although the requirements differ from one type to another, all devices should satisfy certain conditions.

Specificity—The instrument must respond to hydrogen and be insensitive to other gases, combustible or not.

Reproducibility and Accuracy—Readings should duplicate themselves within definite limits when subjected to the same hydrogen concentration. Indicating instruments should meet required standards of accuracy.

Response and Recovery Time—When in use, an instrument should respond to the initial presence of hydrogen and to subsequent changes in hydrogen concentration as rapidly as possible.

Reaction to Environmental Conditions—The performance of an instrument should be little affected by temperature, humidity, wind velocity and other environmental extremes to which it will be subjected.

Linearity—Response should be reasonably linear to facilitate calibration. This will also assure positive indication over the entire range of possible hydrogen concentrations.

Safety—The instrument must not itself be a source of ignition.

Portable detectors sample the atmosphere in their immediate vicinity either by aspiration or diffusion through a porous head. In these instruments reproducibility and accuracy are more important than rapid response and

short recovery time. They tend to be more difficult to maintain because they are battery-powered and because they are only used intermittently.

Fixed detectors usually have a number of remote detector heads with read-out at one console. These heads ordinarily remain activated over a long time and are set to give alarm or switch on automatic equipment when the hydrogen in the air reaches a given concentration.

1. *Portable Detectors*

In general, the portable detectors leave much to be desired as regards accuracy, especially near the lower explosion limit. The catalytic type detector also tends to become less sensitive when kept idle for a time. Thus, it is recommended that these detectors be calibrated frequently and spot checked before being put into use. Sensitivity can usually be restored by subjecting the detector to a high concentration of hydrogen in air. Another disadvantage of the catalytic detectors is their lack of linear response at high hydrogen concentrations. This is especially true at concentrations above the upper explosion limit, although indications become erratic at lower concentrations. Peak readings occur at values ranging from 7 percent to 30 percent hydrogen in air.

2. *Fixed Detectors*

The principle of operation of fixed systems in current use is similar to that of the portable detectors. As hydrogen-laden air passes over a headed catalyst-coated element, the temperature of the element increases and the increase is sensed electronically. In some designs the filament resistance is compared to that of an uncoated filament in a bridge circuit. In others, temperature change is detected either by a thermistor element or by a miniature photocell. Response and recovery times are important for these fixed units. Tests in which the sensing heads of diffusion-type units were exposed rapidly to an atmosphere containing hydrogen gave response and recovery times of about 2-3 seconds. Response and recovery times of diffusion type units may not be improved by increasing the size of the pores of the flame arrestors because of the small quenching distance of hydrogen-air flames.

Reproducibility and accuracy of reading of fixed detectors is typically to within a few percent when an instrument is tested and retested during a series of runs. Moreover, when such instruments are left on for a time in the absence of hydrogen, zero drift is generally low (a few percent). However, if the detectors are turned off for some time, initial response is invariably sluggish or erratic. If the response is corrected by subjecting the detector to high hydrogen concentrations, it is necessary to rezero and check the calibration.

Fixed detectors must be relatively stable when subjected to extremes of temperature, humidity, and hydrogen concentration. Instruments can be designed which are relatively unaffected by extremes of atmospheric temperatures. The effect of humidity is variable, but the available instruments appear to operate satisfactorily even at 100 percent relative humidity. However, the response does deteriorate if instruments are left unenergized in the presence of high humidity. The reaction to extremely high concentrations of hydrogen is erratic. It is desirable that these detectors continue to respond with an alarm as the concentration goes beyond stoichiometric and approaches 100 percent of hydrogen. Since the catalytic combustion cannot be maintained actively when oxygen is nearly absent, the electronic consoles are often designed to lock in an alarm condition until reset manually. This, of course, is not as satisfactory as an instrument that could indicate actual hydrogen concentrations at all levels.

Commercially available hydrogen detectors are of the catalytic combustion type. Other properties such as thermal conductivity, are also used in gas detection apparatus; however, thus far they have not been applied commercially to hydrogen detectors. A detector based on thermal conductivity would have the advantage, in a hydrogen-air mixture, of giving linear readings up to 100 percent concentration. However, the lack of specificity of response poses problems.

To sum up, the adequacy of the currently available instrumentation for hydrogen detection is marginal. Further development is necessary and should emphasize:

1. Increased reliability in the presence of adverse environmental conditions.
2. Higher speed of response and recovery without sacrificing safety.
3. Adequate sensitivity at all levels of hydrogen concentration up to 100 percent.
4. Indication of rate of change of hydrogen concentration in conjunction with the instantaneous measurement of concentration. This, too, requires an inherently more rapid response time.

In general, maintenance of detectors should be emphasized. Each piece of equipment should be tested and calibrated regularly. The ignition hazard presented by the detectors themselves must be recognized. Detectors should be approved with regard to the ignition hazard for use in hydrogen-air mixtures only after appropriate testing by an agency such as Underwriters Laboratories. In this connection it should be noted that equipment safe in hydrogen-air is not necessarily safe in hydrogen-oxygen.

The installation and operational problems of a hydrogen-leak detection system on the Saturn S-IVB static test firing stands were the basis for another evaluation of hydrogen sensors reported in open literature (ref. 30). The J-2 rocket engine powering the Saturn vehicle S-IVB stage uses liquid hydrogen for the fuel and liquid oxygen for the oxidizer. Three types of hydrogen detectors were considered: the palladium thin film, the electrochemical, and the catalytic combustion. The latter was chosen as most applicable. Ten criteria were listed as requirements for the detection system, including operational range from -150° to $+250^{\circ}$ F, 1-second response time, extended period of operation, operation in a nitrogen atmosphere, and explosion proof. The need for a thorough evaluation program prior to implementing an operational system is discussed in reference 30. For example, catalytic combustion units were capable of detecting hydrogen in a nitrogen atmosphere; however, when modified by the vendor to operate at 180° F, the sensor head was no longer capable of detecting hydrogen in this atmosphere.

NEW CONCEPTS OF HYDROGEN LEAK DETECTION

Under a NASA contract (refs. 31, 32), Beckman Instruments, Inc. studied hydrogen gas detection by several means, including

mass spectrography, gas chromatography, palladium resistance films, polarography, and acoustics. Study and development proceeded along parallel paths to develop one hydrogen detector operating on polarographic principles and another operating on acoustical principles.

The polarographic hydrogen detector is an electrochemical device consisting of a semipermeable membrane, an electrolyte reservoir, and electrodes. Hydrogen molecules in the atmosphere diffuse through the membrane, through the electrolyte layer, over the detector anode, and then react to form hydrogen ions at the anode-electrolyte interface. Ionization of the hydrogen molecules yields two electrons, which are the charge supplied for the current level that is proportional to the concentration of hydrogen gas in the sample atmosphere. In the development of the detector, a study of the properties of the anode surface was necessary. The optimum anode surface was found to consist of a gold substrate with light platinum coating. The platinum coating served as a catalytic surface that dissociated the hydrogen molecules to hydrogen atoms and thus rendered them available for oxidation. Stability of the platinized surface was very poor, and experimental work established that it would maintain the anode surface in a highly catalytic state. Using a third electrode, the reactivation process oxidized the working electrode periodically and then reduced all oxides formed during the process. This research was performed over a period of several years, ending in 1966 with the fabrication of a polarographic hydrogen detection system, associated electronic circuitry, and a readout device.

Experimental work also demonstrated that an acoustical sensor could be made specific to hydrogen by employing the thermal molecular relaxation properties of the hydrogen molecule. By operating an acoustic detector at two distinct ultrasonic frequencies that span a center frequency of 10 megacycles and making a comparison of either the speed of sound or the absorption properties, specific detection of hydrogen gas can be accomplished. Experimental work on the polarographic detector led to two other contracts (refs. 33, 34) for the design and fabrication of detection systems.

In 1963 the Bendix Corporation (ref. 35) designed, developed, and fabricated a prototype model of an area hydrogen detector based on the change in resistance of a palladium thin film when it absorbs hydrogen. Three prototypes were delivered to NASA, but no instrument is now available for commercial use.

Parametrics, Inc., examined various techniques for detecting

hazardous vapors of the element propellants, fluorine, and hydrogen. The goal was a rugged, field-type instrument for detecting less than 0.1 ppm of fluorine and less than 1 percent hydrogen. A novel technique based on radio-chemical exchange using kryptonates was investigated. Radioactive krypton-85 was incorporated into a variety of solid materials by placing the solid in contact with krypton-85 under high-temperature and high-pressure conditions. Under these conditions, diffusion of the gas into the solid occurred. This kryptonation resulted in entrapment of krypton-85 molecules in the lattice of the solid. Degassing of the kryptonated material is negligible at room temperatures. A kryptonated solid undergoing a chemical reaction will release krypton-85 because of chemical destruction of the surface layers. The amount of radioactivity released will be proportional to the agent with which the solid is reacting. The possibilities of radiokrypton homologs that can be applied as detection sensors for hydrogen are numerous. A number of metal oxides were also studied by Parametrics, Inc., and the results indicated that kryptonated platinum oxide with a surface coating of molybdenum trioxide would serve as an excellent hydrogen detection system. The final report (ref. 36) stated that a simple rugged instrument capable of continuous unattended operation was feasible.

The research (ref. 25) performed by Rocketdyne Division, North American Rockwell Corporation on the development of a hydrogen-sensitive tape, which changes color, has been discussed in a preceding section. Developmental work on this device is needed to determine its applicability for uses other than monitoring flanges during static rocket engine firings.

Because this survey has been performed over a period of only five months, some research work has undoubtedly been overlooked. Other reports obtained but not reviewed here are listed in the bibliography.

Hydrogen Fire Detection

Fire detectors have been used for many years in buildings, storage areas, aircraft, ships, and submarines. The detectors usually actuate an alarm or indicating device, and sometimes are connected to fire extinguishing and other automatically operated equipment. The fire detector is only one element in an overall fire and safety system and in all practical applications it must be considered in terms of its relationship to other elements in the system.

Pure-hydrogen fires are invisible in all conditions except near darkness. Only impurities burning or heated in the flames are visible. Therefore, even when people occupy or observe a hydrogen storage area, fire detection and visualization devices can be useful in locating fires. The detectors also may be employed more conventionally to monitor areas where hydrogen is stored or used when no personnel are present.

GENERAL CONSIDERATIONS AND REQUIREMENTS

Fire detectors are based on a few basic principles, regardless of the nature of the sensors or sophistication of the control circuitry. First, the fire must have observable physical properties, and there must be a way of transferring information about these properties to a sensor or set of sensors in the detector. All fire detectors have limitations as to the minimum size fire that they can detect at a given distance and the maximum false signals or interferences that they can reject. Depending on the principle applied, either active or passive detectors may identify fires at given points along a line or throughout a volume of space. Principles of fire detection are discussed in references 37, 38, 39, 40.

Characteristics of Hydrogen Fire Detectors

Each situation in which a fire detection system is needed will have a particular set of requirements, and no one system will meet all sets, but some general requisites can be listed. An optimum fire detector should have the following characteristics:

Reliability.—For a fire detector this means that all dangerous or potentially dangerous fires will be detected, but that there will be

no false fire indications. The first of these criteria is met to a greater degree than the second one in most operational systems. The problems and expense that can be brought about by system failures and false alarms are particularly well documented by the airline industry (refs. 40, 41, 42). False alarms can come either from a breakdown in the system or from interference or background signals. The first of these difficulties can be partly overcome by making a fail-safe system, i.e., expected failures such as short circuits do not indicate a fire (ref. 38). The second difficulty is discussed below. Reliability is the most important criterion for a good fire-detection system. In practice, no fire-detection system is wholly reliable but some, especially those with redundant or multiple sensors, approach this ideal more closely than others.

