FLAMMABLE GAS DETECTORS

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The construction and mechanism of operation of
instruments using catalytic detectors for the measure-
ment of flammable gases are described. The practical
advantages and disadvantages which result are outlined
and the reasons for these are discussed. Ways in which
some of these limitations can be met are described and
the directions in which future development could
proceed in order to overcome the present limitations
are outlined.

INTRODUCTION

In recent years, the number of instruments used for the detection and
measurement of flammable gases has increased rapidly. They are in wide use
in many different industries in Britain ranging in interests from the
Post Office to the chemical industry, and in such different places as drying
ovens and pleasure boats. The diversity of users is matched by the diversity
of manufacturers, each with his own design of instrument and hence the range
of instruments produced is wide and varied. However, the vast majority of
these instruments use the same principle of detection of the flammable gas
and hence have many features in common. The object of this paper is to
describe these features and the advantages and disadvantages which result
from them.

All gas detection instruments are composed of four basic units (fig 1)
These are:- (1) the sensing unit which detects the gas to be measured and
produces an anaglogue signal, (2) a central, generally electrical,
processing unit which governs the power supplied to the sensor and processes
the signal from the sensor for display, (3) a display unit which presents
the signal in an appropriate form to the operator or any other necessary
person and/or takes appropriate action and, (4) a power supply to the
processing unit which supplied the appropriate electrical power to the other
three units. The processing unit can range in complexity from a few
resistors in a simple portable instrument to complex circuits with constant
voltage supplies to the sensing unit, alarm circuits etc in fixed continuous
detection instruments. The display unit can be a simple meter, or digital
presentation of the gas concentration but can also include automatic cut-off

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of dangerous machinery, remote visible or audible alarms etc. The power supply unit is generally either a battery in portable equipment or a mains supply in continuously operating fixed equipment. In the latter case, a floating battery is often included in case of mains failure.

The ways in which flammable gas detectors are used have resulted in three main forms of instrument. These are (1) portable spot reading instruments, (2) portable continuously operating instruments and, (3) fixed continuously operating instruments. Instruments of the first type generally weigh about 1 kg, display the gas concentration on a meter and sample the gas either by a simple aspirator system or by diffusion of the gas to the sensing unit. A reading is obtained in about 10 to 20 s. from switching the instrument on after which the instrument is switched off again. Sufficient battery capacity for some hundreds of readings is provided. Such instruments are generally used for surveying an area for flammable gas and to check that a place is safe to enter. The second type of instrument is carried by workmen and provides warning of the presence of flammable gas which may appear in the vicinity whilst work is in progress. Therefore such instruments have sufficient battery capacity to operate continuously through an eight hour shift, are self contained, sample the gas by diffusion and give audible and visible warning signals when the gas concentration exceeds some preset limit. They normally weigh a few kilograms and are readily portable. In general only one sensing unit is present in each instrument but instruments with multiple sensing units are being considered. Fixed continuously operating instruments are generally used to provide protection to personnel and equipment in places where processing or storage of flammable gases and liquids occurs. These range from chemical plant to underground car parks. In general these systems consist of a number of instruments used in parallel. Each one consists of a sensing unit, a processing unit and a meter display but all have a common power supply and alarm display. Systems with up to a hundred or more individual instruments operating in parallel are in use in this country. The "state of the art" of modern electronics is such that the performance of modern flammable gas detectors is governed primarily by the performance of the sensing unit.

Sensing Unit. Although it is possible to have marked differences in the construction and mode of operation of the processing and display units in different instruments, the principle of operation of the sensing unit in most instruments currently in use is the same. The flammable gas is oxidised to carbon dioxide and water on a catalyst using oxygen from air as an oxidant and the heat evolved is measured. This is achieved by incorporating a suitable catalyst into a small transducer containing a temperature sensitive device and oxidising the gas continuously on the catalyst. The heat evolved raises the temperature of the catalyst and this temperature rise is measured by the heat sensitive device. The most suitable catalysts for these oxidation reactions are the metals in Group 8 of the Perodic Table and of this Group, palladium and platinum are by far the most widely used. The most convenient heat sensitive device is a platinum resistance thermometer. Hence the oldest form of transducer is simply a small coil of platinum wire. The gas oxidises on the surface of the platinum, raises the temperature of the coil and the resulting resistance rise is measured by using the coil as one arm of a Wheatstone Bridge and measuring the out-of-balance voltage produced across the bridge (Baker and Firth (1969)). A typical example of such a transducer would be a fifteen turn coil of 75 μm diameter wire with a length of 5 mm and a diameter of 0.5 mm. The coil is heated to a temperature at which oxidation of the combustible gas will take place on the platinum by the electrical current passing through the Wheatstone Bridge. This type of transducer is

