TALKING GAS !

- *Gas Detection principles*

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SECTION 1

WHAT IS GAS?

The name gas comes from the word chaos, which neatly summarises the main feature of the simplest state of matter. A gas is a swarm of particles moving randomly and chaotically, constantly colliding with each other and the walls of any container. The real volume of the particles is minute compared to the total space which they occupy and this is why gases fill any available volume and are readily compressed. The average speeds of gas molecules are of the order of 100s of metres per second and they are colliding with each other billions of times per second. This is why gases mix rapidly and why they exert pressure.

This constant motion is easily demonstrated by releasing a small amount of odorous gas in a room. Within seconds the gas can be smelt in all parts of the room. These properties apply to substances, which are normally gaseous, and to vapours from evaporated liquids.

A volume of any gas at the same temperature and pressure contains the same number of molecules irrespective of what the gas is. This means that measuring gas by volume is very convenient. Gas measurements at higher levels are in % (volume) and at lower levels parts per million, ppm (volume).

Whilst different gases have different densities, they do not totally separate into layers according to their density. Heavy gases tend to sink and light gases tend to rise, but their constant motion means that there is continuous mixing (i.e they do not behave like liquids).

So in a room where there is a natural gas (methane) leak, the gas will tend to rise because it is lighter than air but the constant motion means that there will be a considerable concentration at floor level. This will happen in perfectly still conditions but if there are any air currents, the mixing will be increased.

Air is a mixture of gases, typically:-

Nitrogen	77.2%
Oxygen	20.9%
Water Vapour	0.9%
Argon	0.9%
Carbon Dioxide	0.03%
Other Gases	0.07%

Because its composition is reasonably constant, air is usually considered as a single gas, which simplifies the measurement of toxic and flammable gases for safety and health applications.

SECTION 2

FLAMMABLE RISK

Combustion of Gases and Vapours

Most organic chemical compounds will burn. Burning is a simple chemical reaction in which oxygen from the atmosphere combines rapidly with a substance, producing heat. The simplest organic compounds are those known as hydrocarbons and these are the main constituents of crude oil/gas. They are composed of carbon and hydrogen, the simplest hydrocarbon being methane, each molecule of which consists of one carbon atom and four hydrogen atoms. It is the first compound in the family known as alkanes. The physical properties of alkanes change with increasing number of carbon atoms in the molecule, those with one to four being gases, those with five to ten being volatile liquids, those with 11 to 18 being fuel oils and those with 19 to 40 being lubricating oils. Longer carbon chain hydrocarbons are tars and waxes. The first ten alkanes are:

CH_4	methane (gas)	C_6H_{14}	hexane (liquid)
C_2H_6	ethane (gas)	C_7H_{16}	heptane (liquid)
C_3H_8	propane (gas)	C_8H_{18}	octane (liquid)
C_4H_{10}	butane (gas)	C_9H_{20}	nonane (liquid)
C_5H_{12}	pentane (liquid)	$C_{10}H_{22}$	decane (liquid)

The above compounds are all known as aliphatics. Alkenes are similar but their molecular structure includes double bonds. (Examples are ethylene and propylene.) Alkynes contain triple bonds. (Example is acetylene) Aromatic hydrocarbons such as benzene have a ring molecular structure and burn with a smoky flame).

When hydrocarbons burn they react with oxygen from the atmosphere to produce carbon dioxide and water (although if the combustion is incomplete because there is insufficient oxygen, carbon monoxide will result as well).

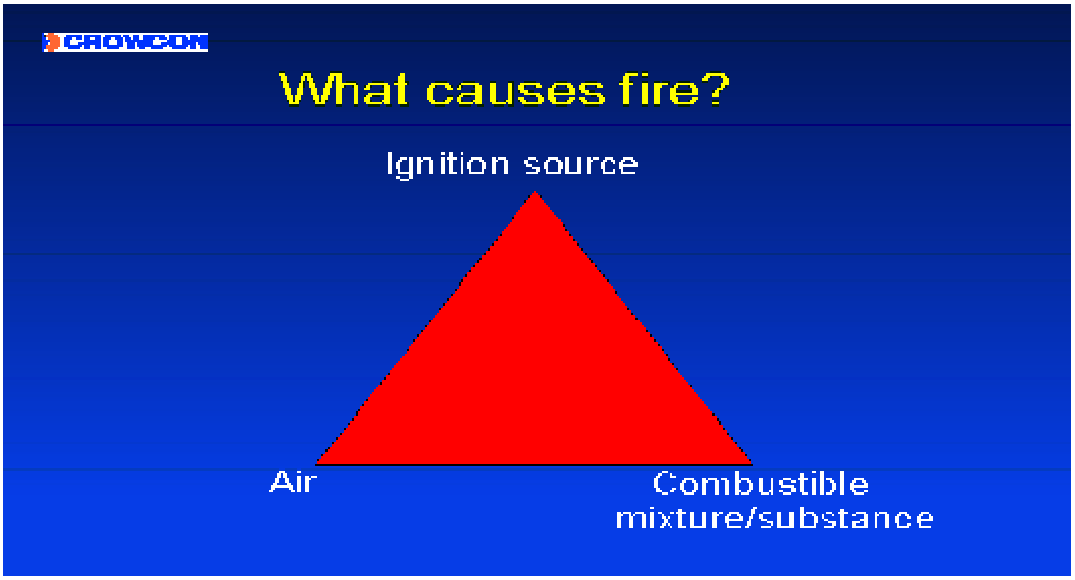
More complex organic compounds contain elements such as oxygen, nitrogen, sulphur, chlorine, bromine or fluorine and if these burn, the products of combustion will include other compounds as well. For example substances containing sulphur such as oil or coal will result in sulphur dioxide whilst those containing chlorine such as methyl chloride or polyvinyl chloride (PVC) will result in hydrogen chloride.

In most industrial environments where there is the risk of explosion or fire because of the presence of flammable gases or vapours, a mixture of compounds is likely to be encountered. In the petrochemical industry, the raw materials are a mixture of chemicals many of which are decomposing naturally or are being altered, by the processes. For example crude oil is 'cracked' to produce many simpler materials.

Explosions

In order for gas to ignite there must be an ignition source typically a spark, or flame or hot surface. For ignition to take place there must be an explosive mixture. This means the concentration of gas or vapour in air must be at a level such that the 'fuel' and oxygen can react chemically.

The power of the explosion depends on the 'fuel' and its concentration in the atmosphere.



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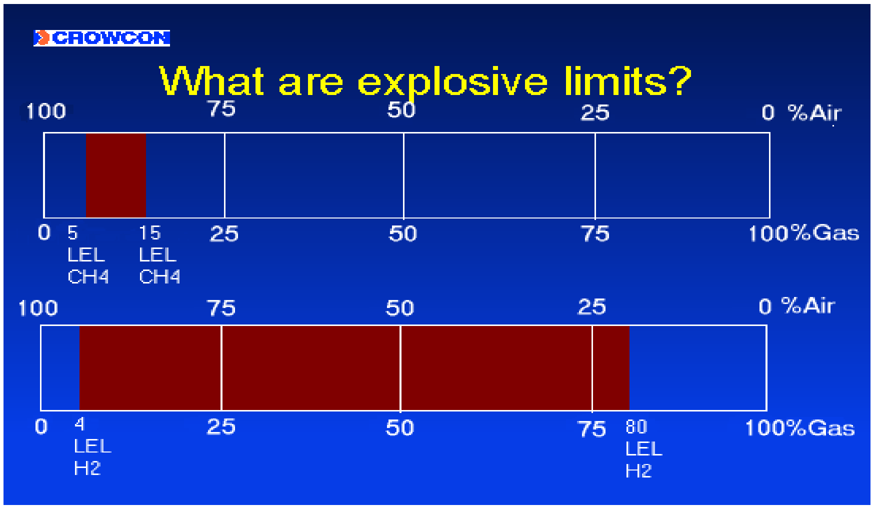
What causes fire?