Specificity.—A fire detector should specifically indicate a fire but not give an indication when a signal is received from a source other than a fire. Discrimination against unwanted signals is a significant problem, which is treated in many ways, depending on the method of detection and the environmental conditions. A trade-off between detector sensitivity and background rejection is frequently necessary. Usually, solutions to this kind of problem can be found only if the properties of the fire, the interference source, the transferring medium, and the sensor are thoroughly understood.

Indication of a fire.—A fire detector must indicate a fire in such a way that timely action can be taken. These may be an audible alarm, warning lights, or both. In automatic systems, a fire indication also results in actions such as shutdown of equipment, closing of valves, or activating a fire extinguisher without human intervention.

Timeliness.—The presence of a fire or explosion must be indicated before major damage occurs. Speed of response depends on the type of sensor and the control circuitry.

Repeatability.—It is desirable for the fire detector to stop indicating a fire after it is extinguished and be able to indicate a fire again if another one occurs.

Resistance to environment.—A fire detector should operate reliably at the predicted ranges of temperature, pressure, sound level, vibration, and humidity. Its response should not be seriously degraded by deposits of various chemicals or other such agents as lubricating oils. One of the obvious problems is to make a sensor capable of withstanding immersion in a flame and yet maintain its repeatability.

Provision for internal testing.—Many current fire-detection sys-

tems provide means for checking their operational status, either by giving an automatic indication of malfunction or by responding to a manual test. This feature has obvious advantages in most situations.

Quantitative output.—The ability to indicate size, location, and type of fire (e.g., small diffusion flame or general deflagration) is desirable in any system, but is especially needed in systems for missiles and aircraft.

Economy.—Reasonable cost is often an important requirement. Considerations of expense must include servicing and replacement, as well as initial cost.

Hydrogen Fire-Detection Principles

Only two types of sensors, thermal and optical, are used as hydrogen fire detectors. Detection is passive, i.e., by radiative or convective transfer of energy from the flames to the sensors. It is conceivable that emission of sound or absorption of infrared radiation by combustion products could be detectable characteristics of hydrogen fires, but they have not been used. Although pressure-sensitive detectors have sometimes been used in explosion suppression systems, the fast-reaction time required for hydrogen-air explosions makes the radiation detector much more desirable. Thermal detectors are less specific than optical detectors. They are the most common type of general fire detector, but because they have some major limitations and do not represent recent advances in fire detection, they will be treated more cursorily than optical detectors.

Optical detection of hydrogen fires falls naturally into two spectral regions: ultraviolet and infrared. In general, different sensors and optical components must be employed in each region; also the background and transmission conditions are peculiar to each region. The following sections will cover the principle of hydrogen fire detection by thermal, ultraviolet, infrared and combination methods.

Although this survey is primarily devoted to fire detectors as instruments capable of remote indications of hydrogen fires, there is another method of detection which should be mentioned—make the flames visible by putting solid materials into them. In this method, the heated material glows, verifying the presence of fire. Some workers in hydrogen facilities throw a handful of dirt in the air or carry a broom held in front of them to locate suspected fires (ref. 30). A dry powder fire extinguisher may be played into the flames so that the extent of the flames may be seen (ref. 4).

THERMAL DETECTORS

Fire detectors designed to detect abnormally high temperatures can be classified as rate-of-temperature-rise detectors and over-heat detectors. Some can be set to indicate either a fast-rate-of-rise before a maximum temperature is reached or warn of a maximum temperature even though the rate-of-rise is slow. The fast rate-of-rise detector functions primarily as a fire detector, whereas the overheat detector will alarm at either a fire or other overheat conditions.

Fixed-temperature detectors often use bimetallic or eutectic materials that warp or melt at present temperatures. A recent development of intumescent paint gives a visual indication of overheat by rapid expansion. The thermocouple detector uses the thermoelectric effect to generate an emf at one junction when referenced to another junction held at a fixed temperature. A thermocouple can be used for both types of response. Another detector uses a thermo-conducting cable with two coaxial or parallel wire conductors upon which a voltage is impressed. In between is an inorganic salt having a resistance that depends on temperature. When a high temperature occurs, the resistance drops and a current flows between the conductors. This detector may detect high temperature along a short length of cable or moderately high temperature along a long length. Typical temperature vs. resistance curves are shown in figure 2.

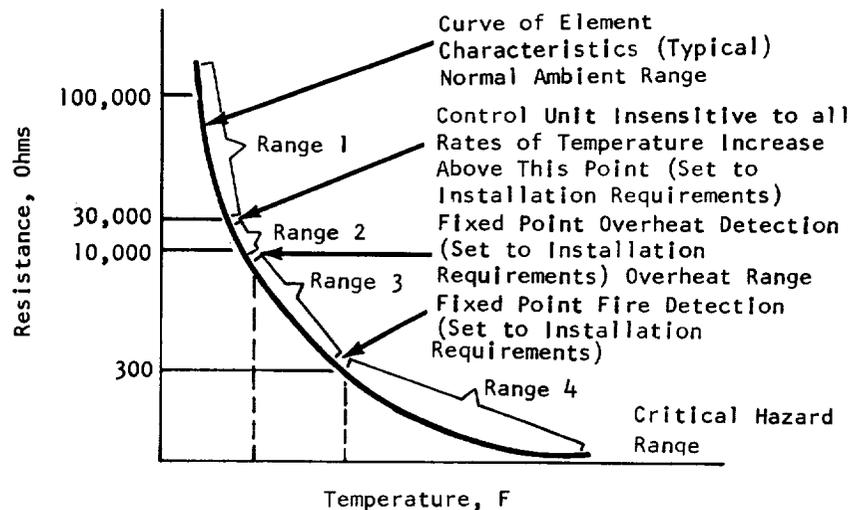


FIGURE 2.—Temperature vs resistance curve.

The pneumatic detector is a common rate-of-rise detector which operates on the principle that the pressure of a confined gas increases when its temperature rises. The sensing element in this detector is small-diameter tubing filled with air. There is a very small hole for bleeding air in or out during slow temperature changes but, if any part of the tube is heated rapidly, the internal pressure rises, setting off the alarm. Most of these detectors can be contained in the form of either unit (small area) or line instruments.

Merits and Disadvantages of Thermal Fire Detectors

Thermal fire detectors have been manufactured for many years, and many of them are rugged, simple, and not subject to frequent failure. The continuous line detectors, for instance, are in standard use in commercial aircraft. Except for eutectic devices, these detectors are repeatable and many of them can withstand, at least momentarily, the heat of a fire. They are relatively economical and now available.

Thermal detectors must be at or very near the site of a fire. To cover a large area or volume, there must be a great many of these detectors. Even then a fire may go undetected for a long time. If they are in the ceiling of a building there will be time delay while hot gases rise from a low fire to the detectors. Indeed, when a detector is immersed in a flame, response is slow compared to optical detectors. Approximate response times of thermocouple detector systems may be 0.05 sec, but continuous element overheat detectors respond in about 5 sec (ref. 43). As stated, they are not specific for hydrogen fires, but thermal detectors are used and will continue to be used as hydrogen-fire detectors where other methods have failed. They also will be used where high reliability or versatility is required in fire-detection systems having two or more sensors. Although many commercial thermal fire detectors are available, only two are known to be used at hydrogen facilities, and both use the thermo-conducting cable described.

ULTRAVIOLET FIRE DETECTION

Detection of ultraviolet radiation from hydrogen flames is a promising method of noticing fires because the flame emission is readily detectable and many sources of background radiation are very faint or completely absent in much of the ultraviolet region. This region of the electromagnetic spectrum covers the wavelength range between about 40 and 4000 Å (ref. 44), but since hydrogen flame emission is detectable only at wavelengths greater than about 2000 Å, this discussion will be restricted to the 2000- to

4000-Å region. Many optical techniques and components applicable to visible light (4000 to 7000 Å) can be used or adapted for ultraviolet radiation. Image tubes, photo tubes, and photocells operate on similar principles in the ultraviolet and visible regions, although some of the materials may be different. Many ultraviolet optical components, such as lens systems, are expensive and difficult to obtain. The spectral characteristics of typical ultraviolet sensors, radiation sources, and transmitting media are shown in figure 3. These characteristics will be discussed below.

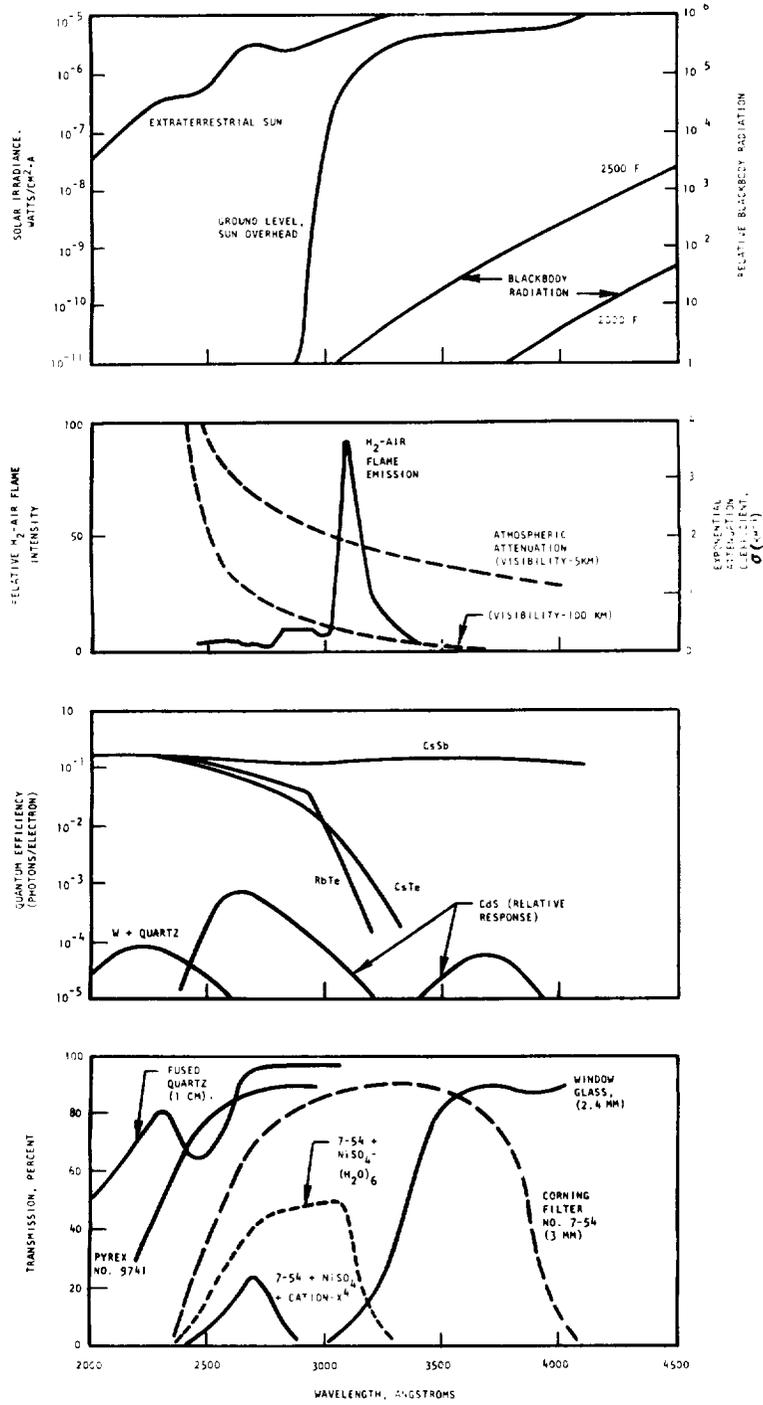
Optical fire detectors which identify fires by detecting ultraviolet radiation have much in common with infrared detectors. They have one significant advantage, however, in that a volume of space, not just a line or point, can be monitored. Any fire of detectable size and within the field of view will be detected more quickly by optics than by any other method. All optical sensors have a maximum range at which fires of a certain size can be detected, the range being a measure of detector sensitivity. When comparing sensitivities, it should be remembered that the flux density of radiation decreases as the square of the distance from a small light source. Other considerations, such as methods of discriminating against nonfire sources of radiation, are also applicable in general to both infrared and ultraviolet detection. For this reason discrimination (a very important consideration), as well as other optical detection principles, will be discussed in some detail; much of this discussion is also applicable to infrared fire detection.