still widely used in portable spot reading instruments. It is not very suitable for use in continuously operating instruments because platinum is a relatively poor catalyst for oxidation of flammable gases, especially methane, and hence the transducer must be operated at high temperatures ($> 800°c$) to obtain sufficient sensitivity. At this temperature platinum evaporates from the coil, especially in the presence of combustible gas (Bussiere et al, (1956)), resulting in a reduction of the cross-sectional area of the wire and hence an increase in its resistance and an early "burn-out" of the coil.

Attempts to overcome this deficiency of the simple platinum coil have led to improved forms of transducer which are now in wide use. One of the first attempts was to prevent excessive heating of the platinum coil occurring at its centre when used for detecting leaded petrol vapours. Decomposition of tetraethyl and tetramethyl lead on the platinum coil forms a monolayer of adsorbed lead oxide which poisons the oxidation of flammable gas. To overcome this it is necessary to operate the transducer at even higher temperatures ($>900°c$) where the problems associated with evaporation are even more serious. The temperature of the coil is highest at is centre and this of course increases when gas is oxidised on the transducer. Therefore, Strange (Strange (1955)) coated the centre turns of the platinum coil with glass thus reducing the temperature rise produced by oxidation of the gas in this area and giving some increased mechanical strength to the coil. These transducers are widely used for the detection of leaded petrol vapour.

Other transducers have been developed which operate at lower temperatures by using more active catalysts than platinum wire. In each case the platinum wire coil is retained as a temperature sensing device but the catalyst is separated from it. One example is the element first described by Baker (Baker (1958)) which is shown in fig 2. This transducer uses palladium supported on thoria as a catalyst which is deposited on the surface of a refractory bead of ~ 1mm. diameter encapsulating the platinum coil. Palladium is more active than platinum and readily oxidised gases such as methane at temperatures about 300°C less than platinum. Moreover, this type of construction enables a catalyst with a higher surface area to be used producing similar sensitivities to a particular gas at lower operating temperatures of the transducer. The spherical symmetry of this type of device makes it insensitive to changes in orientation and the encapsulation of the coil produces resistance to mechanical shock. This transducer is widely used in all types of gas detection instruments.

Another successful transducer using a more active catalyst than platinum wire is that described by Sieger (Sieger (1958)). A core of woven silica fibre is wound about with the platinum resistance thermometer and impregnated with a supported catalyst generally containing some palladium. This method of construction makes the transducer resistance to mechanical shock and enables it to be produced in a range of sizes for different applications. It is widely used in continuously operating gas instruments.

A more recent transducer using a platinum catalyst with a larger surface area has been described by Young Ho Kim (Young Ho Kim (1971)). This transducer is similar in basic design to the Baker transducer described above but is more complex in construction. It has a layer structure of ceramic and glass with an outer coating of the platinum catalyst. It is claimed that this construction produces greater stability and enables the detection range for combustible gases to be extended towards lower concentrations (~ 100 p.p.m.)

Many other forms of catalytic transducers have been described in the literature during the past decade but the four types described above account for the vast majority of instruments in use in this country at the present time.

The effects of orientation and of both thermal and mechanical shock on a transducer and other physical effects such as power consumption are determined by its physical construction and shape. Ideally a transducer should be spherically symmetrical, mechanically very strong and of minimum size to reduce these effects to a minimum. The effects of gases, both those to be measured and those which may interfere with the signal and the long term stability of the signal are determined by the catalyst. There is obviously greater flexibility in the design of the catalyst in those transducers where the catalyst is separated from the resistance thermometer.