Ignition source

Air

Combustible mixture/substance

Not all concentrations of flammable gas or vapour in air will burn or explode. The LOWER EXPLOSIVE LIMIT(LEL) is the lowest concentration of 'fuel' in air which will burn and for most flammable gases and vapours it is less than 5% by volume. So there is a high risk of explosion even when relatively small concentrations of gas or vapour escape into the atmosphere.



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What are explosive limits?

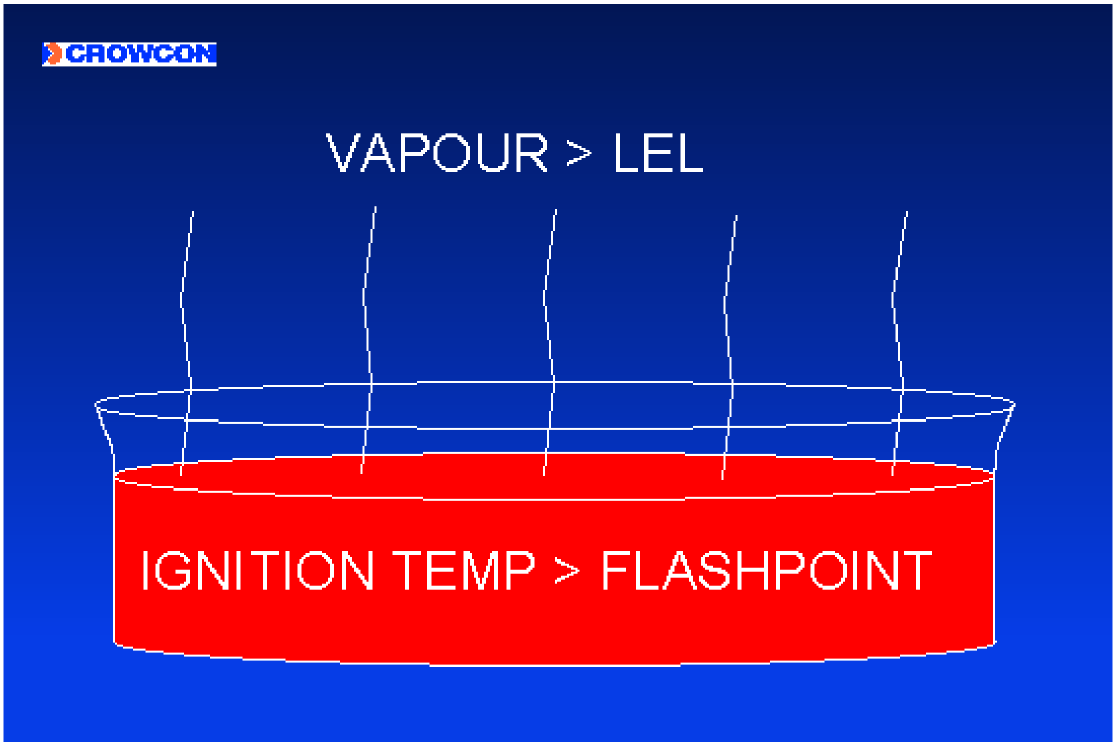
100 75 50 25 0 %Air

0 5 LEL CH4 15 LEL CH4 25 50 75 100%Gas

100 75 50 25 0 %Air

0 4 LEL H2 25 50 75 80 LEL H2 100%Gas

The UPPER EXPLOSIVE LIMIT (UEL) is the maximum concentration of 'fuel' in air which will burn. Concentrations above the UEL will not burn because there is insufficient atmospheric oxygen available.



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VAPOUR > LEL

IGNITION TEMP > FLASHPOINT

Flammable liquids generally have a low FLASH POINT. This is the lowest temperature at which vapour is given off at sufficient rate to form an explosive mixture with air. Liquids with flash points below normal ambient temperatures automatically release vapour in sufficient volume to provide an explosive mixture, so leakage of such liquids is potentially as dangerous as a flammable gas leak.

VAPOUR DENSITY is a measure of the density of a gas or vapour relative to air. Gases or vapours with a vapour density of less than one are lighter than air and they tend to rise from the point of escape and may therefore be readily dispersed (or they may be trapped at a higher level).

Gases or vapours with a vapour density of greater than one are heavier than air and tend to sink to lower levels and can spread around forming concentrations between the LEL and UEL. Such heavy gases can remain trapped for a long time in ducts, inspection pits, etc, ready to explode as soon as a source of ignition is introduced.

When an explosive mixture of gas or vapour and air has developed, it can be ignited either by a spark of sufficient energy or if it is exposed to a surface at a sufficiently high temperature. The lowest temperature, which will cause a mixture to burn or explode, is called the IGNITION TEMPERATURE.

Equipment Safety

Areas where there is the possibility of the presence of an explosive mixture of flammable gas or vapour and air are known as 'hazardous' and other areas as 'safe' or 'non-hazardous'. Any electrical equipment used in hazardous areas, including gas detection equipment, must be specially tested and approved to ensure that, in use even under a fault condition, it cannot initiate an explosion.

Crowcon equipment meets European, American and other international standards for electrical equipment used in hazardous areas.

In Europe, hazardous areas are generally defined as follows:

Zone 0	An area where an explosive mixture is likely to be present at all times under normal operating conditions.
Zone 1	An area where an explosive, mixture is likely to occur in normal operation.
Zone 2	An area where an explosive mixture is not likely to occur in normal operation, and if it does it is only for short periods.
	In the United States, hazardous areas are classified by two Divisions. **Division 1** equates to Zone 0 and Zone 1 and **Division 2** equates to Zone 2.

in Europe gas detection equipment, certified for use in hazardous areas in Europe, normally falls into one of the following categories.

Intrinsically Safe	denoted as EEx ia or EEx ib	For use in Zones 0, 1 or 2 Zones 1 or 2
Flameproof	denoted as EEx d	For use in Zones 1 or 2
Increased Safety	denoted as EEx e	For use in Zones 1 or 2

Intrinsic safety differs from other forms of protection because it is based on the principle that the equipment is electrically safe. The definition of an intrinsically safe circuit is generally one that does not contain sufficient electrical energy, even under fault conditions, to cause a spark or generate sufficient heat to ignite a combustible gas mixture. Under the current standards, Ex ia equipment is tested with two coincident faults applied to the system. Ex ib equipment is tested with one fault.

Intrinsic safety requirements are covered by European Standards BS EN50014, EN50020 and EN50039, and the guidance Standard EN50073. In the United States the relevant Standard is UL 913 "Intrinsically Safe and Associated Apparatus (for use in Class I, II and III Division 1, Hazardous (Classified) Locations)."

Other forms of protection are based on mechanical safety and for flameproof equipment the equipment enclosure should be capable of containing an explosion within it, thereby avoiding the possibility of the system becoming an external ignition source.

Flameproof requirements are covered by European Standard EN50018, BS4683 : Part 2 :1971, BS5001 : Part 5 1977 and the guidance Standard EN50073. In the United States the relevant Standard is UL 1203 "Explosion Protected and Associated Apparatus (for use in Class I, II and III Division 1, Hazardous (Classified) Locations)."

When selecting intrinsically safe equipment for a particular application it is necessary to know what the IGNITION TEMPERATURE of the gas or vapour is and in what GAS GROUP it is. The following tables provide the classifications to be found in the EN50014 series and also provide information on equivalent Standards.