Transmission of the Ultraviolet

Before optical emission from a fire can be detected it must be transmitted through the atmosphere to the sensor. Background radiation is similarly transmitted. Although oxygen and nitrogen molecules in the air strongly absorb radiation below approximately 1850 Å, attenuation at longer wavelengths results mainly from scattering. This scattering occurs because of molecules and small particles and droplets (also called aerosols) suspended in the atmosphere. Fewer molecules and lower aerosol content naturally diminish the scattering coefficient (K). As the wavelength is shortened, the attenuation from scattering increases rapidly. Plots of K vs wavelength for different conditions at sea level are shown in figure 3 (ref. 45). This scattering can be a severe problem at cryogenic installations where water vapor sometimes condenses to form thick clouds of fog.

For sunlight transmitted through the atmosphere there is an

→
FIGURE 3.—Ultraviolet spectral characteristics of sources and materials.



additional attenuator, ozone. This gas, formed in the upper atmosphere by photochemical processes, is concentrated mainly in a layer about 30 000 feet thick, centered at an altitude of about 90 000 feet (ref. 46). The total amount of ozone is equivalent to a layer only 2 or 3 mm thick at normal temperature and pressure, but its absorption is extremely strong. The absorption is strongest at about 2600 Å, but is only 50 percent at about 2750 and 2280 Å. The atmosphere is virtually opaque to extraterrestrial radiation below 2863 Å, the shortest solar ultraviolet wavelength ever measured at the Earth's surface (ref. 44). The attenuation of solar irradiation at short wavelengths decreases with altitude even below the ozone layer; above the ozone layer there is virtually no attenuation.

Transmission of Materials

Ultraviolet transmission of solid materials is of interest for fire detection because the optical components used must transmit the radiation in the desired spectral region. With ordinary window glass, having a thickness of 2 mm or greater, the transmission falls off rapidly below 3600 Å, and the glass is practically opaque to ultraviolet wavelengths shorter than 3000 Å. A 2-mm thickness of pyrex is nearly cut off by 2800 Å (ref. 44). Special ultraviolet transmitting glasses and clear, fused quartz transmit as low as 1800 to 2000 Å. Sapphire is another commonly used ultraviolet transmitting material. Other materials used as filters transmit only in a selected wavelength range.

The process of absorption may be molecular or by interference. Of primary interest in hydrogen fire detection are filters with sharp cutoffs on the long wavelengths side at about 2800 to 1900 Å, and as high a transmission as possible toward the shorter wavelengths. Such a transmission-attenuation characteristic would block out sea level solar radiation and transmit the OH radiation of 2600 Å and above. Transmission curves are also shown in figure 3. For a more thorough discussion of ultraviolet transmission, see references 44 and 47.

The attenuation of ultraviolet radiation by liquids may be a problem if detectors or detector windows are accidentally splashed with liquids. Pure water has a fairly high transmission in the ultraviolet. Even as low as 2000 Å in wavelength, a 1-inch thickness of distilled water transmits 82 percent of the incident radiation (ref. 44). Limited measurements of lubricating oil and hydraulic fluid (refs. 37 and 13, respectively) show that both fluids begin attenuating at 3500 Å and are strongly attenuating at wavelengths of 3000 Å or shorter.

Ultraviolet Background Radiation

Since a great many hydrogen handling facilities are out of doors, the most serious problem in ultraviolet background radiation is solar irradiation. A plot of solar irradiance at sea level is shown in figure 3 (refs. 46, 48). It should be understood these values are for a clear day with the Sun directly overhead. The amplitude will diminish as the Sun departs from the zenith or if the day is cloudy or hazy. Sunlight reflected from metal and glass is also quite strong (refs. 44, 48).

For fire detection in air vehicles, it should be recalled that short-wavelength solar irradiation increases with altitude because the atmospheric attenuation decreases. For instance, the intensity of solar irradiation at 2950 Å nearly doubles in going from sea level to an altitude of 40 000 feet (ref. 44). Above the ozone layer, solar ultraviolet radiation is much more intense than flame radiation in the ultraviolet. Because the intensity of sunlight as compared to flame radiation is a significant problem in optical detection of fires, the development of "solar-blind" (at or near sea level) ultraviolet detectors, which would be insensitive to radiation at wavelengths longer than about 2850 Å, has aroused considerable interest.

Terrestrial sources of ultraviolet can also be troublesome. Radiation from heated solid materials, sometimes called blackbody radiation, does not produce a serious interference problem as long as the temperature is lower than approximately 2100° F. The ultraviolet emission from a heated solid decreases very rapidly in the ultraviolet region toward shorter wavelengths. Other ultraviolet sources, against which discrimination has not been achieved are: (1) other flames in the field of view, such as matches, intentional fires, burning exhaust gases, and, especially, welder's torches; (2) unfiltered carbon arc lamps or other illuminating sources strong in ultraviolet; and (3) lightning. Ordinary incandescent or fluorescent lamps do not present as severe a problem because their glass envelopes eliminate short-wavelength ultraviolet.

Ultraviolet Sensors for Hydrogen Fire Detection

A variety of ultraviolet sensors has become available only in the last few years, partly because of requirements for instruments in rocket and satellite research. One of the most common means of detecting ultraviolet radiation is by photoelectric emission. The sensor can be a simple photodiode tube or a complicated high-gain photomultiplier tube, with tube envelopes made of fused

quartz or other highly ultraviolet transmitting material. Numerous photoemissive cathode materials in the ultraviolet have recently become available. Sensors that may be used for hydrogen fire detection include:

Photomultiplier tubes.—These tubes can be built to operate at temperatures up to 1000° F, but they require high voltages and are normally sensitive to high-frequency vibration. Although rugged photomultipliers are relatively expensive, they have high sensitivity, low noise, and very fast response. Cs-Sb is the most common cathode material used in photomultiplier tubes; this material's response extends into the visible region (fig. 3). More recently, tubes in which Rb-Te and Cs-Te photocathodes are used have been available, with good response at 2500 Å and much lower response above 3000 Å. Although these tubes are solar blind, those with Cs-Te photocathodes have been known to saturate when exposed to sunlight. Even with filtering to reduce longer wavelength response, one test (ref. 22) showed the response to reflected skylight was four times the response to a 2800-cc/minute hydrogen-diffusion flame (distance unspecified). This was still an improvement over the Cs-Sb cathode tube. In applications where solar radiation is not of concern, these tubes are quite useful for hydrogen fire detection.

Phototubes.—A variation of the phototubes is a gas-filled tube with pure metal photoelectrodes, usually referred to as a Geiger-Mueller tube. At the proper electrode potential, a photoelectron emitted from the cathode ionizes the gas and an electrical pulse is formed. With a tungsten photocathode the useful spectral response for fire detection is between 2000 and 2800 Å. Such a tube made by McGraw-Edison Inc., is used on their own and in several other detectors. When the sensitivity of this tube and circuitry is kept at a low-enough level, it appears to be truly solar blind (refs. 20, 22) at sea level. Its maximum response is at 2200 Å, a wavelength at which OH radiation has not been measured.

Solid-state detectors.—A few solid-state ultraviolet photocells are now available or being developed. Detecting materials include silicon, selenium, silicon carbide, cadmium sulfide, and cadmium selenide. Only relative spectral response to radiation is available. Data on temperature limitations are not available, but each undergoes a change in sensitivity and spectral response as the temperature is raised. None of them is solar blind, nor can they be filtered to make them so. The silicon carbide detectors will respond up to almost 1000° F. An extensive developmental effort on these detectors has been made by Westinghouse Corporation (ref. 50), at

least partially for the purpose of fire detection. The peak spectral response can be tailored, by construction of the sensor, to vary between 2000 Å and 3800 Å, but the longer-wavelength portion of the response curve extends into the region of solar radiation. All of these rugged, very small photocell sensors can be protected by fused quartz or other short-wavelength transmitting material.

Image tubes.—Ultraviolet imaging devices provide a different class of detector. These devices have obvious usefulness in hydrogen fire detection by enabling the viewer to see the size and location of the flame, just as with ordinary fires. There are two types of ultraviolet imaging detectors—the image converter and the television tube. The image converter uses a photo-emissive coating deposited on an ultraviolet transmitting face plate. The emitted electrons are focused on a phosphor screen, which fluoresces, producing a visible image. Only one ultraviolet image converter, the RCA model 7404 tube, is known to be in production.

Because Cs-Sb is used in the photocathode, its spectral response is similar to that of the photomultipliers of the same material. A high voltage (12 kV) is required to operate the tube. With suitable optics and power supply, one of these tubes can be used as a hand-held monocular to survey an area for hydrogen fire (ref. 51).

An ultraviolet-television-camera tube is based on the same principles as visible-light tubes. Such tubes, now largely developmental, have a visible-ultraviolet photosensitive element and window materials that transmit short-wavelength radiation. Tubes that have been made include vidicons that can detect to as low as approximately 2000 Å. Care must be exercised with some of these tubes to ensure that the faceplate temperature is kept at a moderate level. The ultraviolet vidicon can be used in a conventional television camera with one major difference—the lens must be adjustable and correctable; and, it must transmit below 3000 Å. Because of manufacturing difficulties and lack of a widespread demand, ultraviolet lenses are not generally available and are quite expensive. With suitable optical filtering, an ultraviolet television system can produce a satisfactory image of a hydrogen flame (ref. 51).

Background Discriminating Techniques

Several techniques which can be used for discriminating against ultraviolet background sources, are discussed below:

Spectral selection.—The most common technique for background discrimination is to make the detection spectrally selective, so that it does not occur at the wavelengths of radiation from an interfering source. Particularly in the case of solar background

discrimination, a penalty is paid for the exclusion of wavelengths above 2850 to 2900 Å, because the hydrogen flame emission at shorter wavelengths is very much weaker than the principal OH emission band between 3064 and about 3200 Å. The detector responses and filter curves do not drop off sharply above the desired wavelength, which means that the peak of the response curve must be at an even shorter wavelength than 2850 Å. Narrow-band filters, with relatively sharp cutoffs, tend to attenuate strongly even at the peak of transmission. One that is often used, a nearly solar-blind filter, consists of Corning 7-54 glass, plus a thickness of $\text{N}_2\text{SO}_4 \cdot (\text{H}_2\text{O})_x$ crystal, and a film of Cation-X. Its peak transmission is at about 2650 Å, and is nearly cut off at 2400 and 2900 Å. One manufacturer of interference filters specifies 30 to 35 percent transmission for filter widths of about 120 to 500 Å in the ultraviolet. If there is no solar background where a hydrogen fire is to be detected but there are other sources of illumination, it may be feasible to filter the light sources. Ordinary glass reduces much of the ultraviolet, and special glass can be bought to eliminate longer wavelength ultraviolet without seriously affecting the quality of the transmitted visible light.