In addition to the transducer itself the other main component of the sensing unit is the gas flow system which enables the gas to reach the transducer. Such systems are of relatively simple design (Baker and Firth (1969)) and are generally diffusion systems in continuously operating instruments and either diffusion or aspirating systems in portable spot reading instruments. In both systems the transducer is contained in a cavity to which gas enters by diffusion. Often an identical transducer carrying no catalyst is also exposed to the gas in a similar cavity. This transducer forms the balancing arm of the Wheatstone Bridge and compensates for the effects of changes in the thermal conductivity of the gas to be measured. In simple instruments this compensating transducer also eliminates the effects of variations in the voltage applied to the bridge. In diffusion systems gas reaches the transducer cavity after diffusion through a sinter or gauze system which eliminates the effects that airspeed variations would have on the transducer signal. In aspirator systems, the gas is pumped past the end of the cavity containing the transducer. Often a gauze or sinter is positioned at the end of the cavity so that no turbulence occurs inside (Baker and Firth (1960)). The main design criterion of both systems is that far more gas should be capable of entering the cavity or volume around the element than is oxidised by the transducer.

MODE OF OPERATION

The size of the signal from all catalytic transducers in a given concentration of flammable gas is governed by the rate of oxidation of that gas on the catalyst and the heat of oxidation. The rate of oxidation of any gas on a catalyst is governed by the surface area of the catalyst and the kinetics of the reaction. There will obviously be variations in the surface area between transducers and wide differences in the kinetics of the reaction for different gases at a given catalyst temperature. To overcome these effects, transducers are operated at a temperature which is sufficiently high to ensure that the reaction rate is controlled by the rate of diffusion of the gas to the catalyst surface and not by its subsequent reaction on the surface (Firth (1969)). This also ensures that the signal from the transducer is tolerably independent of slight temperature fluctuations. Under these conditions it can be shown (Firth et al (1973)) that the signal (V) produced across a Wheatstone Bridge by a transducer operating in a flammable gas/air mixture of concentration C at concentrations up to the lower explosive limit (LEL) is given by

$$V = K. D. \Delta H.C. \tag{1}$$

where D is the diffusion coefficient of the gas in air, ΔH is the enthalpy of the gas and K is a constant. Good agreement has been found between the signals predicted by equation (1) and experimentally determined values. A list of values of $D.\Delta H. \overline{/LEL/}$ for 93 gases has been published (Firth et al (1973)).

Since, under diffusion controlled conditions, all the flammable gas reaching the surface of the catalyst is oxidised, the signal $V_{(tot)}$ from a mixture of gases will be the sum of the signals from each gas in the mixture. Therefore from equation (1).

$$V_{(tot.)} = \sum_i K D_i \Delta H_i C_i \qquad (2)$$

The validity of equation 2 has been tested with mixtures of gases of widely ranging individual LEL values and the results are shown in table (1). There is good agreement between the observed signals and those predicted by equation 2.

The mechanisim of the reaction of gases on the transducer, the limitations of the devices already outlined and equation (1) and (2) enable the performance of flammable gas detectors in different environments to be predicted. It is also possible to evaluate the effects of the approximations made in the use of the detector on its accuracy.

PRACTICAL USE

Effects of Different Gases.

A flammable gas detector is used to measure the hazard from combustible gases and ideally therefore should display a signal at a given concentration of a gas expressed as a percentage of its LEL which is independent of the gas being measured. Thus a 50% LEL mixture of hydrogen in air should give the same signal as a 50% LEL mixture of propane in air. Indeed it is normal for flammable gas detectors to have a scale calibrated 0-100% LEL and to be used on the assumption that the ideal situation exists in practice. For this to be so the function $D.\Delta H. \overline{/LEL/}$ would have to be constant for all flammable gases. It has been shown (Firth et al (1973)) that although many gases have values which are within 20% of a mean-value then are many common gases which lie outside this range. It is therefore advisable to calibrate the instrument with the gas which is to be measured. If this is not done, then it is often necessary to apply a correction factor to the reading shown by the instrument in order to obtain the true concentration of the gas. This correction factor is the ratio of $D.\Delta H. \overline{/LEL/}$ of the gas being measured and $D.\Delta H. \overline{/LEL/}$ of the gas used to calibrate the instrument. It is common practice to use pentane as a calibration gas. Table 2 shows the correction factors (ie the factor by which the instrument reading must be multiplied to give the correct concentration) which must be used with such an instrument when measuring a number of common gases. The figures given here are calculated from published data (Firth et al (1973)) and have an accuracy of about $\pm$ 10 per cent. Many gases (Nos 8-20) can be estimated reasonably well ($\pm$ 20%) with an instrument calibrated against pentane without using a correction factor but a number of common gases (1-7) will give high readings whilst others (21-26) will give low readings. More accurate readings will be obtained with the former gases if the instrument is calibrated with hydrogen, and with the latter gases if it is calibrated with n-hexane.