Gas Groupings

Representative Gas	Cenelec EN50018 BS5501 Pt 5 IEC 79-1 Group	Non-harmonised EEC Standards UK BS4683 Pt 2 Group	France C12-320 Group	Germany VDE0171 Class	USA UL698 Group
Methane (mining use)	I	I	IA or IB	1	D
Propane	IIA	IIA	IIA or IIB	1	D
Ethylene	IIB	IIB	IIIA	2	C
Hydrogen	IIC	IIC	-	3a	B
Carbon disulphide	IIC	-	-	3	
Acetylene	IIC	-	-	3c	A

Temperature Classifications

Maximum Surface Temperature °C	EN50014, BS5501 Pt 1 BS4683 Pt 1, IEC79-1	USA UL 698
450	T1	
300	T2	
280		T2A
260		T2B
230		T2C
215		T3
180		T3A
165		T3C
135	T4	T4
120		T4A
100	T5	T5
85	T6	T6

Approval Codes

To check whether an instrument is suitable for a particular gas or vapour, reference to its APPROVAL CODE is necessary, eg: EEx is IIC T4.

E - Approved to European Norm.
Ex - Explosion Proof.
ia - Intrinsically safe, suitable for Zones 0, 1, and 2.
IIC - Suitable for gases or vapours in Groups IIA, IIB and IIC.
T4 - Suitable for gases or vapours with ignition temperatures greater than 135°C.

SECTION 3

TOXIC RISK

MONITORING FOR TOXIC GASES IN AREAS WHERE PEOPLE WORK AND IN THE GENERAL ENVIRONMENT

The most important factor in the demand for toxic gas monitoring in the UK is the legislation known as the **CONTROL OF SUBSTANCES HAZARDOUS TO HEALTH REGULATIONS 1988 (COSHH).** Similar legislation exists elsewhere or is being introduced and COSHH takes into account the European Commission Directive 80/ 1107/EEC. COSHH covers all toxic substances except those which have their own legislation (asbestos, lead, radioactive materials and materials present in mines).

The regulations spell out what employers and in a few cases employees have to do. (Failure to comply is subject to the penalties of the HEALTH AND SAFETY AT WORK ACT 1974). The requirements are:

- Assess the risks to health and what precautions are needed
- Introduce measures to prevent or control the risk
- Maintain equipment and observe procedures
- Monitor exposure of workers and carry out health surveillance
- Train employees about the risks and precautions

The assessment is done by the employer with help from the Health and Safety Executive (HSE) if needed. The best way of controlling a risk is to prevent exposure but if this is not possible, a process may have to be enclosed or ventilation and extraction equipment used or special handling procedures employed. It should be possible for most people to work in a safe environment day after day and HSE publishes Guidance Note EH40 each year to help employers to control their processes adequately so that workers are not exposed to levels of toxic materials above the recognised safe levels.

EH40 sets out OCCUPATIONAL EXPOSURE LEVELS in two categories.

MAXIMUM EXPOSURE LEVELS, MELs are for the more dangerous substances and exposure to materials with MELs should be as low as possible and certainly not above their MEL.

OCCUPATIONAL EXPOSURE STANDARDS, OESs for the less dangerous materials are the exposures, which can be viewed as safe, and employees can work in them day after day.

EH40 lists OCCUPATIONAL EXPOSURE LIMITS (OELs) showing substances with MELs separately from those with OESs. The list gives LONG TERM (8 hour) EXPOSURE LIMITS (LTELs) applicable to exposure during a normal working day and SHORT TERM (15 minute) EXPOSURE LIMITS (STELs) applicable to occasional exposure to higher levels. (Where no 15-minute limit is given a level of three times the 8-hour limit is used).

When mixtures of toxic gases are encountered the effects on health are often additive and this needs to be taken into account (exposure to two gases with similar effects, each at 50% of their OELs may be equivalent to working at an OEL or the two gases together may have an enhanced effect).

Exposure to toxic substances has to be calculated on a TIME WEIGHTED AVERAGE (TWA) basis, so for example a person working at an OEL for 7 hours with a 1 hour lunch break will have had an exposure of 7/8 of the LTEL.

The following data has been extracted from EH40/2000:-

			LTEL	STEL
1	GASES WITH MELs		(8 HR TWA)	(15 MIN TWA)
	Ethylene oxide	C_2H_4O	5	-
	Formaldehyde	HCHO	2	2
	Hydrogen Cyanide	HCN	-	10
2	GASES WITH OESs			
	Ammonia	NH_3	25	35
	Carbon dioxide	CO_2	5000	15000
	Carbon monoxide	CO	30	200
	Chlorine	Cl_2	0.5	1
	Chlorine dioxide	ClO_2	0.1	0.3
	Fluorine	F_2	-	1
	Hydrogen bromide	HBr	1	3
	Hydrogen chloride	HCl	-	5
	Hydrogen fluoride	HF	-	3
	Hydrogen sulphide	H_2S	10	15
	Nitric acid	HNO_3	2	4
	Nitrogen dioxide	NO_2	3	5
	Nitric oxide	NO	25	35
	Ozone	O_3	-	0.2
	Phosphine	PH_3	-	0.3
	Sulphur dioxide	SO_2	2	5
	Sulphur hexafluoride	SF_6	1000	1250

The monitoring aspect of COSHH is particularly relevant to Crowcon's products because monitoring is required

- If the failure of control measures would lead to serious health risks
- If it is not certain that exposure limits are not being exceeded
- If it is not clear that control measures are working properly

When monitoring of exposure is called for records of the monitoring must be kept and employees must be told about their risks, the precautions and the results of any monitoring and health surveillance.

Gaseous toxic substances are especially dangerous because they are usually invisible and often odourless. Also their physical behaviour is not always predictable since their temperature and pressure affect their properties dramatically as do the effects of draughts. Crowcon's toxic gas detectors and their accessories have been designed with this in mind and the need for continuous monitoring has led to the development of data logging facilities.

As well as monitoring conditions in the work place, there is increasing emphasis on Environmental Monitoring because it is recognised that everyone's health and well-being is suffering because pollution from industrial processes, traffic fumes and the decay of waste is already at serious levels. Crowcon's fixed systems with data loggers are in use for general pollution monitoring.

Carbon Monoxide (CO)

Carbon monoxide, which is odourless and colourless is the most abundant toxic gas. Different authorities put maximum safe exposure limits at 30 to 50 ppm and even lower levels have the effect of causing drowsiness. Having a similar density to air, it is readily inhaled and detectors need to be mounted at head height.

Any process where there is incomplete combustion of carbon fuel leads to the production of carbon monoxide, eg petrol and diesel engines, coal, gas and oil boilers, even smoking. Its presence in mines is due to the slow combustion of coal.

It is also used in enormous quantities as a cheap chemical reducing agent eg in steel production and other metal refining and heat treatment and in the production of methanol by reaction with hydrogen.

Hydrogen Sulphide (H_2S)

Hydrogen sulphide is well known because of its bad egg odour, which can be smelt down to less than 0.1 ppm. A maximum safe exposure limit is 10 ppm but high concentrations cannot be smelt and can lead to instant paralysis. It has almost the same density as air so detectors are mounted at head height or near potential sources of leaks.

It is produced during the decay of organic materials, extracted with oil (when the oil is said to be sour) and is often found underground during tunnelling and in sewers. It is a constituent of biogas. It has some industrial uses and is produced as a by-product in others (eg fibre manufacture).

Sulphur Dioxide (SO_2) (For Sulphur Trioxide, see Acid Gases)

This gas is colourless and has a characteristic choking smell. It is formed on burning sulphur and materials containing sulphur such as oil and coal and it is highly acidic, forming sulphurous acid when dissolved in water. With the oxides of nitrogen it is a cause of acid rain and in the atmosphere, especially when it is foggy, it affects many people's respiratory systems.

In industry its maximum safe level is 2 ppm. It is found in industrial areas and near power stations and it is a raw material for many processes. It has a use in the treatment of water to displace excess chlorine and because of its sterilising properties it is used in food processing. It is twice as heavy as air and it tends to fall to ground level so the Crowcon Environmental Sampling Unit sited near the ground ensures rapid detection in the event of a leak.

Chlorine (Cl_2)

Chlorine is a pungent smelling, corrosive, green/yellow gas. The best known use is in water purification for domestic supplies and in swimming pools but the bulk of it is used to make chlorinated compounds such as PVC and for bleaching paper and fabrics. It is a very heavy gas and is readily absorbed by most materials. The behaviour of chlorine makes it a very difficult gas to detect (so difficult that even calibration requires special techniques).