Two-color method.—When complete spectral selectivity is not feasible, there are other methods of discrimination against occasional background ultraviolet, such as in the two-color method (spectral comparison). The ratio of the intensities of flame and background radiation in two spectral regions is often distinctly different. As a typical example, the ratio of pure hydrogen flame radiation at 3100 Å to that at 6000 Å is much greater than one, whereas the same ratio is much less than one for sunlight. A two-color detector takes the signals from two sensors and compares them, and can be set to indicate a fire for sensor output ratios less than one, and give no indication for ratios greater than one. This principle is used by at least one manufacturer of fire detectors. Limitations are imposed if the background level is sufficiently high to obscure flame radiation and/or saturate the detectors.

Temporal variation of radiation.—Temporal variation of emitted radiation is another distinguishing characteristic of flames and explosions. Detector control circuits may allow only the output of ac components of the sensor to pass. A band-pass filter is used to include most of the flame-light modulation frequencies but exclude unwanted frequencies, such as the 120-cycle radiation modulation from fluorescent and incandescent lamps. The use of flicker discrimination slows the overall response time of the detectors.

Sensitivity is also lowered, since only a part of the flame radiation (namely, that which is time varying) is accepted. This technique has not been used in commercially available ultraviolet fire detectors, but its feasibility has been demonstrated in developmental systems (ref. 13). Some detectors can be made to respond to radiation only if it persists for a certain duration, which also slows the response time, but is useful in discriminating against momentary flashes such as sunlight or lightning. The rapid rise in radiation intensity at the onset of an explosion can also be used with the proper circuitry to detect an explosion and actuate suppression devices.

Radiation level.—A discrimination technique in which radiation levels are compared could be used in the ultraviolet fire detector, but so far it has not been considered attractive. If the maximum expected background irradiance of the detector is lower than the minimum expected flame irradiance, the detector could be designed to indicate a fire only when the level of irradiation is greater than a certain threshold value. In a situation where maximum sensitivity is desired or the background level is high or unpredictable, this would not be a practicable method of discrimination.

Ultraviolet Fire Detectors

A few commercial ultraviolet-sensing fire detectors are now available. The McGraw-Edison and RCA detectors may be considered off-the-shelf items. The others are either developmental types or more-or-less made to order. Some installations with indoor fire-detection problems have fabricated their own ultraviolet fire detectors using photomultiplier tubes for high sensitivity.

INFRARED FIRE DETECTION

The emission from hot water in hydrogen-air flames is strong in certain portions of the infrared spectrum, especially around the 2.7-micron wavelength. Infrared sensors have fairly fast response and some are quite economical. The transmission characteristics of optical materials create a minor problem in the near infrared. Background radiation, however, causes a significant problem with infrared detection. A composite graph of the spectral characteristics of typical infrared background sources, sensors, flames, and transmitting media is shown in figure 4.

Transmission of Infrared

Infrared radiation is not strongly scattered in its passage through air, but it is absorbed by water and CO₂ in the same bands hot water emits. However, some hot water radiation will

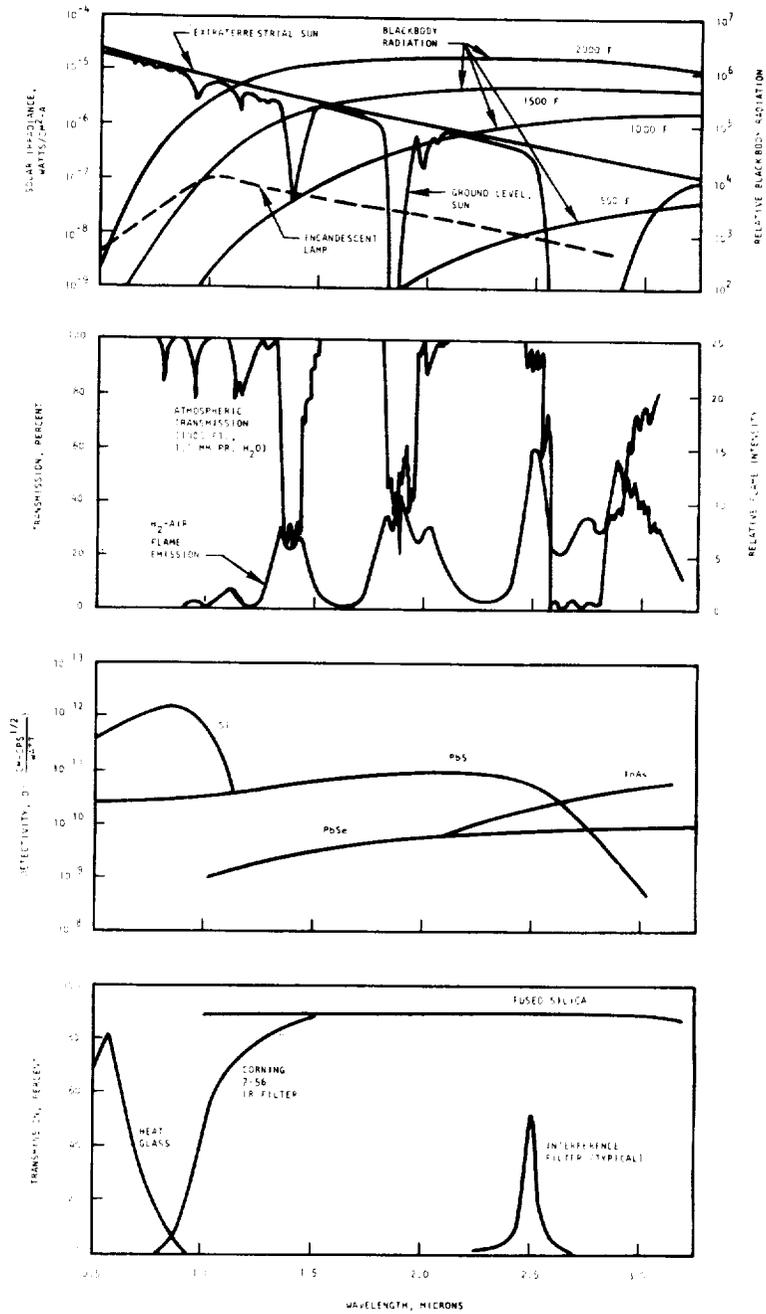


FIGURE 4.—Infrared spectral characteristics of sources and materials.

not be attenuated because the bandwidth or wavelength range of the radiation emitted by the hot water is greater than the bandwidth of absorption by the cooler water in the air (fig. 4). The lower atmosphere also attenuates solar radiation very strongly, so that between 1.81 and 1.88 microns, and 2.55 and 2.9 microns almost no solar radiation reaches the Earth's surface. At an altitude of 16 000 feet, and on a very clear day, the Sun's radiation is attenuated only about 50 percent at 1.75 microns, about 97 percent at 2.7 microns, and about 30 percent at 2.5 and 2.9 microns (ref. 46). On cloudy or humid days the attenuation of sunlight will be greater. The shorter-wavelength water bands are also attenuated, but less strongly. Infrared materials such as glasses do not have spectral characteristics that cause a great problem up to about 3 microns, although water in the material will cause some absorption. Some optical glasses (fused silica) and Vycor are quite transparent in this region. Block or band-pass filters such as interference, long-pass, and short-pass filters, and infrared-absorbing glasses can also be applied in this region. Liquid water absorbs in the same regions as water vapor (ref. 52).

Infrared Background Radiation

Interference radiation in the infrared region comes not only from the Sun but also from hot materials. Incandescent lamps, heaters, and hot walls in an engine space can emit troublesome interference radiation. Heated solids usually emit radiation similar to blackbody radiation. A 100-watt tungsten lamp (4700° F) has its peak radiation at about 1 micron, whereas the peak radiation of a blackbody occurs at about 2.5 microns for a temperature of 1300° F, and at 7.4 microns for a temperature of 500° F. Radiation from heated bodies in the field of view of a detector will be attenuated about the same amount as flame radiation, whereas solar radiation is entirely removed in certain bands. The radiation from these sources can be modulated by reflection from moving or rippling surfaces, or by passing through fan blades or "heat waves" in the air. Aside from the above sources, hot exhaust gases and other flames (such as matches and welding torches) can cause false signals. Interference radiation from fluorescent lamps is less troublesome than that from other sources.

Infrared Sensors for Hydrogen Fire Detection

Three sensors are used for infrared fire detection: photoemissive, photovoltaic, and photoconducting. The photoemissive types are photomultipliers, and the other two are used in photocells. Ag-O-Cs is the most common photoemissive cathode material. Its

spectral response is greatest at 0.8 micron (8000 Å), and extends only into the very-near infrared, cutting off at 1.2 microns (S-1 response). Photovoltaic cells employ silicon (Si), and indium arsenide (InAs), and photoconductive cells use lead sulfide (PbS) and lead selenide (PbSe). All these detectors can operate without being cooled, but the sensitivity of some can be greatly increased by cooling to the temperature of liquid nitrogen. Probably the best detector for water-band emission is the lead-sulfide (PbS) detector. Its sensitivity at room temperature peaks around 2.7 microns, and it is cheap and readily available. PbSe is a factor of 10 lower in sensitivity than PbS, and InAs is even less sensitive.

The spectral response of silicon is unfavorable to longer-wavelength detection. Silicon detectors have peak response at 0.85 to 1.05 microns and cut off at 1.5 microns. Silicon cells have been used in general fire detectors, but it is questionable whether detection of the near-infrared bands of water at 1.1 microns and shorter wavelengths is satisfactory for most hydrogen fire detection devices. Background radiation from the Sun would be more of a problem in this region because solar intensity is greater and flame emission is lower near 1.1 microns than at 2.7 microns. Infrared-imaging devices are more common than ultraviolet units, and do not require rare and expensive optical components. Infrared vidicon tubes that can be used in conventional vidicon cameras are now available, and most lenses for ordinary television can be used in the near infrared with a slight loss of resolution. The response of both tubes extends to over 2 microns. The development of infrared-image converters for nighttime surveillance and communication in military operations has brought about tubes that are cheap and easy to acquire. These tubes use the Ag-O-Cs photocathode and have an S-1 spectral response, which does not respond to wavelengths greater than 1.2 microns. They can be used in monoculars with built-in power supplies. A hydrogen flame can be easily seen through them, but they are of limited use when the background illumination is high in infrared content.

Background Discrimination Techniques

General methods for discrimination against interference radiation were discussed in the section on ultraviolet fire detectors. These techniques are also applicable to the infrared region. The most favored technique in the infrared region is by modulation (or flicker) discrimination. The Sun and most heated solids do not emit flickering radiation. However, incandescent lamps have a time-varying radiation component modulated at 120 Hz. Band-

pass filters for fire detectors usually do not pass frequencies above 30 Hz, so as to avoid this problem, and yet include most of the flame frequencies. Another popular discrimination technique is by radiation level (refs. 53 and 54). Detector sensitivity is lowered until ambient radiation levels do not cause an alarm, but a fire of sufficient size will activate the device. Two-color discrimination is also a technique that can be used. Spectral selection can be used either by itself or in conjunction with other techniques.