TABLE 1

Gas	Concs (% vol)	LEL (vol %)	LEL mixture (vol %)	Observed signal (mv)	Calculated signal (mv)
Methane Hydrogen	0.5 0.5	5.3 4.0	4.6	19.0	20.0
Methane Hydrogen Propane	0.33 0.33 0.33	5.3 4.0 2.2	3.4	21.1	19.4
Carbon Monoxide Methanol	3.0 1.9	12.5 7.3	9.8	43.2	42.8
Carbon Monoxide Methanol Methane	1.5 1.9 0.5	12.5 7.3 5.3	8.3	43.4	43.3
Methane Ethane	0.5 0.5	5.3 3.0	4.2	18.8	19.4
Methane Ethane Propane	0.33 0.33 0.33	5.3 3.0 2.2	3.1	23.2	21.5
Carbon Monoxide Hexane	3.0 0.5	12.5 1.1	5.1	44.1	37.1
Carbon Monoxide Hexane Methane	1.5 0.5 0.5	12.5 1.1 5.3	3.7	43.1	37.6

TABLE 2

No.	Gas	LEL (vol %)	Correction factor (1)	Correction factor (2)	Correction factor (3)
1	Methane	5.3	0.51		
2	Methanol	7.3	0.54	0.89	
3	Hydrogen	4.0	0.61	1.0	
4	Carbon Monoxide	12.5	0.62	1.01	
5	Ethanol	4.3	0.63	1.04	
6	Ethylene	3.1	0.66	1.07	
7	Ethane	3.0	0.68	1.12	
8	n-Butane	1.8	0.79		
9	Acetylene	2.5	0.81		
10	Propane	2.2	0.84		
11	Acetone	2.6	0.90		
12	Ethyl Acetate	2.5	0.90		
13	cis-Butene-2	1.7	0.95		
14	Pentane	1.5	1.0		
15	Diethylether	1.9	1.0		
16	Methyl Ethyl ketone	1.8	1.12		
17	Benzene	1.3	1.13		
18	Cyclo-hexane	1.3	1.13		
19	Toluene	1.2	1.15		
20	Xylene	1.1	1.19		
21	n-Heptane	1.2	1.20		0.96
22	n-Hexane	1.1	1.25		1.00
23	Octane	1.0	1.24		0.99
24	n-Buty-Alcohol	1.4	1.35		1.07
25	n-Amyl-Alcohol	1.2	1.41		1.13
26	Nonane	0.8	1.47		1.17

(1) Calibration gas pentane
(2) Calibration gas hydrogen
(3) Calibration gas n-hexane

It is worth noting that the correction factor needed for methane may be different if the sensing element is a single platinum coil or one with the centre turns coated with glass. This is because platinum is a poor catalyst for the oxidation of methane. Thus it is not possible to operate such a transducer at a temperature which is sufficiently high to ensure that the oxidation is controlled by diffusion, without shortening the useful life of the transducer. Hence the signal is lower because not all the gas reaching the catalyst surface is oxidised and correction factors of 0.77 are commonly used for methane for such an instrument calibrated with pentane. In general, the signal obtained from a catalytic transducer operating in methane is much higher than it is for other gases and, since methane is now one of the most common of combustible gases, instruments to measure it should be calibrated with methane.

The signal obtained from mixtures of flammable gases is the sum of the signals from each gas in the mixture. An instrument which is to be used for measuring the hazard from a gas mixture should be calibrated with that mixture. If, however, the instrument is calibrated with pentane then high readings will be obtained from mixtures where each component could give a high reading and low readings will be obtained from mixture where each component will give a low reading. This is illustrated in table 3 with mixtures of hydrogen methane, carbon monoxide, ethane, methanol and propane, each of which will give a high signal. More accurate signals are obtained from such mixtures if hydrogen is used as a calibration gas.