Use of the Crowcon Environmental Sampling Unit is the best way to detect it successfully and this minimises the number of detectors required.

Oxides of Nitrogen - Nitric Oxide (NO) and Nitrogen Dioxide (NO_2)

There are three oxides nitrogen . Nitrous oxide (NO_2) (or dinitrogen oxide) is not poisonous. It is used as an anaesthetic and as a propellant for whipped cream. Nitric oxide NO (modern name nitrogen monoxide) and nitrogen dioxide NO_2 are the constituents of so called NOx which with sulphur dioxide causes acid rain. The main cause of these gases in the atmosphere is petrol and diesel engines. At the point of exhaust, nitric oxide accounts for about 90% of NOx. However it reacts spontaneously with oxygen in the open atmosphere to give nitrogen dioxide. Nitric oxide is a colourless gas but nitrogen dioxide is an acid, pungent smelling, brown gas. The maximum safe level for nitric oxide is 25ppm and for nitrogen dioxide 35ppm. Both can be detected by electrochemical sensors. In the open environment it is best to monitor for nitrogen dioxide.

Carbon Dioxide (CO_2)

Despite the fact that we breathe out carbon dioxide and that it is present in the atmosphere to the extent of about 400ppm, its maximum safe level is 5000ppm (0.5%). It is produced during combustion and in brewing and other fermentation processes, and is one of the main constituents, with methane, of landfill gas and sewage treatment digester gas. There are hazards in the brewing industry, particularly as the gas is heavier than air and collects at low levels. There is some degree of risk in crowded, badly ventilated places, and this problem is often worsened by oxygen deficiency. CO2 is also used to increase plant growth by elevating normal levels in greenhouses etc.

It is odourless and colourless and difficult to measure in ppm levels. Infrared absorption is the usual detection technique.

Hydrogen Cyanide (HCN)

This well-known poison is a colourless, sweet smelling gas with a 15 minute maximum safe level of 10ppm. It is easily detected with the main industrial application in gold refining.

Hydrogen Chloride (HCl)

This pungent smelling gas is highly corrosive and dissolves readily in water to form hydrochloric acid. It is used in and produced by many chemical processes. It is also emitted from waste incinerators in which PVC is burnt. There is a sensor for hydrogen chloride although care in its use is necessary because of cross sensitivities.

Acid Gases

Hydrogen chloride, hydrogen fluoride, nitrogen dioxide and sulphur dioxide are all strong acid gases dissolving in water to give acids.

Fumes from other acids eg nitric acid can be similarly detected.

Carbon dioxide and hydrogen cyanide are weakly acidic and are unlikely to be detected with an acid gas sensor.

There are many processes where acid gases are used or produced as by-products.

NOTE: sulphur trioxide $S0_3$ is encountered in the exhaust from power stations. It is not a gas but a solid, which readily sublimes (ie it goes from the solid state to the gas state on heating). Acid gas sensors, however, cannot be used to detect sulphur trioxide or sulphur dioxide because these substances destroy them quickly.

Applications for the general acid gas sensor include detecting the leakage of - hydrogen fluoride used in the production of lead free petrol and the detection of acid fume leakage in chemical processing.

Ammonia (NH_3)

Ammonia is the only common alkaline gas. Its density is about half that of air and it has a characteristic smell. Its maximum safe level is 25ppm but its alkalinity makes it highly reactive with acid gases and chlorine and its presence in atmospheres containing other gases is often masked by this. For instance, if ammonia and chlorine are present in equal concentrations, the result is a cloud of ammonium chloride and neither of the two gases.

Ammonia is flammable with an LEL of 15%. It is produced in vast quantities all over the world to provide fertilisers, urea for resins, explosives and fibres such as nylon. It is also used as a refrigerant. This application is increasing with the demise of CFCs. Another application is to maintain the sterility of water supplies after treatment with chlorine and sulphur dioxide.

It can be detected in ppm levels electrochemically and in LEL concentrations by pellistor sensors.

Ozone (O_3)

Ozone is not a stable gas and is generated, as it is required. It is increasingly used instead of chlorine for treatment of water. It can be detected at low ppm levels, electrochemically but the sensors also react to chlorine and nitrogen dioxide.

INDUSTRIES WHERE TOXIC GASES ARE FOUND

CARBON MONOXIDE
Car Parks
Power Stations
Steel Works
Generating Plant
Mine Shafts
Chemical Companies
Garages
Metal Refinery & Heat Treatment
Underground Work

Nuclear Engineering
Laboratory
Car Manufacturing Plant
Tunnels

HYDROGEN SULPHIDE
Dirty Waste Water Sites
Petrochemical Companies
Offshore Companies
Tunnelling Contractors
Man Entry Applications
Chemical Companies
Laboratories
Dye Makers
Mines

SULPHUR DIOXIDE
Water Purification
Unclean Water Sites
Light Bulb Manufacturers
Power Stations
Paper Mills
Pet Food Manufacturers
Power Generating Plant
Steel Manufacturing

HYDROGEN FLUORIDE
Hospitals
Pharmaceutical
Leaded Petrol Manufacturing
Chemical Companies

CHLORINE
Clean Water Plant
Paper Manufacturers
Chemicals & Plastic Manufacturers
Food Industry
Textiles

NITRIC OXIDE & NITROGEN DIOXIDE
All situations where there are combustible emissions therefore tunnels, car parks, loading bays etc.

CARBON DIOXIDE
Breweries
Food Manufacture
Mushroom Growing
Landfill Sites
Water & Sewage Plant
Refrigeration Plant
Chemical Industries

HYDROGEN CYANIDE
Gold Refining
Acid Gases
Petrochemical Plant
Chemical Engineers
Laboratory
Pharmaceutical Manufacture
Hospitals

AMMONIA
Refrigeration Plant
Clean Water Sites
Chemical Manufacturers
Fertiliser Manufacturers
Refrigerated Storage Depots
Food Processing Engineers
Plastics & Foams
Currency Manufacture

SECTION 4

OXYGEN RISK

ENSURING THAT THERE IS A SAFE LEVEL OF OXYGEN

The usual concentration of oxygen in the atmosphere is 20.9%. Unless there is adequate ventilation the level is reduced surprisingly quickly by breathing and combustion. Other ways of depleting the oxygen level include dilution by other gases such as carbon dioxide (but note that 0.5% is the maximum safe level) and nitrogen and chemical absorption by corrosion processes and similar reactions.

The table below shows the effect of a diluting gas on the level of oxygen.

CONCENTRATION OF DILUTING GAS	RESULTING OXYGEN CONCENTRATION
0.5%	20.8%
1 %	20.7%
5%	19.9%
10%	19.0%
15%	18.2%
20%	17.4%
25%	16.7%

Instruments for monitoring oxygen normally provide alarms at 18 or 19% because most people begin to behave abnormally when the level reaches 17% and death comes very quickly if the level drops only 2 or 3% more. Exposure to atmospheres containing between 10% and 13% oxygen can bring about unconsciousness so quickly that the individual cannot help or protect himself. There are more deaths from oxygen deficiency than from any other gas hazard because the possibility of low oxygen levels is forgotten whereas flammable and toxic gases are more often considered.

Oxygen enrichment can dramatically increase the flammability of anything, which will burn. If the level exceeds 24% even materials such as clothing, which might normally just smoulder, will burst into flame.

SECTION 5

GAS DETECTION APPLICATIONS

There are many examples where gas detection is used and Crowcon can provide detailed data sheets about some of the following applications.

Oil Rigs and Platforms, Refineries and Petrochemical Plant

Exploring and producing natural gas and crude oil has a whole variety of hazards. Flammable gas will be continually present during the processes involved; therefore, plant and personnel will need to be monitored for risk levels.