Infrared Fire Detectors

There are more sources of infrared fire detectors than of ultraviolet ones. Some fire detectors with near-infrared detectors (wavelengths less than 1.3 microns) will be relatively insensitive and subject to background problems; however, it might be possible to modify these systems to take PbS sensors or they may be used in applications without a strong infrared background.

DETECTION LIMITS AND PERFORMANCE SPECIFICATIONS

There is no one standard for expressing sensitivity of fire detectors. Thermal detector specifications as to size of a fire and distance from the fire would be almost impossible to give in a general sense, because convective heat transfer is a function of highly variable factors. Designers of heat-actuated automatic sprinkler systems can specify the number of sensing elements necessary to protect a room of a given geometry from disastrous fire, but the minimum-size detectable fire is not given. When a heat detector is immersed in a fire, the response time depends on convective and conductive heat transfer, the fixed temperature trip level, and, for continuous detectors, the length of sensor element actually in the flame.

A description of the performance limitations for radiation-sensing detectors regarding size of fire, type of fire, maximum detecting distance, field of view, and response time should be fairly straightforward in principle. The problem arises from a lack of standards. Because of the varying emissivities and spectral distributions of radiation from different kinds of fires, and the various spectral responses of the sensors, it is difficult to compare the sensitivities. There are even different ways in which a detectable flame is specified. In some cases the flame is described by its height, and in others, by the rate of flow and pressure of the fuel. The problem is not lessened by the reluctance of some, but not all, manufacturers to reveal either the specific kind of sensor or the spectral response. An additional complication is that interference radiation may lower the sensitivity of some detectors, particularly

infrared detectors, or make the use of others impractical. Except for claims to solar blindness, almost no manufacturer specifies background limitations.

Some radiation detectors have sensitivities specified in terms of a 5-inch-diameter pan fire of gasoline. This is because of standards for aircraft fire detectors (radiation-sensing type established by the Federal Aviation Agency (FAA)). The minimum performance standards and specifications are spelled out in considerable detail. The adverse condition under which aircraft fire detectors must function imposes rather severe requirements of vibration, temperature, and other environmental extremes. The specification on response is that the sensor of the instrument shall be exposed, at a distance of 4 feet to a test flame produced by a burning gasoline pan 5 in. in diameter. The response time shall not exceed 5 sec. Other specifications include time-to-clear after saturation by flame radiation and removal of flame, repeat response time, freedom from false alarms under various conditions, fire resistance, unimpaired sensitivity due to a coating of oil, and resistance to water, salt spray, and blowing sand. One of the most severe tests is the ability to discriminate against direct sunlight and sunlight modulated from 0 to 100 Hz. The manufacturer is also required to supply data on the cone of vision (field of view) and the maximum effective range at field extremities.

The FAA standards are a good example of the data necessary to determine radiation detector usefulness in a given situation. For a given fuel and size of fire, detector sensitivity could be well specified by giving maximum detection distance in the center and at the edges of the field of view. If data could be found to compare radiant intensities of two different size fires, then data on the sensitivities of two detectors with disparate sensitivity specifications could be compared. It should be kept in mind that the irradiance at the sensor is inversely proportional to the square of its distance from the fire. The data in reference 19 can be used for this purpose when comparing sensitivities given for hydrogen fires (if the hydrogen rate of flow and orifice size are known), provided the spectral bandwidths are accounted for. However, it is impossible at present to compare sensitivities specified for different fuels because the difference in radiation output is not known. The best procedure to follow in determining the validity of a detector is to observe its performance for a specific type of fire.

The most sensitive radiation fire detectors use photomultiplier tubes as sensors, small hydrogen fires being detected at over 100 ft. Among the least sensitive but most reliable detectors are the

solar-blind Geiger-Mueller ones. Those in which photocells are used have sensitivities between these two extremes, the response being considerably enhanced by the addition of light-gathering optics (lenses and focusing mirrors).

Specificity, as applied to hydrogen fire detection, should mean the same thing as applied to fire detection in general, i.e., the detector should indicate a fire only when a fire occurs and not when an interference signal is received. It is possible to conceive of a fire detector which would indicate a pure hydrogen fire as opposed to most other fires, but it is difficult to imagine that such a device would have any practical value. Any accidental fuel fire, hydrogen or otherwise, can be a hazard. Because of the small number of observables in hydrogen fires and the relatively low intensity of some of them, any detector capable of sensing a hydrogen fire can detect a hydrocarbon-fuel fire, but the reverse is not necessarily true. In hydrogen fire detection, as in other fire detection, the principal problem is one of achieving acceptable sensitivity while rejecting interferences.

Ideally, a fire detector should be tried under the actual conditions in which it must operate. Sometimes modifications will be necessary, e.g., sensitivity may have to be decreased or filters added to optical detectors. In one installation using solar-blind ultraviolet detectors, specially designed shields were made to block out light from unwanted sources but to allow monitoring of the desired areas. Continuous strip thermal detectors must be installed where they will not be stepped on or otherwise abraded or dented. It should be kept in mind that for each installation careful consideration must be given to the selection, placement, and quantity of fire detectors to meet the particular requirements.

Research in Hydrogen Fire Detection

FIRE VISUALIZATION AT ROCKET ENGINE TEST AREAS

The probability of leaks and fires is highest in those facilities where hardware is frequently changed and modified, a situation normally found at rocket testing facilities. For example, a number of problems involving hydrogen fires developed at Rocketdyne's Santa Susana Field Laboratory near Los Angeles. A method for visual detection of these fires was needed, especially for the critical periods during engine firings. Ordinary closed-circuit television and direct observation proved inadequate for timely detection of fires and subsequent location of the leak sites. Accordingly, a program was conducted to develop techniques for the visualization of hydrogen fires in the presence of strong background illumination (ref. 51). The investigation included television, viewing telescopes, and photography in both the infrared and ultraviolet spectral regions.

Infrared Television

Infrared television (IRTV) proved to be a very useful technique for the visual detection of hydrogen fires. The background radiation in test stand areas comes from the Sun, floodlights, and (during test firing) from the rocket engine or turbine exhausts. Selected optical filters were necessary to allow radiation from the hydrogen flame to be received by the vidicon and at the same time block most of the background radiation. With the proper selection of filters, good definition and contrast between the flame and its surroundings were achieved. A Hamamatsu vidicon tube with response to wavelengths up to approximately 2.2 microns was used. The filters were set in a filter wheel between the camera lens and the vidicon. The filters found most useful for the particular lighting conditions were: (1) a silicon window for low-level background illumination, (2) a long-pass filter transmitting at 1.3 microns and longer wavelengths for detection in a sunlit or floodlit environment, and (3) a long-pass filter transmitting beyond 1.6 microns for intensely lighted backgrounds.

The IRTV system has been used to monitor accidental hydrogen

fires during tests of liquid hydrogen turbopumps and large rocket engine firings, and a number of fires have been detected that could not have been seen by eye. After the firings, video tape replays revealed the locations of burning hydrogen leaks, whereas ordinary cameras and televisions could not always locate the flame. An additional advantage of IRTV is that it can "see through" some of the fog produced by the presence of cryogenic lines. Figure 5 is a photograph of two simultaneous television pictures, one conventional and the other with an infrared vidicon, showing a hydrogen diffusion flame in sunlight reflected from a metal plate.

Ultraviolet Television

Ultraviolet television (UVTV) was also tested successfully for hydrogen flame visualization against almost all lighting and background conditions. A Westinghouse vidicon tube having a sensitivity to wavelength as short as 2000 Å was used. A Barnes Engineering ultraviolet transmitting lens was found to operate reasonably well. Interference filters having different bandwidths and peak transmission points were tried, and a few were found suitable for observing the most intense OH radiation at 3064 Å against

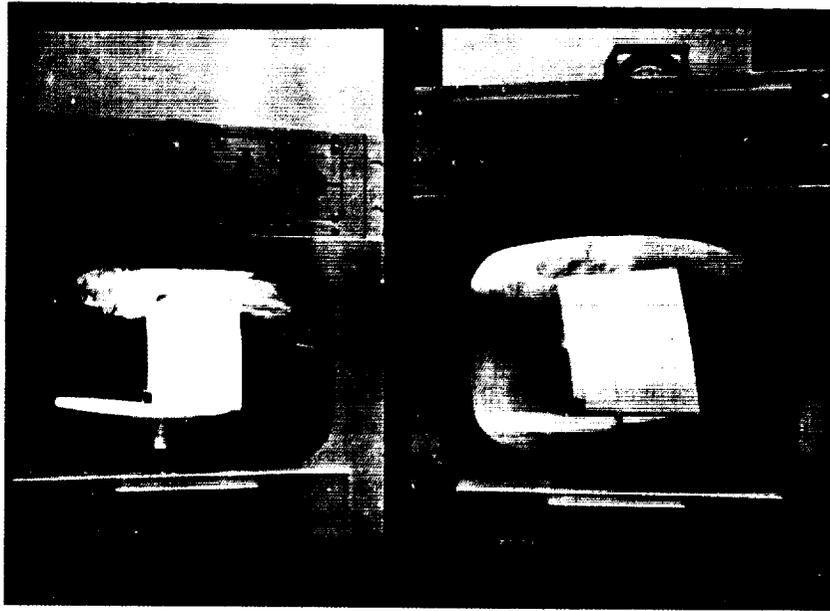


FIGURE 5.—Hydrogen diffusion flame; conventional television (left) and infrared television (right).

solar and other backgrounds. UVTV was not used extensively, however, primarily because ultraviolet-transmitting optics were too expensive.

Telescopes for Observing Hydrogen Fires

Image-converter tubes, both infrared and ultraviolet, were used in telescopes for viewing hydrogen flames. Infrared telescopes (sometimes called "snooper scopes") with optics and power supply were available commercially, but the ultraviolet telescope had to be constructed. Quality of the ultraviolet image was limited by the lens employed but, with proper filters (such as those used with the UVTV) the technique was shown to be quite feasible. The infrared telescopes have a spectral response up to approximately 1.3 microns, and with proper filters (depending on background illumination) they can be used to see hydrogen fires about 1 ft. long, burning from a 0.25-in.-diameter tube at a distance up to 50 ft. The value of these devices is extremely limited when extraneous radiation is high in infrared content.

HYDROGEN-AIR FIRE AND EXPLOSION DETECTION FOR AEROSPACE VEHICLES

Research has been conducted on the observable properties of hydrogen-air fires and explosions at atmospheric and lower pressures (refs. 19, 22), and a prototype detection system developed on the basis of some of these findings. This is one of the few studies in which quantitative measurements (ref. 19) of the emitted radiation from hydrogen fires and deflagration have been reported. Also of interest are the behavior of infrared and ultraviolet radiation as the pressure is lowered, which are useful for aircraft as well as missile fire detectors and detectors in altitude-simulation chambers.