However if a gas which gives a low signal (e.g. hexane) is mixed with one which gives a high signal (e.g. carbon monoxide) then the signal obtained will depend markedly on the relative concentrations of each gas and, as can be seen from table 3, accurate readings will not be obtained if either hydrogen or pentane is used as a calibration gas. In such cases, unless the ratio of each gas is fixed and the instrument is calibrated with the mixture the signals should be interpreted with caution.

Effects of High Concentrations of Gas.

Since oxidation of the combustible gas is used to obtain a signal from the instruments, it is apparent that if the concentration of oxygen in the gas mixture is too low for complete oxidation of the combustible gas to occur, then the signal obtained will be low. Hence as the concentration of a flammable gas is increased in air from zero, the signal from the transducer increases to a maximum at the stoichiometric ratio for complete oxidation and then decreases to zero at a concentration of 100 per cent combustible gas (Baker and Firth (1969)). Therefore there is a range of high concentrations of gas in air which will give readings which indicate that the gas is below the LEL. For methane, this concentration range is approximately 40 to 100 per cent.

Various methods of overcoming this problem are employed. The simplest method involves careful observation of the instrument reading as the gas enters the sampling chamber. As the concentration inside the cavity containing the transducer rises, the signal will rapidly rise above 100 per cent LEL before returning on scale. As the instrument is withdrawn from the gas to air, the signal will again rise above 100 per cent LEL before returning on scale.

Some instruments incorporate a mixing valve which allows air to be added to the gas being sampled before it reaches the transducer. The true

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TABLE 3

Gas Mixture	Composition (vol %)	LEL mixture (vol %)	Signal at 50% LEL (1)	Signal at 50% LEL (2)
Methane Hydrogen	50 50	4.6	87	52
Methane Hydrogen Propane	33 33 33	3.4	72	43
Carbon Monoxide Methanol	61 29	9.8	86	50
Carbon Monoxide Methanol Methane	39 49 12	8.3	93	55
Methane Ethane	50 50	4.2	79	47
Methane Ethane Propane	33 33 33	3.1	74	44
Carbon Monoxide Hexane	86 14	5.1	66	40
Carbon Monoxide Hexane Methane	60 20 20	3.7	82	49

(1) Instrument calibrated with pentane
(2) Instrument calibrated with hydrogen

concentration of gas can be estimated by multiplying the instrument reading by the mixing ratio. Other instruments employ a separate transducer measuring the thermal conductivity change produced by the combustible gas (Klauer (1967)). This signal is added to the signal from the catalytic transducer so that when the concentration is above the stoichiometric ratio the signal is always above that at the LEL of the gas.

When a transducer is operated in high concentrations of hydrocarbons the incomplete oxidation which occurs results in the deposition of carbon on the catalyst (Firth and Holland (1971)). If the catalyst is porous then disruption of the catalyst can occur and permanent damage of the transducer can result. Such damage only occurs during prolonged exposure but is a problem with early forms of the Baker element if exposure exceeds 45 minutes (Baker and Firth (1969)). It is not a problem with the other transducers or with later versions of the Baker device.

Catalyst Poisons.

Gases which are more strongly adsorbed onto the catalyst than the combustible gas or oxygen will prevent adsorption of these gases onto the catalyst so that a low signal will result. Gases which are particularly strongly adsorbed are those containing halogen atoms. A few parts per million of such gases can reduce the signal from a combustible gas by more than 50 per cent (Firth et al (1972 a)). The effect is temporary and when the halogen containing gas is removed the transducer recovers its sensitivity. Various methods have been employed to overcome this effect. The simplest uses a charcoal filter to absorb the inhibiting gas before it reaches the transducer but this method will also remove hydrocarbons with a molecular weight greater than that of propane.