Oil companies often hire portable cabins to use for temporary accommodation or as laboratories for occasional investigations and these are situated in hazardous areas. Flameproof systems with gas and smoke detectors are fitted inside these cabins which usually operate at positive pressure to prevent gas ingress. Detection of gas or smoke at the air intakes causes alarms to sound and the shutting down of the electrical supply other than for the safety system and flameproof lighting. Combined gas detection and purge systems ensure that a cabin cannot be used until the atmosphere is safe.

Flameproof systems (i.e with a flameproof control unit) are also installed with detectors sited near drilling blocks, valves, and accommodation areas.

Workers are often asked to enter vessels, tanks or pontoons or other normally enclosed spaces such as the legs of a platform. These are of steel construction and may have been closed for along time. Rusting or corrosion will have taken place leaving insufficient oxygen to sustain life and anyone entering without carrying out a proper check with a portable instrument faces sudden death. Once inside it makes sense to have an alarm instrument running continuously. Other gas hazards, flammable and toxic, for example hydrogen sulphide, also exist in such places and this is why the Crowcon multi-gas instruments were developed.

Purging of tanks, which have held flammable liquids, is done with nitrogen and portable instruments are used to check that purging is complete.

Onshore, the demand for flameproof systems is less because there is usually a safe area available for the control unit. However there is a wider variety of flammable gases encountered either because they are being manufactured or are by-products or are used as reactants in a process.

Confined Spaces

Workers should never enter confined spaces if the gas concentration at the entry point exceeds 20% of the LEL because the concentration will vary at different places and it is likely that there will be pockets of gas or vapour inside which will exceed the LEL. Portable instruments can be used for spot sampling and can also be taken inside to provide continuous assurance that all is well.

In addition to places of obvious risk, there are many unmanned buildings used by electricity, telecommunications, broadcasting and sewage utilities where it is possible for methane to build up, often because of the decay of natural vegetation or seepage from domestic and industrial landfill sites. Portable instruments are used to check these places prior to entry.

Pipeline and sewage system construction and maintenance, tunnelling and working in deep holes are all risky as far as gas hazards are concerned and many reports have been published about accidents in these situations.

As well as the possibility of encountering toxic or flammable gas or vapour, because of leakage from the gas mains or a petrol pipe or tank or because someone has been there before and has left something dangerous behind, the oxygen level may be low because natural decay has absorbed it. In some places hydrogen sulphide is present and it is not unknown for carbon dioxide to have been formed by a chemical or biological reaction. For example, if an engine was running in a confined underground space, which was visited infrequently, it could deplete the oxygen and leave carbon monoxide behind. This will remain in the area for some time as it has almost the same density as air.

Many places can become confined spaces under certain conditions, for example an open ditch with poor air circulation or a structure of irregular shape which may allow pockets of gas to accumulate. Sometimes an inert gas such as nitrogen is used to purge pipes before welding and this can quickly dilute the oxygen.

Cutting and welding using compressed oxygen and acetylene leads to the other oxygen risk, enrichment, which can cause a rapidly burning fire or explosion, especially if combined with acetylene.

Risks in Tanks, Sewers, Containers and Holds

Vessels used for food processing, brewing, fermentation and distilling and chemical processing have to be cleaned and, if this is done by entering them, there is the possibility of oxygen having been absorbed by the process or carbon dioxide or other gas diluting the oxygen. Ships' holds are particularly dangerous as they are often `purged' with engine exhaust gases.

In sewage treatment plants, in addition to the hazards of flammable methane and toxic hydrogen sulphide, displacement of oxygen in dry and wet wells is a frequent problem.

Steel Industry

Due to the processes involved in steel making, it is essential that personnel are protected against carbon monoxide poisoning in surrounding areas and asphyxiation due to lack of oxygen when they are carrying out maintenance in confined spaces or ovens, in and around the blast furnaces, power plant and coke ovens. Due to the use of nitrogen and argon, oxygen monitors are also needed. Fixed systems are used in areas where gas can unexpectedly build up. Areas such as lifts and mess rooms, have fixed systems installed, as well as the plant in general. If there is any leakage of gas, the sensors will give an early warning, before maintenance personnel equipped with portable instruments enter the area.

Fire Brigades

Although Fire Brigades can run into a variety of gas hazards they are primarily interested in monitoring flammable gas and oxygen levels. Typical examples of situations where gas detection could be required are gas leakage incidents, testing of storm drains, spillages from road or rail transport of chemicals and underground rescues, and petrol vapour build-up in car parks.

Storage Areas

Most storage of flammable gases or liquids is outside or occurs in well ventilated buildings. However spillage during loading of vehicles and leaks lead to fire hazard. Fixed gas and flame detectors are usual and there may also be a need for portable gas detection instruments.

Sulphur dioxide, chlorine and ammonia are stored by water treatment companies. Fixed detectors or sampling systems are used to detect spillages and leaks.

Crowcon detectors are suitable for outside use. Spray deflectors and weatherproof cases for control units are needed if the conditions are particularly arduous. Environmental sampling units aid the detection of heavy gases.

Marine and Vehicles

Ships' engine rooms are hazardous and can be protected by systems with flammable gas and fire detectors. Smaller vessels including pleasure craft often have a very serious risk of explosion because they use LPG or propane for heating and cooking. These heavier than air gases, with LELs as low as 2%, collect in the hull if there are leaks from fittings (even small ones) or during cylinder changing.

Cranes and lift trucks sometimes work in hazardous areas. Fixed detectors, often with flameproof control units are used to warn of gas or vapour clouds.

Road vehicles carrying flammable materials, which are involved in accidents, can cause a hazard to other road users and fire brigades are responsible for clearing spillage. They use portable detectors to check that conditions are safe. Vehicle operators often use sampling portables for checking tanks after cleaning.

Everyday Places

Gas or oil fired boilers are widely used in hospitals, hotels, banks, schools, sports centres, factories and offices and they usually run continuously and automatically. There is always a risk, usually minor, of leakage because of loose fittings or pipe fracture. Extremes of temperature or a heavy vehicle outside the building may cause fracture of underground pipes and the gas or oil may seep along the pipework into the boiler room. If methane is the fuel, collector cones on ceiling mounted detectors are fitted whereas with propane, butane (or LPG) the detectors need to be at ground level or more important in any ducts. A low level Crowcon Environmental Sampling Unit is often used in these situations. System outputs provide facilities for boiler shutdown, fan control etc, as well as alarms.

Refuse has been dumped in landfill sites for many years. The decay of the organic material underneath the topsoil produces a mixture of methane and carbon dioxide. Landfill sites are used for the building of factories, out of town shopping centres and even houses.

The bulk of the gas is normally extracted under controlled conditions via boreholes but there is always some seepage. It is therefore necessary to monitor for the build-up of gas inside the buildings and particularly in the wall cavities and enclosed places like toilets and switchrooms.

Power Generation

Ambient Air Monitoring For Flammable Gas Around Boiler Front & Associated Areas

Traditionally oil and coal have been used as the main fuels for power stations. Two fuels are required as coal fired boilers are only suitable for high load applications. At low load oil is used for close control of the stations output. In European and American markets oil and coal stations are being converted to gas and coal or gas, oil and coal. The reasons for this include:

- Gas is a cheaper source of fuel (easier to produce, transport and store)

- More flexible fuel i.e. can be used at low and high load
- Lower SOx and NOx emissions associated with gas fired stations

Where natural gas is used there is a real risk of leaks occurring around the pipework and burners at the front of the boiler and creating potentially hazardous conditions. Fixed point flammable gas detectors are used to monitor boiler fronts, gas burners and the associated pipelines carrying natural gas. The gas detectors are controlled using control units which provide audible and visual alarms should flammable gas be detected at 40% LEL. If 60% LEL gas is detected plant is shutdown.