Further radiation measurements of hydrogen-air deflagrations were made (ref. 22). A series of simulated leak tests, with ignition occurring in partially mixed, nonhomogeneous hydrogen-air systems proved that the time rate of growth of radiation and pressure were highly variable and depended not on an overall mixture ratio but upon the relative positions of leak and ignition source, leak rate and orientation, and chamber geometry. These factors influence the degree of mixing attained at the time of ignition. As a part of this research, three commercially available ultraviolet photoemissive detectors were evaluated for solar-blind operations. A model detection system was designed and constructed to determine the existence and location of incipient deflagration through the use of dual detectors and logic circuitry.

FIRE DETECTION IN AEROSPACE VEHICLES

At present the fire detectors in missiles, as in most aircraft, are thermal detectors. However, it would be desirable to monitor for fires throughout the volume around vulnerable components and to have a more rapid response than is given by these detectors. A program was carried out to develop a model detection system for the upper stages of the Saturn vehicle, based on observing the radiative properties of hydrogen fires. As an aid to designing this system, some data on the properties of hydrogen fires at sea level and at other altitudes were also obtained (ref. 13) :

1. The lower flammability limit of hydrogen-oxygen mixtures was determined to be 0.43 torr. This pressure corresponds to an altitude of 175 000 ft.
2. The lower limits of ignition for flammable hydrogen mixtures were determined to be 0.43 torr for a spark ignition source, and 2.5 torr for a hot-metal ignition source.
3. Discrimination of hydrogen-fire radiation from hydrogen-fueled rocket plume radiation can be accomplished by utilizing the difference in the temporal variation of the radiation from fires and plume.
4. Discrimination of hydrogen-fire radiation from sea level and extraterrestrial sunlight radiation can be accomplished by a two-color technique, which utilizes the spectral distribution of energy from the Sun.
5. The temporal variation of the radiation from hydrogen-diffusion flames undergoes a drastic reduction in amplitude when the ambient pressure drops below 150 torrs.
6. A fire-detection system can be employed in the Saturn vehicle, which utilizes the steady-state component of the ultraviolet radiation from the OH radical as the indicator of accidental hydrogen fires, two-color discrimination against false signals from sunlight, and high frequency discrimination against J-2 plume radiation false signals.
7. A system solely dependent on the temporal variation in the radiation from fires and backgrounds will not reliably detect accidental fires onboard the Saturn vehicle above an altitude of 35 000 ft.

INTUMESCENT PAINT

Intumescent paint is a simple and inexpensive means of detecting hydrogen fires. Such organic compounds as the sulfuric acid salt of paranitroaniline decompose at approximately 385° F to give copious quantities of sulfur dioxide and produce an extremely heat stable black polymeric char. A paint has been prepared con-

taining this agent and a resin-based lacquer which, when applied to a surface, appears no different than an ordinary paint film. However, if a flame is impinged on the paint film, it blackens, swells, and sulfur dioxide is generated. The blackening of the paint, the swelling of the area around the site of flame impingement, and the odor of the sulfur dioxide can disclose a hydrogen fire.

PORTABLE FIRE DETECTORS

Two recent programs have been conducted to develop handheld fire detectors (not telescopes). One of these programs resulted in the development of an infrared sensitive detector (refs. 55, 56). As a result of an in-house effort by the U.S. Air Force, an ultraviolet detector was designed to sense hydrogen flames in the presence of sunlight (ref. 20). Both systems have light-gathering optics and have an audible-tone fire indicator.

The infrared detector was developed to enable firemen to locate fires which are concealed by heavy smoke or debris or are located in confined spaces. A lead sulfide cell, filtered by a Corning 7-57 infrared filter, was the sensing element responsive to wavelengths between 0.9 and 2.5 microns with a lens to collect the radiation. The signal, a constant audible tone into an earphone at about 200 to 300 cps increased in frequency when a hot spot was detected. Four versions of this detector consisting of four different fields of view, two electronic circuits, and a pistol grip or flashlight-style holder were tested by a fire department. All units could detect a 1-sq. ft blackbody at 300° F through smoke sufficiently thick to obscure the blackbody from visual detection. It was found that a narrow field of view was the most satisfactory, partly because heat sources such as incandescent bulbs gave false signals when the detector was pointed at them. This detector might be useful indoors or, with caution, outdoors.

The objective of the ultraviolet detector work was to design and demonstrate a prototype of a portable hydrogen fire detector for ground support facilities. The McGraw-Edison Geiger-Mueller tube was selected as a sensor. An ellipsoidal, 8-in.-diameter aluminum mirror is employed to increase the optical gain of the system. The mirror is mounted on the front of a cylindrical chassis containing some of the electronics and is held by a pistol grip. The power supply is carried separately on a shoulder strap. Readouts consist of an audible tone and a flashing light. The tone is not continuous but occurs when a fire is detected in "tone bursts," which become a constant hum when the detector is close to a large flame. This detector can sense a 1-in.-high hydrogen-air diffusion

flame (1000 cc/min of hydrogen from a 1.75-cm orifice) at 80 ft. With the proper scanning technique, the operator can determine the approximate size and location of the flame.

RELATED RESEARCH AND DEVELOPMENT

Ultraviolet Sensors

Recent research programs on fire detection components and techniques include work on solid-state ultraviolet detectors (ref. 57). Two materials, SnO₂ and ZnS-MgS solid solution, were found to be promising for photo-conductive detection at 2850 Å. The shortest cutoff wavelength observed was at 3270 Å. Research on photoemissive ultraviolet detectors (ref. 58) for detecting fires and explosions using radiation at wavelengths shorter than 2900 Å has been conducted. As a result of this work, a sensor with a quartz envelope and molybdenum photocathodes was developed. Hydrogen-filler gas has been used to provide gas amplification of photo currents in such tubes as the McGraw-Edison with a long-wavelength cutoff near 3600 Å, and a peak response at approximately 2600 to 2800 Å. These tubes were capable of operating up to 590° C (1100° F).

Fiber Optics

The use of ultraviolet fiber optics for the detection of fire and explosion can overcome the temperature limitations of optical sensors. Fiber optics of quartz or similar material can withstand high temperatures and transmit the radiation to a remotely mounted sensor. One effort to develop ultraviolet fiber optics for the detection of fire and explosion is reported in reference 59. Bundles of fused quartz fibers clad with magnesium fluoride were fabricated to lengths up to 12.5 ft. Transmission properties were not as good as expected, but a 4-ft-long bundle had appreciable transmittance down to 2500 Å; the same length of glass fiber transmits negligible radiation below 3700 Å.

Computers

For difficult conditions, fast response, and stringent reliability requirements, a multi-sensor approach to fire detection is often recommended. Recent developments in fire detection for such conditions (refs. 13, 23, 38) have taken advantage of the availability of compact logic circuitry in computer applications. Information from a number of sensors of different types can be processed so as to indicate fire, overheating, or failure somewhere in the system.

A description of a fire and overheating detection system concept is given in reference 38. A computer was designed to process signals from ultraviolet, infrared, and continuous-strip thermal detectors. False alarms and failure can be reduced by designing a fail safe system that employs redundant sensors. The computer for this program would weigh only a few ounces.

Survey of Hydrogen Fire and Leak Detection Practices

The extent to which hydrogen leaks and fires are a problem is highly variable, and persons responsible for safety tend to view similar situations with differing degrees of concern. Hydrogen leakage poses the greatest problem when there are extremes of temperature (high or low) and high pressure. Additional problems are created if the equipment is not operated continuously but is cycled in temperature and pressure, or if there are frequent changes or modifications of hardware. Although leaks can happen any time, they are most likely to occur after reassembly of hardware. The use of hydrogen (especially liquid) indoors causes some concern. The rapid dissipation of hydrogen in the atmosphere considerably lessens the hazard outside.

Of the facilities visited during the survey, the type of plant requiring the least surveillance for hydrogen leaks and fires (1) had all its hydrogen equipment outside, (2) operated with gaseous hydrogen at moderate pressure, (3) operated continuously for many months, (4) had few personnel in the area where hydrogen is used, and (5) had only rugged, nonflammable equipment for handling hydrogen. Hydrogen leaks were allowed to burn as long as the plant was operating, provided they did not create a hazard or represent a significant economic loss. Near the other end of the spectrum was a facility in which liquid hydrogen was used inside a building that housed some 300 to 400 persons and was surrounded by delicate, expensive experimental equipment sometimes operated at high voltages. It should be reemphasized, however, that these cases involved a degree of danger. Serious hydrogen explosions and fires in such facilities were reported during this survey, sometimes with considerable loss of property and, occasionally, lives.

Certain findings from the survey of hydrogen leak and fire detection practices are summarized in table 3. The type of facilities visited or contacted by telephone is included, plus one found in the literature (ref. 60). Some of the plants or laboratories had facilities that could be considered separately from each other be-

TABLE 3.—*Survey of Hydrogen Fire*

Type of facility	LH ₂ or GH ₂	Inside or outside	Pressure and/or temperature	Capacity and/or usage	Leak check methods
Storage	GH ₂	Out	2000 and 600 psi	120,000 cu ft (2 trailers)	Soap bubbles when connecting trailers; tape around flanges, look for ruptures or bulges
Test cell, mixing characteristics	GH ₂	In	600 psi	About 0.1 lb/sec	Unperforated tape around flanges, semi-permanent leak-detecting system
Production and use of hydrogen for catalytic hydrocracking	GH ₂	Out	-----	Several million cu ft/day	Tape and bubble liquid
Liquid hydrogen facility	Both	Both	From 1900° F at 250 psi to 40.5 R at 10 psi	200,000 gal/day 680,000 gallons storage	Bubble compound and tape with punched holes
Hydrogen production for hydrogenation processes	GH ₂	Both	1600° to 2000° F at about 200 psi, to ambient temperature, 0.4 psi	10 to 15 × 10 ³ cu ft/mo 150,000 cu ft storage	-----
Research laboratory	LH ₂	In	1 to 5 atmospheres	Few thousand gallons	Portable detectors
Hydrogenation and other processes	GH ₂	Both	1 atmosphere to 100 psi; one operation at 2000 psi	30 × 10 ⁶ cu ft/year. Storage about 50,000 cu ft	Pressure decay and soap bubbles
Propulsion laboratory	GH ₂ (from LH ₂)	Both	GH ₂ at 3500 psi	2 × 10 ⁶ gal/year LH ₂ (vaporized) ² 100,000 gallons storage	-----
Heat transfer laboratory	Both	Out (Partially enclosed)	GH ₂ —up to 2000 psi at 500° F. LH ₂ —up to 4000 psi	200 gallons, LH ₂	Portable detector
Storage (at least ½ mile from other facilities)	LH ₂	Out	-----	26,000 gallons permanent; 150 to 5000 gallons portable dewars	Visual observation of frosting during transfer
Storage facility (50 to 500 feet from test facility)	LH ₂	Out	-----	20,000 gallons	-----

and Leak Detection Practices

Portable hydrogen detectors (principle)	Fixed hydrogen detectors			Hydrogen fire detectors	Remarks
	Principle	Sampling heads	Number of heads		
None	None	-----	-----	None	Considering hydrogen detection tapes.
None	None	-----	-----	None	
Catalytic combustion (2 manufacturers)	None (except tape)	-----	-----	None	Hydrogen produced is not pure; therefore, flames are somewhat easier to see than pure hydrogen flames. Detectors also used for other combustible gases. Fixed head locations: liquifier, chemistry laboratory, control room, propane compressor, and electrical power room. Alarm at 25 and 40 percent LEL.
Catalytic combustion (2 manufacturers)	Catalytic combustion	Aspirated	12	None	
Catalytic combustion	None	-----	-----	None (ultraviolet sensor used as furnace flame monitor)	
Catalytic combustion	Catalytic combustion	Diffusion	≈50	Overheat detectors in building	Warning and alarm concentrations at 4 and 10 percent LEL. Automatic shutdown of experimental electronics near hydrogen and activation of high-speed fans.
Ultrasonic	None	-----	-----	None (sprinkler system in buildings)	
-----	Catalytic combustion	Aspirated	4 or 5 in each room	None	Alarm at 50 percent LEL, if detected by at least two sampling points in a given indoor area. Sampling points in upper part of room.
Catalytic combustion	None	-----	-----	None	Flares used in test areas to ignite accidentally escaping hydrogen.
None	None	-----	-----	None	
-----	Catalytic combustion	Diffusion	2	Thermal type triggers deluge system	One sensor over storage tank, one over vent stack.