Catalysts which are resistant to halogen inhibitors to a certain extent have been developed and are commercially available. The formulations are proprietary but allow transducers to be used for measuring higher hydrocarbons in the presence of low concentrations of gases such as vinyl chloride. Since the rate of reaction of the flammable gas is controlled by diffusion only a fraction of the catalyst surface is used in the reaction. This fraction reduces as the temperature of the catalyst increases. The excess catalyst area, not being used in the reaction, can adsorb an inhibiting gas without effecting the reaction of combustible gas and hence increasing the catalyst temperature enables higher concentrations of inhibitor to be tolerated.

Gases which can be oxidised to form a solid product can permanently effect the sensitivity of a transducer by covering the surface of the catalyst with a solid residue. Such gases are those containing silicon, phosphorus or metal atoms. For the reasons described above, increasing catalyst temperature reduces the effect since coverage of the catalyst surface by the residue is not complete; the oxides tend to grow from preferred area of the catalyst. Hence the Strange element (Strange (1955)) obtains resistance to tetraethyl lead in petrol by operation at high temperatures. It is worth remembering that since the excess area of the catalyst has to be covered before the sensitivity of the transducer is effected and deposition of the residue is a continuous process it is often possible for a transducer to operate for some considerable time in the poison gas before the effect becomes apparent. However continuous exposure to a few parts per million of silicones will eventually poison most instruments and it is important that instruments operated in such conditions are frequently checked with known concentrations of flammable gas.

Some instruments are provided with a tube of paradichlorobenzene for use when measuring leaded petrol. The reagent combines with tetraethyl lead and acts as a filter, preventing the tetraethyl lead reaching the trandducer. The device described by Young Ho Kim (Young Ho Kim (1971)) is often enveloped in a fibrous filter which is heated by the transducer and or which tetraethyl lead is decomposed to give lead oxide before it reaches the surface of the catalyst. It is claimed that such a combination is more than two orders of magnitude more resistant than an unprotected transducer.

Effects of Temperature

Ambient temperature changes can affect the readings given by catalytic transducers. Instruments operated at $65^\circ C$ have given readings of 85-90% LEL when exposed to flammable gases with concentrations of 100% LEL (Fardell (1973)). Larger deviations have been observed at higher temperatures. These changes are produced by the effect of temperatures on the rate of diffusion of flammable gas to the surface of the catalyst, the LEL of the gas and the enthalpy of the gas. To a first approximation the latter effect can be ignored.

The effect of temperature changes on the rate of diffusion of gas to the catalyst is determined by the temperature dependence of the diffusion coefficient, (Satterfield and Sherwood (1963)) and temperature dependence of the number of flammable gas molecules per unit volume (ie the density) in the gas phase around the catalytic transducer. Therefore from equation (1) the ratio of signal S_T produced at T° K to the signal S, produced at the temperature (T_o°K) at which the instrument is calibrated is given by

$$\frac{S_T}{S_o} = \frac{T_o}{T} \left(\frac{T'}{T_o'}\right)^{1/2} \tag{3}$$

where T' and T_o' are the average temperatures in the depletion layer around the transducer at ambient temperatures T and T_o. Since the transducer is generally operating above $500^\circ C$ the function $\left\{\frac{T'}{T_o'}\right\}^{1/2}$

is approximately unity.

It can be shown from the data of Coward and Jones (Coward and Jones (1952)) and the constant value for many gases, of the product ΔH /LEL/ that the LELs of many flammable gases decreases almost linearly with temperature. Hence the ratio of the LEL of a gas at temperature $T^\circ C$ to the LEL at temperature $T_o^\circ C$ is given by

$$\frac{(LEL_T)}{(LEL_{T_o})} = \left[1 - 6.6 \times 10^{-4}(T - T_o)\right] \tag{4}$$

Equation (3) and (4) can be combined to derive a correction factor, X, by which the reading given by an instrument at $T^\circ K$ must be multiplied to obtain a true measure of the gas concentration.

Thus

$$X = \frac{T}{T_o} \left[1 - 6.6 \times 10^{-4}(T - T_o)\right]^{-1} \tag{5}$$

Because of the assumptions used in deriving equation (5) values of X calculated from it are only approximate. However it shows that at 65°C the signal from 100% LEL of a flammable gas will be 86%, in agreement with the findings of Fardell.