Boiler Deadspace Monitoring

Oil, coal or gas is burned in the boiler, which superheats water passing through hundreds of pipes around the boiler wall. These pipes pass through the top of the boiler into a deadspace sometimes known as the Penthouse. The Penthouse is insulated from the very high temperatures of the boiler, however temperatures in this area can reach 400 to 500 °C. During normal operation the Penthouse is sealed, however when the boiler is non operational pipework contracts and it is then possible for unburned natural gas to leak into the deadspace. Once the boiler is put into operation again surface temperatures of metal work in the Penthouse will eventually exceed the ignition temperature of natural gas and so cause an explosion.

To combat this hazardous situation gas sampling equipment is installed to extract samples of air from the deadspace and monitor for flammable gas.

Fire & Gas Detection For Turbines

The superheated steam produced in the boiler is passed through a steam driven turbine, which produces electricity. In addition gas driven turbines are used to supplement the power output of the station during peak load. As a gas turbine can be started quickly they are also used to power essential equipment required to start up the main boilers and turbines. Gas turbines are usually monitored for a build up of flammable gas in the load compartment, exhaust ducts and gas compressor compartment.

In addition heat detectors are used to detect fires which may result from overheating due to loss of cooling equipment or loss of lubricants resulting in overheating bearings.

Fire Detection In Coal Silos, Feeders, Mills and Classifiers

Coal for use in the combustion process is delivered to the power station by rail and automatically unloaded into hoppers before being transported by conveyer to the coal silos for storage. From the silos coal is passed at a predetermined rate by the feeder to the mill. The mill pulverises the coal, which is then carried by forced ventilation fans through the classifier. The classifier grades the coal allowing only finely pulverised coal to pass through to the burners for combustion and returning larger particles to the mill to be pulverised further. In all of these areas there is a real risk of spontaneous combustion of coal dust deposits. Prior to combustion smouldering occurs which results in detectable levels of carbon monoxide being produced. At this stage there is no fire and so preventative action can be taken, such as steam/nitrogen inerting, at the operators discretion. Fire detection is further implemented by positioning thermocouples at strategic locations throughout the plant. The thermocouples provide direct information on increases in temperature due to the presence of a fire. All shutdown actions are manually operated. Gas Sampling Systems are used to detect carbon monoxide around the plant.

Protection of Personnel

Coal fired electricity production is a combustion process which produces various by-products. For example the incomplete combustion of coal results in large quantities of carbon monoxide being produced in the process. In addition, contaminants in coal when burnt produce oxides of nitrogen and sulphur. Should a leak occur in any process line carrying these gases it is possible to exceed the occupational exposure limits. As it is not possible to economically cover all leakage points using a fixed system, personnel are issued with portable instruments.

Waste Disposal on Landfill Sites

Most waste in the UK is dumped in large holes in the ground often left after quarrying or brick making. The Department of the Environment has issued guidelines in Waste Management Papers WMPs 4, 26 and 27. The last deals with the increasing problem of gas evolution from these sites. A rough analysis of typical rubbish is:-

Paper	30%
Vegetable and wood	25%
Ash and cinders	10%
Glass	10%
Plastic	10%
Textile	10%
Metal	5%

Paper, vegetable and wood, textiles and some plastic (ie more than 65% of the total waste) are bio-degradable. When a landfill site is first set up there is plenty of oxygen present in the mass of rubbish and as it becomes damp, aerobic degradation occurs, producing carbon dioxide and water and sometimes other gases such as hydrogen. As the oxygen is used up, under the right conditions of acidity and temperature, anaerobic degradation begins to take place, forming methane and carbon dioxide. A landfill site therefore undergoes changes chemically, biologically and physically at a rate depending on the composition of the waste, the bacteria present, the acidity and the temperature.

It takes about two years for a site to be generating gases at a reasonably stable rate and at this stage the main constituents are methane (70%) and carbon dioxide (30%) with a little hydrogen and hydrogen sulphide, although there will be variation depending on conditions. Typically, 5m3 of methane is produced per tonne of waste each year and it may take 20 years for all of the gas to be evolved at which time nitrogen is generated.

In addition to the safety monitoring of buildings on a landfill site and searching for seepage of gas, Crowcon is able to provide PC controlled sampling equipment to monitor the site's gas evolution by regularly (usually daily) drawing samples from boreholes and measuring the concentrations of methane and carbon dioxide by infrared absorption and of oxygen by electrochemical sensor. Fluctuations in atmospheric pressure determine gas evolution and the methane concentrations of the ingredients. For example, during a fall in pressure, gas evolution increases and the concentration of methane increases. Hence, sample monitoring of methane by transportable instruments gives misleading data on gas evolution and Crowcon's landfill system has been shown by the Waste Consultants, Aspinwall and Company, to provide reliable data. Using computers and modems, Crowcon's systems allow all of the data to be monitored remotely.

Crowcon also produces systems to assist in the control of the disposal or use of the gas. Whether the methane/carbon dioxide mixture is burnt to dispose of it, to heat plant and buildings or to provide electrical power it is necessary to monitor the ratio of the two gases because if the carbon dioxide concentration exceeds 40% the mixture will not burn and some other fuel has to be added.

Emission Monitoring

Many emission monitoring applications are difficult to deal with because of the temperature of the gases. However, high temperature flammable detecting heads have been used up to 200°C. One application is to monitor a cocktail of flammable gases from a fibre making plant to warn of any explosive risk in the plant. This was done using stainless steel duct air sampling units.

Electrochemical gas detectors can provide a cost effective means of emission monitoring. Successful results can be obtained by withdrawing samples from stacks, cooling and drying them and then passing them over appropriate electrochemical gas detectors. The drying process is normally done using Permapure gas drying membrane, this preventing variations in readings due to humidity changes.

In the UK, emission control is regulated under the Environmental Protection Act, 1990. Her Majesty's Inspectorate of Pollution (now known as the "Environment Agency") has issued "Chief Inspector's Guidance Notes to Inspectors" for various industries and these give details of the required maximum emissions of various substances and the regulations governing their control. A fundamental principle adopted in these notes is to ensure that the best available techniques not entailing excessive cost (BATNEEC) are used. Hence there will be a tendency for less expensive but none-the-less effective techniques to be used.

In these guidance notes, it states that the emission measurements must be corrected for a temperature of 0°C, pressure of one atmosphere, dry gas and 11 % by volume oxygen. This means that oxygen measurement needs to be carried out for this correction to be made. (This is to avoid distorted readings in the event of excessive air being bled into the emission system). When using electrochemical detectors, it is essential that due regard is paid to the cross sensitivities. Knowledge of what gases are likely to be present is essential before a scheme is designed and indeed there will be many applications for which electrochemical sensors are not suitable. Crowcon has successfully measured carbon monoxide, hydrogen sulphide, sulphur dioxide and oxygen in emissions. Crowcon's emission monitoring systems are PC controlled to allow algorithms to be written to correct many cross sensitivity effects. The PC also calculates the readings to the 11% oxygen base and into mg/m^3.

Digester Gas Monitoring

Since the privatisation of the UK water industry, the water companies have become increasingly involved in revenue activities outside their core business. An example of this is electricity generation from sewage sludge, with the resultant electricity being used both for on site consumption and for sale to the national grid.

Combustion engines are used to generate the electricity using a gas fuel called Biogas, which is generated from sewage sludge in an oxygen free tank or digester. Because the process is oxygen free the process is said to be anaerobic.

There are a large number of constituent gases in Biogas and listed below are the more significant ones:

Methane	58.5%
Carbon Dioxide	40%
Nitrogen	1
Oxygen	0.5%
Hydrogen Sulphide	3000ppm
Hydrogen	40ppm

Clearly, with the high level of methane present, this represents a rich source of energy; the problem is the high level of hydrogen sulphide, which at 3000ppm will readily cause corrosion, and mechanical failure of the generating engine.

One of the techniques employed to combat the high concentrations of hydrogen sulphide is to use a scrubber, which chemically absorbs the hydrogen sulphide and is situated between the digester and the engine. Obviously these is a need to measure the levels of hydrogen sulphide before and after the scrubber to monitor its efficiency, shutting the engine off or switching to an alternative fuel supply if the level rises too high or if the methane concentration drops below preset limits.