TABLE 3.—*Survey of Hydrogen Fire*

Type of facility	LH ₂ or GH ₂	Inside or outside	Pressure and/or temperature	Capacity and/or usage	Leak check methods
Shock tube research	GH ₂	In	5000 psi (intermittent)	-----	-----
Brazing furnace	GH ₂	In	~.1 psi at 1200° to 2000° F.	8000 cu ft/hr maximum	Bubble compound and portable detector
Storage Propulsion research	GH ₂ Both	Out (Partially enclosed)	2000 psi	~250 gallons LH ₂	Portable detector
Production and use of hydrogen for hydro-cracking	GH ₂	Out	-----	Millions of cu ft/day	Breaks in plastic tape; portable detectors
Flame studies laboratory	GH ₂	In	-----	Small	-----
Storage	LH ₂	Out	-----	200,000 and 20,000 gallons	-----
Rocket engine test	Both	Out	1500 psi	50,000 gallons	Helium-pressurized bubble compound; portable detector
Pump and high-pressure storage	GH ₂	Out	5000 psi	8-inch by 80-foot bottle	-----
Shock tube (under construction)	GH ₂	In	12,000 psi up to 600° K	-----	-----
Compressor for pipeline system	GH ₂	Partially enclosed	5000 psi	-----	-----
Rocket engine testing	LH ₂	Both	-----	15,000 gal/mo	-----
Storage and LH ₂ vaporizer	Both	Out	-----	5000 gallons, plus 20 GH ₂ bottles (2 by 20 feet)	-----
Production and use of hydrogen for reaction processes	GH ₂	Both	From 3 to 8 psi at ambient temperature; to 5000 psi at 900° F.	7 × 10 ⁴ cu ft/day 100,000 cu ft storage	-----

and Leak Detection Practices—Continued

Portable hydrogen detectors (principle)	Fixed hydrogen detectors			Hydrogen fire detectors	Remarks
	Principle	Sampling heads	Number of heads		
-----	Catalytic combustion	Diffusion	5	None	Sensor location: (1) one at highest point in room, 12 to 15 feet above equipment; (2) three along tube about 4 inches above it; and (3) one in exhaust vent.
Thermal conductivity	None	-----	-----	None	Leaks at high temperature occur in container inside furnace above auto-ignition temperature.
None	None	-----	-----	None	
Catalytic combustion	Catalytic combustion	Diffusion	4	None	Sensors under roofs at, or near, hydrogen areas.
Catalytic combustion (2 models)	None	-----	-----	None	Visual detection of accidental fires; small fires seen at night. Leaks sometimes diluted with steam.
-----	Catalytic combustion	Diffusion	4	None	Placement: three sensors in laboratory—two in corners (14 feet above floor), one above burner; one sensor in control room.
None	None	-----	-----	None	
Catalytic combustion	Catalytic combustion	Diffusion	2	Infrared television	Sensor heads attached to cable; can be moved and repositioned around test facility.
None	None	-----	-----	None	
-----	Catalytic combustion	Diffusion	-----	None	
-----	Catalytic combustion	Diffusion	4	None	Sensors above compressors and in roof. Replace aspiration-head system.
Catalytic combustion	Catalytic combustion	Aspiration	8	Flame monitor in exhaust scrubber	Sampling points 0 to 100 feet from analyzer: (1) one 10 feet over LH ₂ run tank; (2) one 12 feet over engine; (3) four in exhaust scrubber; (4) one in fuel pit, and (5) one in GH ₂ storage pit.
-----	Catalytic combustion	Diffusion	3	Thermal detectors trigger extinguisher	Diffusion heads over storage tank, vent stack, and vaporizer.
Catalytic combustion; ultrasonic	Catalytic combustion	Aspiration	4	None	Alarm at 20 percent LEL, automatic shutdown of certain apparatus for a local concentration of 40 percent LEL.

TABLE 3.—*Survey of Hydrogen Fire*

Type of facility	LH ₂ or GH ₂	Inside or outside	Pressure and/or temperature	Capacity and/or usage	Leak check methods
Launch complex for space vehicles	Both	Out	-----	Hundreds of thousands of gallons	-----
Cryogenic testing of materials, (six, open test cells)	LH ₂	Both	Ambient pressure	2000 gal/mo	-----
Rocket engine and structural testing	Both	Out	-----	Hundreds of thousands of gallons	-----
Testing of rocket engine at simulated altitude	LH ₂	In	-----	-----	-----
Hydrogenation processes	GH ₂	Both	9 to 15 psig and 150 psig	≈30,000 cu ft/hr	Soap bubbles
Production and use of hydrogen in hydrocracking and other processes	GH ₂	Out	Up to 3000 psi at several hundred °F.	Up to 14 × 10 ⁶ cu ft/day	Tape, tape with holes, and bubble compound
Propulsion test all (combustion studies)	GH ₂	In	600 psi	Up to 1 lb/sec for 15 or 20 seconds	-----

cause they performed distinctly different functions and each had a complete set of detection equipment. Emphasis was placed on the type of remote detection equipment used, but some information was also obtained about portable leak-detection equipment. A horizontal line drawn in any column indicates that the information was not obtained for that facility. The first four columns summarize some of the operating conditions of the facility, including whether liquid or gaseous hydrogen was used. Very often gaseous hydrogen (GH₂) is present with liquid hydrogen (LH₂) because the gas phase is obtained from liquid by a vaporizer or is a pressurant for the liquid. When there are fixed fire or leak detectors, the location is discussed in the remarks.

and Leak Detection Practices—Continued

Portable hydrogen detectors (principle)	Fixed hydrogen detectors			Hydrogen fire detectors	Remarks
	Principle	Sampling heads	Number of heads		
-----	Catalytic combustion	Diffusion	≈154	Ultraviolet fire detectors; G-M tube (about 60); thermal wire at flanges; etc. (42)	Output of each sensor to panels in control center and to event recorder. Hydrogen detectors alarm at 25 percent LEL. Infrared television being considered.
Catalytic combustion	Catalytic combustion	Aspiration	6	Ultraviolet sensor (furnace-monitor type) at one enclosed test cell for fire detection	Fixed leak detectors, one above each cell, indicate when area is safe to enter (less than 20 percent LEL).
Catalytic combustion	Catalytic combustion	Diffusion	-----	Ultraviolet fire detectors (G-M tube); thermal wire	Only false fire alarm due to welding torch.
-----	Catalytic combustion	Aspiration	-----	Considering infrared television	
Ultrasonic; catalytic combustion	None	-----	-----	None	Some difficulty with ultrasonic detector due to background noise level.
Catalytic combustion	None	-----	-----	None	Visual detection of fires, usually at night.
-----	Catalytic combustion	Diffusion	1	Ultraviolet flame detector used to ensure ignition	Rapid air flow causes false alarms from fixed H ₂ sensor; helped by wrapping head with asbestos cloth. Head is 10 to 20 feet above and to side of flame area.

HYDROGEN-LEAK-DETECTION PRACTICES***Types of Detectors Used***

It is obvious from table 3 that catalytic combustion-type detectors are overwhelmingly preferred to others for hydrogen leak detection. Ultrasonic leak devices were the next most used detectors. Even then, two of the three plants that reported using ultrasonic leak detectors also indicated that they employed catalytic combustion detectors. The one facility using a thermal conductivity detector also had a need to check for leaks of noncombustible gases such as argon and carbon dioxide.

The thermal conductivity meter can be used to detect all gases, although each one requires a different calibration. Both portable and fixed leak detectors were being used to monitor for such combustible gases as propane, methane, and hydrogen at several installations. In these cases, calibration was usually made with a gas having intermediate properties between hydrogen and the other gas to be detected. Table 3 shows none of the more recently developed leak detection equipment in use. A few facilities were considering the leak detecting tape, but its use on a regular basis was not planned.

Aspiration-type heads, which lead the gas through piping to a remote central console, were found in use less frequently than in the past. Older installations were replacing such systems with the diffusion-convection heads containing individual sensors, for both speed of response and sensitivity. In some areas, where fast response is not considered necessary, the aspirated system is still considered satisfactory. At least one installation using a diffusion-convection head reported false signals because of rapid air flow when the ventilation system was operating. This was partially remedied by wrapping the sensor head in asbestos cloth.

Placement of Fixed Sensors

Certain practices in the placement of fixed leak detectors were fairly common and more or less standard. If a roof covers an area of hydrogen equipment, at least one sensor is placed just beneath the roof at the highest point. If the roof is flat and horizontal, the sensor is located just over the equipment or in a corner where the gas is liable to accumulate. This is often done even if the roofed area is only partially enclosed, such as one with only one side wall or no side walls.

Sometimes fixed hydrogen detecting heads are located a few feet above the equipment. Usually in these cases there are also sensors in the roof. In a few outdoor operations employing liquid hydrogen, fixed sensors are mounted within an inch or two of potential leak sites such as flanges, valves, and compressors. Even so, wind leaves detection rather to chance.

Sensors are often placed in enclosed spaces adjacent to hydrogen-handling areas. Most commonly, such places are control rooms, but rooms with ignition sources, such as electrical switching rooms or motor-generator enclosures are also included. In addition, sensors are located inside hardware such as vents, at intakes to compressors, or above open containers of LH_2 .

Aside from certain common-sense practices regarding placement of sensors, there seems to be no standard set of rules as to

how many fixed sensors there should be and where they should be located. According to one liquid hydrogen manual (ref. 4), the number and distribution of points should be based on the possible rate of leakage, the ventilation, and the size of the room. However, beyond this, there is no quantitative method for determining placement and number of sensors. The enormous variation in such important factors as ventilation patterns, amount and operating conditions of the hydrogen, remoteness of location, ruggedness or delicacy of equipment, and geometry of the facility, almost precludes a general rule on sensor placement.

One interesting method of determining optimum positions of sensing points was reported during the survey. In this method, the facility used hydrogen inside a large, high-ceiling room with roll-up doors and two sets of dual-speed ventilating fans, one set in the roof and the other set operating the exhaust system directly over the hydrogen equipment. Sensors were placed near the ceiling and in large "hoods" over the local areas, their location having been determined by placing smoke generators at the sites of potential leaks and observing flow patterns under various conditions of ventilation; e.g., placing a sensor directly beneath a ceiling vent was found to be less desirable than placing it to one side. It was also determined that, when the fans were turned to high speed, under some conditions a greater hazard was created by rolling up the outer doors than by leaving them closed.