Effects of Pressure

Changes in absolute pressure have little effect on the accuracy of most instruments. Since the diffusion coefficient D in equation 1 is inversely proportional to the absolute pressure (Satterfield and Sherwood (1963)) and the number of molecules entering the depletion layer above the catalyst is directly proportional the absolute pressure, the signal from the transducer is almost independent of the absolute pressure of the gas mixture being measured. Moreover, the LEL of a gas, expressed as percent by volume, is almost independent of the absolute pressure (Coward and Jones (1952)). Hence the signal would be expected to be a measure of the explosiveness of a gas which is independent of small changes about atmospheric pressure. In practice a small degree of pressure dependence is observed. The signal is directly proportional to absolute pressure with proportional constant of approximately 2.5×10^{-2} when pressure is expressed in torr and signal in percent LEL. Thus for an increase in pressure of 100 torr the signal from gas concentration of 40% LEL at atmospheric pressure will rise to 41% LEL.

Effects of Oxygen Concentration

The signal from most transducers is independent of variations in oxygen concentration provided sufficient oxygen is present to completely oxidise the gas. However, because platinum is a relatively inactive catalyst for the oxidation of methane, many platinum coil type transducers do not operate in a completely diffusion controlled conditions when measuring this gas and the kinetics of the oxidation reactions on the catalyst surface can affect the signal obtained. It has been shown (Firth and Holland (1969)) that oxygen can inhibit the oxidation of methane on platinum and hence it is found that on such transducers reduction of oxygen concentration can result in an increase in the signal from a fixed concentration of flammable gas. This effect is shown in table 4. It is, of course, not observed with more easily oxidisable gases where the signal is controlled by diffusion.

TABLE 4

Effect of oxygen concentration on signal from platinum coil at atmospheric pressure

Oxygen Conc vol %	Signal in 40% LEL methane
21	40
15	46
10	50
6	62

Sampling Systems. It is obvious that an instrument can only measure the concentration of flammable gas which is immediately adjacent to the transducer. Thus if gas is conveyed to the transducer through a sampling system in which dilution of the mixture or loss of the flammable gas can occur then the signal given by the instrument will not be a measure of the atmosphere being tested. There are a number of ways in which the flammable gas concentration can be changed especially where the gas is conveyed to the instrument through a tube. The simplest case is the entry of air into the sample through leaks and hence all connections should be checked. Many plastic tubes are able to absorb higher molecular weights compounds such as hexane and reduce the concentration of flammable gas reaching the transducer. Where such possibilities exist the gas should be sampled through a metal tube.

In some cases instruments which are at ambient temperatures are used to measure atmospheres which are at temperatures well above ambient. If such atmospheres contain a flammable gas whose partial pressure is above its saturated vapour pressure at ambient temperatures, the gas will condense in the sampling system and a low estimate of its concentration will be obtained. In such cases the detection unit of the instrument should be at a temperature high enough to prevent condensation.

CONCLUSIONS

The mechanism by which flammable gas detectors produce a signal is now well understood and it is possible to predict the effects of environmental variables on their performance. Automatic electronic compensation for these effects, especially these produced by temperature variations, could be incorporated into instruments.

The signals which are produced in different gases can be predicted and it would be possible to incorporate a selection switch for different gases in instruments and thus to remove the need to use calibration factors. However, the situation with mixtures of flammable gases which could have varying compositions is more complex and no satisfactory way of dealing with it is available for use with present transducers.

The most serious limitations of present devices is their susceptibility to catalyst poisons. A number of possible ways of overcoming this problem are becoming apparent. Since poisons are necessarily strongly adsorbed, then it is possible to remove them on a catalyst or filter surface immediately adjacent to the catalyst of the transducer. Such a filter would be at a temperature too low to oxidise the flammable gas. This would be particularly useful for inhibitors such as halogens and would also markedly improve the performance to poisons such as tetraethyl lead. Many poisons, although strongly adsorbed on the transducer catalyst are mobile on its surface, area. Such effects have been observed (Firth et al (1974)) where water vapour is an inhibitor.

The constancy of the product of ΔH and the LEL of many gases has been reported, and an instrument which measured only the calorific value of the flammable atmosphere would give a signal which is much more independent of the nature of the flammable gas than will present devices (Firth et al (1973)). This advantage would be particularly significant for variable mixtures of flammable gases. An instrument using this principle of detection is under development (Firth et al (1972 b)).