It is necessary to condition the gas before presenting it to the measuring detectors and water is removed by hydrophobic water barriers. Flow fail monitoring is provided by a pressure transducer measuring in the 0 to 1000 millibar range. Alarm levels can be set corresponding to both blocked gas path and leaking components within the system. The biogas is usually at atmospheric pressure so a pump is needed to retrieve the sample from the digester.

From the gas composition above it can be seen that biogas is explosive and it must not be allowed to accumulate undetected in a confined space, such as a cubicle. The atmosphere inside the system cubicle is therefore continuously monitored and controlled for both temperature via a thermostat and leaks of sample gas by a local gas detector. If the temperature rises above 35°C or a gas leak is detected, a ventilation fan is turned on changing the air inside the cubicle. In the case of a gas leak, the pump is also turned off.

Two different types of gas sensor are used to monitor the biogas, Infrared methane and electrochemical for hydrogen sulphide. The methane measurement is in the range 0-100% by volume and is continuous.

The hydrogen sulphide concentrations are too high for normal use of electrochemical sensors and a sample/purge arrangement using two detecting heads needs to be employed to maximise the sensor performance. The fresh air purge allows the electrochemical sensor to recover from its exposure to the gas. Using two hydrogen sulphide detectors a sample period of ten minutes in every hour is achieved.

SECTION 6

FIXED SYSTEMS INSTALLATION

SITING OF GAS AND FIRE DETECTORS

Remote Gas Detectors

There is not much in the way of official guidance on the siting of gas detectors and good practice has developed in the industry through experience at various sites. Crowcon are able to provide assistance to ensure that cost effective, efficient fixed gas detection systems are installed.

BS6959:1988 - "British Standard Code of Practice for Selection Installation, Use and Maintenance of Apparatus for the Detection and Measurement of Combustible Gases. (Other than for Mining Applications or Explosives Processing and Manufacture)" provides assistance but as its title admits, its scope is limited.

Basic considerations for installing a fixed system are:-

1 To install it so that it will monitor every part of the plant or premises where a risk exists.

2 The system must give early warning of the presence and location of gas in order to initiate one or more of the following:-

   a) evacuation of the premises
   b) fire fighting
   c) shutdown of the process or plant
   d) control of ventilation

There are no hard and fast rules about detector location (unlike fire detection systems). To quote BS6959, clause 5.2, "Sensors should be located in positions determined by those who have knowledge of gas dispersion, the process plant systems and equipment involved and in consultation with both safety and electrical engineering personnel. The agreement reached on the locations of sensors should be formally recorded".

Protection must be provided by locating detectors adjacent to likely sources of hazard and at the perimeter of a plant. Both types of siting should be used because localised detection can be affected by wind and its direction whilst perimeter detection gives delayed response and would need to be extensive to give total protection.

Having considered suitable locations for gas detectors, the mounting height has to be decided. In general, for gases lighter than air the detectors should be above the area where leaks are likely and for gases heavier than air the detectors must be at floor level or in inspection pits or ducts into which heavy gas may flow.

However gases do not separate out into discrete layers according to their densities. If they did, air would not exist as a homogeneous mixture but the heavy carbon dioxide would be at ground level with oxygen, which is heavier than nitrogen, next with a layer of nitrogen on top. If gases behaved like this, they would in fact be behaving like liquids. (Also consider how CFCs which are heavy vapours get into the ozone layer). It is better to view gases as tending to rise if they are light and tending to sink if they are heavy and to think about other phenomena which might affect the gas dispersion.

For example, if carbon monoxide, which is only slightly lighter than air, is under pressure and is suddenly released into the atmosphere a drop in temperature is caused resulting in an increase in density. This may cause the gas to fall to floor level.

Also, the nearer in density to air a gas is, the more easily it will flow with air due to draughts and ventilation etc. Therefore a compromise with gases like carbon monoxide and also gases only slightly heavier than air such as hydrogen sulphide and nitric oxide, is to mount the detectors at a height as close as possible to the breathing areas of personnel being protected.

When monitoring deficiency of oxygen, which is slightly heavier than air, it is necessary to consider what might be displacing it. For example carbon dioxide which is heavier will tend to sink to floor level so this is where the detectors should be. Conversely if helium is displacing the oxygen, the detectors should be mounted at a high level. On the other hand, if combustion is consuming oxygen, the whole volume of air would gradually become depleted in oxygen and detector location would not be so critical.

When installing gas detectors it is advisable to ensure that the gas inlet is not exposed to liquid or dust contamination by positioning the unit downwards (Splash deflectors should be used when water or other liquid is continually present).

People often ask what the area of coverage of a gas detector is in an open location. There is no official figure, but we often use 100m^2 per detector, adding more detectors at points where leakage could occur.

Fire Detectors

There is much more guidance in siting smoke and heat detectors, and BS5839: Part 1 : 1988 gives the detail.

The area of coverage of a smoke detector is 100m2 providing it meets BS5445: Part 7 (EN54: Part 7: 1984).

SMOKE DETECTOR SITING

The following table summarises spacing and ceiling height:

Spacing	Maximum area of coverage Maximum distance of detectors to any point Distance between detectors, general Distance between detectors, in corridors	100m^2 7m 12m max 8m max
Mounting Height	Normal maximum If satisfactory fire tests are done	10.5m 12-15m

Heat detectors should cover no more than 50m^2 and the maximum distance from a detector to any point should not exceed 5.3m. Mounting heights are as follows:

HEAT DETECTOR SITING

	Mounting Height	Maximum Normal Ambient Temperature °C
Grade 1, rate of rise 60°C	9m	45
Grade 2 60°C	7.5m	45
Grade 3 75°C	6m	60
High Temperature 85°C	6m	70
High Temperature 95°C	6m	80

No zone on a fire detection system should cover more than 2000m^2.

CABLING FOR FLAMMABLE AND THERMAL CONDUCTIVITY DETECTORS

Detectors using pellistor sensors or thermistors require three of four core cables, each conductor not exceeding 6.25 ohms (12.5 ohms loop) for Flamgard. In hazardous areas the cable should be mineral insulated (eg BICC type 4L1 PVC covered) or steel wire armoured (eg BICC type 6944). Suitable cable glands must be used.

Cable length calculations (Flamgard detector)

1 mm^2 cross section conductor is 17 ohms/1000m

Therefore maximum cable length $\frac{1000 \times 6.25}{17}$ = 368 m

CABLING FOR TOXIC GAS/OXYGEN DETECTORS

Detectors using electrochemical sensors require two core cable. For use in hazardous areas, because they are intrinsically safe, they must be wired with a suitable Zener barrier between them and the control unit. With a Zener barrier each conductor must not exceed 12 ohms (24 ohms loop). The loop resistance must not exceed 180 ohms when no Zener barrier is used. Flameproof cabling is not essential but for mechanical security we recommend the use of mineral insulated or armoured (eg BICC 2L1 or 6942). Note also that the Zener barrier will need a low resistance (less than 1 ohm) intrinsic safety earth.

Cable length calculations:
1 mm^2 cross section conductor is 17 ohms/1000m
Therefore maximum cable length = $\frac{1000 \times 12}{17} = 706 \, \text{metres}$

The use of copper conductors having greater cross-sectional areas (eg 2.5mm^2) reduces the cable resistance and allows longer cable lengths to be achieved.

SECTION 7

SAMPLING SYSTEMS

Most fixed gas detection systems have their remote detector located in accordance with the guidelines given in Section 3. In the majority of applications, where gas detectors are used for hazardous area monitoring, they operate by gas diffusing into the sensor. In other applications such as those listed below, the use of a sampling system provides better results.