Leak Indicators and Actions Taken

Both the concentration level at which an alarm is given and the action taken are determined by individual needs and preferences. The alarm or warning level for a fixed sensor system varies from 4 to 50 degrees LEL (0.16 to 2 percent H₂ by volume). The most flexible systems have a two-level alarm, the lower level as a warning and the upper level a full-scale alert. Most fixed detection systems only give alarms by horns and lights, and only by lights when the alarm-level concentration has been sensed. In situations where more than one group of people is involved in the operation, alarms and readouts may be located in two or more places. Human judgment is allowed before action is taken that may be inconvenient or result in damage or expensive downtime. Automatic action can take such forms as the shutdown of local electronic equipment, shutdown of a compressor, closing of valves, or activation of high-speed fans.

Portable leak detectors for hydrogen are used to check fittings after the assembly or reassembly of hardware, often in conjunction with bubble compounds. Sometimes a flange is investigated as

is; at other times the flange is wrapped with tape and a hole is punched to localize the leaking gas. Portable detectors are also used for periodic monitoring of equipment; e.g., in a pressure vessel consisting of layers of stressed metal, a narrow channel was drilled through the outer layers and a probe inserted into it to detect incipient leakage in the interior of the vessel. Checking hydrogen concentration around a leak that is allowed to remain is another use for such meters. Hydrogen leaks and even vented hydrogen are often diluted by steam jets or gaseous nitrogen, whichever is available and cheapest to use at the particular plant.

Another potential hazard that can be monitored with a portable leak detector occurs in certain low-pressure gas-storage tanks, called holders. These tanks maintain pressures of a few p.s.i.g. and have a variable volume for the stored gas. One such device features a flexible diaphragm attached to the walls of the tank. In these tanks hydrogen is stored on the under side of the diaphragm, and there is air in the upper part that has a number of ventilating holes. When the diaphragm leaks, an explosive mixture may eventually form in the top. An explosion that demolished one such holder was reported. In one installation surveyed, a portable leak detector was used to investigate the hydrogen concentration in the air above the diaphragm at weekly intervals.

Calibration of Hydrogen Leak Detectors

The catalytic combustion detectors require regular maintenance and calibration. Most facilities have a regular program calling for recalibration at 1- to 3-month intervals. For large rocket engine or launch vehicle firings, calibrations of fixed sensors are performed before every test. Calibrating a diffusion-convection head with its own control module can involve removing the head and module to a calibration laboratory. The sensing head is inserted into a container with a known concentration of hydrogen and the module is adjusted to give the correct reading. It is generally agreed that this recalibration procedure is necessary. Sometimes these periodic checks reveal a plugging of the sintered metal shields on diffusion sensors. In addition to partial plugging by dust, these shields are not often given a coating of paint.

At one of the laboratories surveyed the fixed detector calibration is simplified by having a polyethylene hose installed between a control center and a fitting on the outside of the sintered shield. To calibrate a sensor, a standard mixture of hydrogen and air is pumped through the hose to the sensor and the meter in the sensor control module is adjusted to give the correct reading. This process saves much time eliminating the time and effort needed to

climb up to each of the sensors to either calibrate them in place or take them down for calibration.

HYDROGEN-FIRE-DETECTION PRACTICES

As shown in table 3 hydrogen fire detection is not nearly so great a concern as is hydrogen leak detection. Many hydrogen users say they do not worry about hydrogen fires and would not use a fire detector if they had one, because at a particular facility, small fires at leak sites do little damage and can be seen at night; or an inexpensive and convenient means of detecting hydrogen fires has not been available.

In facilities where fixed hydrogen fire detectors are employed, ultraviolet sensors are clearly preferred, particularly those supposed to be solar-blind. Combined ultraviolet and thermal wire detectors were found in operation at two liquid hydrogen-fuel rocket facilities. This combination, plus hydrogen gas detectors, is considered highly satisfactory by personnel having experience with the system. Fire detectors may be used as flame monitors to ensure that ignition has taken place.

Infrared television (IRTV) is the only equipment in use or under consideration as hydrogen-flame-imaging devices at the facilities that were surveyed. IRTV is unquestionably useful under certain circumstances; but the systems are expensive and require more and different kinds of adjustments than conventional television systems. In one facility such a system was reported to be frequently in need of repair, at least partly because of the inexperience or impatience of the operators.

In none of the places with optical fire detectors was there a device automatically actuated when a fire was detected. In a few cases thermal detectors actuated sprinkler or deluge systems, just as in ordinary industrial plants and warehouses.

The calibration of fire detectors is not so great a problem as that of leak detectors. The resistance of the thermal wire can be checked periodically and the operating condition of the control circuitry can be readily ascertained. Optical detectors should be visually inspected for dirt on the window or lens. Commercial detectors have built-in methods for electrical checks. One set of specially made ultraviolet detectors is calibrated in the field by an ultraviolet lamp held at the end of a flexible cable leading to a portable power supply. The distance and the angular range at which the lamp can be detected is a check on the sensitivity and field-of-view of the detector. One common practice is to light a match in front of the detector for a rough check of its operating condition.

Conclusions and Recommendations

HYDROGEN LEAK DETECTION

The catalytic combustion detector is the commercial leader from the standpoint of number of manufacturers and application at hydrogen facilities. A number of improvements in the catalytic combustion detectors have been made in recent years, including:

1. Better flame arrestors
2. The use of diffusion-type sensor heads to provide remote sensing
3. Sensors designed and engineered for hydrogen usage
4. A means to make the catalytic filament hydrogen-specific

Of continuing importance in the future should be investigations to overcome the shortcomings of catalytic detectors listed below:

1. Full reliability in the presence of adverse weather conditions
2. Accuracy at all levels of hydrogen up to 100 percent
3. Inherent hazard of sensors. If the flame arrestor is damaged because of such things as abuse, aging, and corrosion, and it is unknown to operating engineers, the instrument is a potential ignition source.
4. Most instruments are not now hydrogen specific
5. Limited usage in inert atmospheres and in vacuum
6. Frequent calibration, especially after periods of nonuse

A number of new ideas and principles have been advanced during the last ten years and they have been put to some specific uses, usually as part of government-sponsored programs. However, new techniques have not yet become commercial on-the-shelf items for hydrogen detection. The users of hydrogen in both commercial and governmental facilities have expressed a great deal of interest in these new hydrogen detection devices. As more uses of liquid and gaseous hydrogen develop, hydrogen leak detection demands will increase.

Further development of some of the new techniques is needed to

broaden their applicability. Research and development agencies should be encouraged to develop detectors that will fully meet future needs. Research efforts should be oriented toward unique physical and chemical properties of hydrogen that have not yet been exploited for hydrogen detection.

HYDROGEN FIRE DETECTION

The need for hydrogen fire detectors in many industrial and laboratory situations is not considered to be as great as that for hydrogen leak detectors. This attitude may be ascribed partly to a real lack of hydrogen fire problems and partly to a lack of convenient, economical, and reliable fire detectors.

Ultraviolet fire detectors are preferred in ground installations. Infrared television is a useful hydrogen fire visualization technique where fires are likely and potential damage is great, provided the expense and environmental problems are not prohibitive. Ultraviolet visualization techniques are hampered by unavailability of reasonably priced components.

Recent developments from government-sponsored programs have contributed to improvements in fire detection. Examples are sensor systems with greater resistance to environmental conditions and multi-sensor-computer approaches to provide more reliable fire detection. Government-sponsored research also has yielded information on properties of hydrogen fires and explosions necessary both for defining hazards and for reliable and appropriate detection.

The technology of fire detection is adequate for many needs, but few manufacturers can produce economical and convenient devices or initiate vigorous marketing programs necessary to establish sufficient demand. Certain fire detection problems, such as occur under very difficult conditions of environment and interference, are not well met at present. For example, optical sensors capable of operating reliably and rapidly in flight vehicles (particularly supersonic vehicles) have not been successfully tested.

Additional data on spectral radiant intensity and radiation modulation spectra of hydrogen and possibly other fuel fires should be obtained. Developments should continue in the areas of rugged, heat-resistant sensors, fiber optics, and solar-blind radiation sensors and sensor-filter combinations.

The development of fire detection systems suitable for high-speed aircraft and launch vehicles should be continued beyond the prototype or model stage.

APPENDIX A

INSTRUMENT PERFORMANCE DETERMINATION BY TEST

TEST A—LINEARITY OF RESPONSE

In this test, the sensing head was placed in a closed 5-liter container equipped with gas inlet and outlet ports. The response was measured for a series of hydrogen-air or other specified mixtures passed slowly through the chamber. An auxiliary recorder measured the detector signal in each trial.

TEST B—RESPONSE AND RECOVERY TIMES (DIFFUSION HEADS)

To determine the response, the detector head was exposed to a series of uniform hydrogen-air mixtures in a vertical 2-in.-diameter pipe equipped with gas inlet and outlet ports and with a horizontal sliding plate actuated by a rapid solenoid. The detector head was placed in a second 2-in. pipe located immediately above the horizontal plate. In making a run, the horizontal sliding plate was closed and the lower chamber filled with a hydrogen-air mixture at a rate of flow of 100 cc/sec. The response time was taken to be the interval between the time the solenoid was actuated and the time the signal response reached a value of approximately two-thirds of the maximum. At hydrogen concentrations of 4 percent and more, maximum response was considered to be the signal obtained with 4 percent hydrogen.

Recovery times were determined with the same apparatus by removing the sliding plate and passing a 2 percent hydrogen-air mixture through the 2-in. pipe. Recovery time was that required following removal of the detector head from the 2-in. pipe for the signal response to drop to approximately one-third of its maximum.

TEST C—EFFECT OF AMBIENT TEMPERATURE AND HUMIDITY

In this test, the sensing element is placed in a closed 5-liter container fitted with a gas inlet and outlet through which a uni-

form hydrogen-air mixture (or other mixture of known composition) is passed. For the low-temperature trials the chamber was cooled with dry ice. To change the humidity, moist room air was substituted for the dry cylinder air normally used or the gases were bubbled through a water-filled container.

TEST D—IGNITION HAZARD FROM AN INTERNAL EXPLOSION

Each sensing-head assembly was modified to include a 0.005-in.-diameter nickel wire that acted as an ignition source when fused, and a thermocouple to serve as witness of an internal explosion. The modified assembly was placed in the closed 5-liter container used in test C, which was equipped with a pressure release vent for the present test. Prior to ignition, a hydrogen-air mixture was passed through the container for 15 min, allowing the gases within the sensing head to equilibrate with the external gases. Ignition of the gases in the outer chamber was noted by a loud report and rupture of the pressure diaphragm.

TEST E—WIND TEST

Wind to which an unprotected sensing element might be subjected was simulated by a 1/2-horsepower blower of 1275 c.f.m. fitted at the exhaust port with a 2-ft-long, 7-in.-diameter extension pipe. The sensing heads were placed at selected positions in front of this outlet in air flowing at measured velocities at 1000, 2000, 3000, and 4000 ft/min.

TEST F—RESPONSE TIME AND LINEARITY OF RESPONSE (ASPIRATING UNITS)

Response time and linearity of response of the aspirating units were measured by inserting a vacuum pump in the flow system, effecting a continuous measurable flow. Lengths of 0.4-cm ID hose, 15 and 30 cm long, were connected to the detector gas inlet and to a three-way stopcock. The stopcock permitted either atmospheric air or a quiescent hydrogen-air mixture in the 5-liter chamber to be drawn through the detector. Response time was measured from the time interval between initiation of flow of premixed gas to the detector and the time the signal response reached approximately two-thirds of the maximum value.

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