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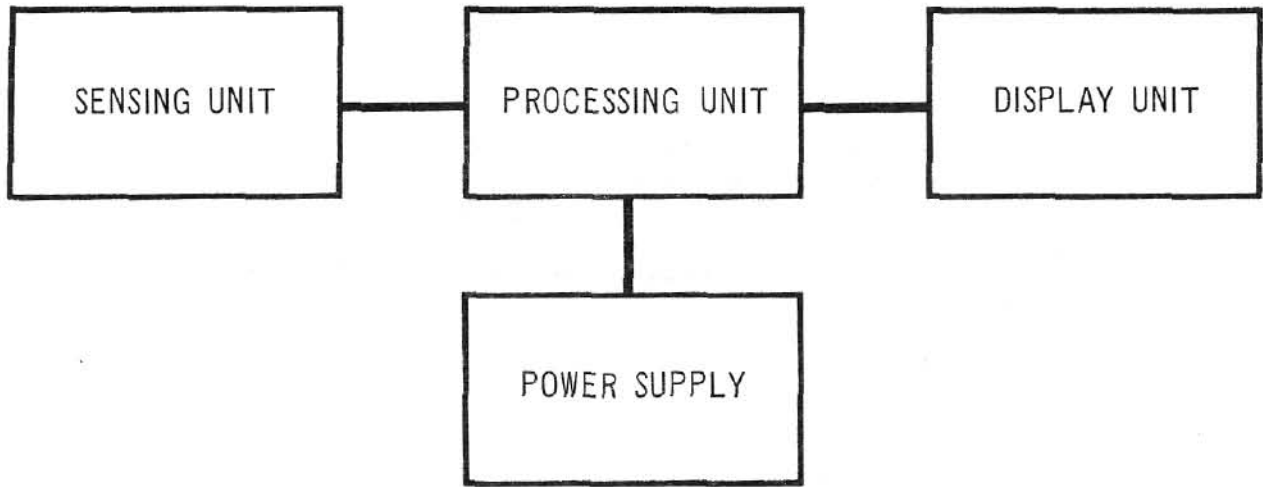
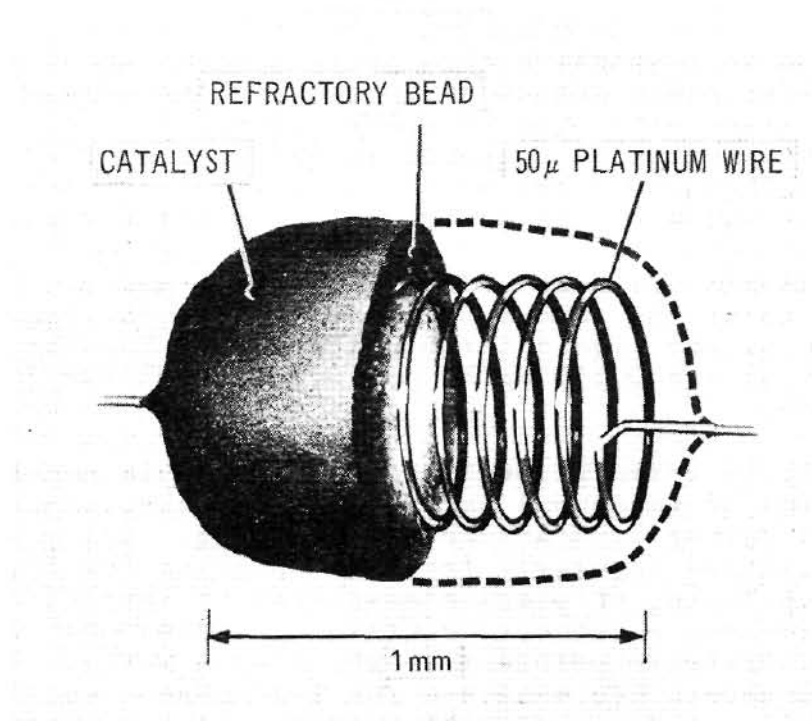Fig.1—Instrument components

Fig.2—Catalytic transducer