- Measurement of gas concentration in inaccessible or confined locations where a detecting head cannot be installed such as in a process plant.
- To take gas from a Zone 0 hazardous area when using a detector suitable only for Zones 1 or 2.
- To measure gas, which needs to be dried or cooled before a meaningful reading, can be taken.
- To dilute the gas to be measured with an inert gas by a known ratio to bring its concentration down to a measurable value.
- To monitor gas which by its nature does not readily diffuse and mix in air.

Crowcon has developed various types of sampling system to cope with the wide variety of applications.

Piped Sample Systems

Crowcon's sample systems are designed in modules for ease of manufacture and servicing. A cubicle, normally wall mounting, contains the complete gas sampling and detection system. With standard units, a control unit is fitted to the inner door of the system and this operates up to three standard gas detectors and a pressure/flow transducer. The cubicle contains a power supply and timing equipment, which operates automatic drain valves on dust/water filters and water barriers. The temperature within the cubicle is controlled thermostatically to below 35°C by means of a cooling fan, incoming air being cleaned by a dust filter. A cubicle gas monitor is fitted so that if a flammable gas leaks within the cubicle an alarm is provided, the sample pump is turned off and the extract fan is turned on.

Pellistor, thermal conductivity, electrochemical or infrared sensors can be used so that a wide variety of gases can be monitored. To ensure that reliable readings are taken, all of the plumbing is in PTFE and pumps are fitted with Viton diaphragms.

Electrochemical sensors are a well established means of monitoring low ppm levels of toxic gases but Crowcon has developed techniques to use these sensors for measuring higher levels. These involve allowing the sensor to rest by purging with fresh air periodically and by using special dilution techniques.

The use of infrared is necessary for percentage levels of carbon dioxide and methane and auto-zeroing is normally provided.

Sequential Sampling Systems

Crowcon's sequential sampling systems enable gas samples to be taken from up to eight remote points but utilising a single gas conditioning and monitoring unit. These units can be combined together for more sampling points. The construction is similar to the standard piped sampling system.

Between each measuring period, the detector line is purged by fresh air. Samples are drawn from each point continuously at ten litres per minute and during the sampling period, one litre per minute is taken through the gas detectors. This is accomplished by means of a double-headed pump.

Environmental Sampling Unit

This has been designed primarily to monitor heavy gases such as chlorine or propane (LPG) which because of their nature flow to low points and do not diffuse readily in the general atmosphere.

The equipment comprises a sampling chamber, an explosion proof electric fan and collection pipes which allow the gas to be brought to the sampling chamber. The pipes can be open at their ends or have holes drilled along their length, with the ends closed.

Flow tests have shown that 12 metres of collection pipes can be connected to the inlet to the gas sampling chamber whilst maintaining a flow velocity of 0.4m/sec which ensures detector response within 60 seconds. Where two sampling pipes are used, their combined lengths should not exceed 12 metres.

Because of the very low pressure developed by the unit, care must be taken with siting the pipes to ensure that extraneous pressure effects are eliminated. This means ensuring that the open ends are positioned to avoid the effects of wind and any thermal currents. Bends and Ts in the pipes count as 2 metres of pipe.

The collection pipes are mounted horizontally near the ground or can be mounted vertically, for example in a pit or well. Where the water in a well may rise or fall, use of the collection pipe with an open end and with holes drilled along its length allows water to lap up the pipe with no fear of it entering the sample chamber.

Air Sampling Unit

If a forced ventilation system is used in a building, the first signs of a gas leak or discharge could be provided by a detector monitoring the air in a ventilation duct. The air sampling unit was originally developed by our sister company Apollo for detecting smoke in ducts and it works just as well in detecting low levels of gas. Two probes from a sampling chamber are inserted into the duct, the inlet having holes drilled along its length and the outlet being chamfered. By a Venturi effect about 1 % of the flow is sampled and this provides rapid response by a detector mounted in the unit.

The unit will not work unless the duct width is between 300 and 1500mm and it is essential that all the joints between the air sampling unit and duct are perfectly sealed. The air velocity needs to be at least 5 metres/sec.

The following data shows the response time to achieve 95% of the duct level in the sampling chamber (to which needs to be added detector response time).

Duct Flow rate Metres/Sec	Response Time Seconds
5	12
10	8
15	5
20	4

The air sampling unit is convenient because it has no electrically powered components and it also facilitates calibration and cleaning of the detector. It is suitable for the whole range of Crowcon remote detectors. It is normally made from polycarbonate but a special stainless steel one is also available.

Air Aspirator

The Air Aspirator provides the facility of extracting a gas sample from a remote position without the use of electric pumps. It can be fitted with any of Crowcon's gas detectors and is ideally suited for use in hazardous areas as, apart from the detector and an optional flow failure alarm, no electrical power is required for operation.

The Aspirator obtains its pumping action by passing high pressure air through a small orifice in the eductor venturi. The vacuum so formed extracts a continuous sample through a pipe from a remote position. Since there are no moving parts the Aspirator is virtually maintenance free and can be expected to have a long life.

The Aspirator is available in single or multi channel configuration and is constructed in stainless steel. It requires a supply of compressed air at a nominal pressure of 100 p.s.i. to instrument air quality to give the required flow of 0.5 to 1.5 litres per minute.

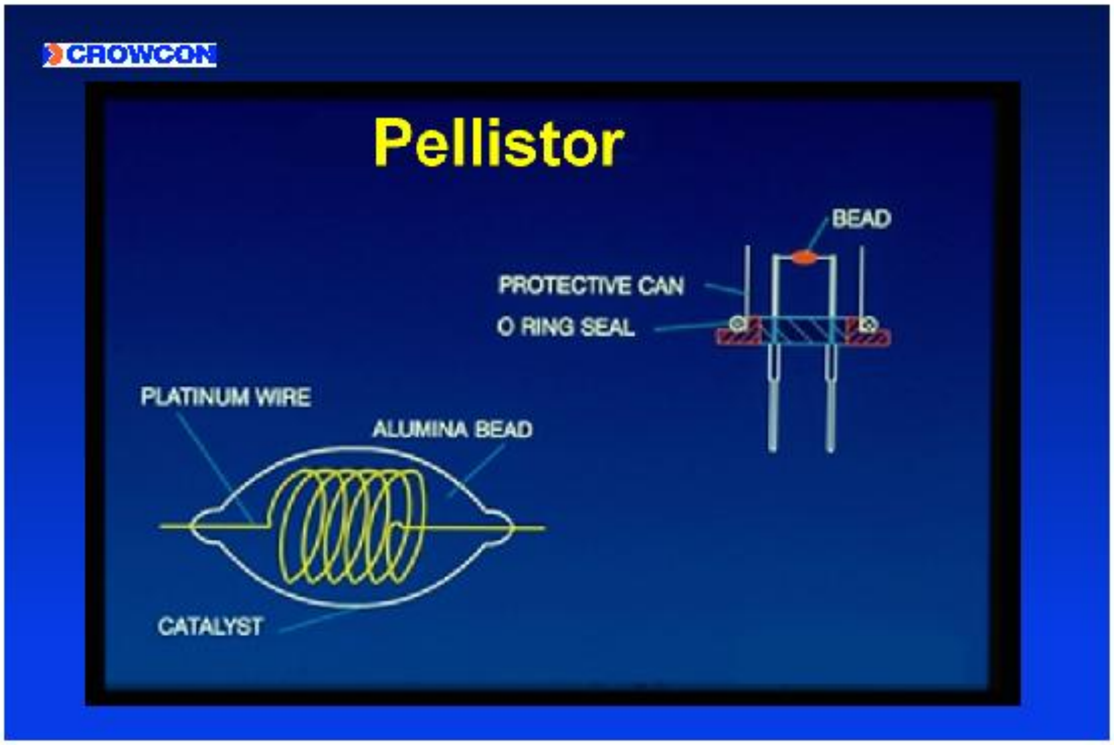
SECTION 8

PELLISTOR SENSORS

Operation

Catalytic pellistor sensors are sensitive to most flammable gases and vapours. It is possible therefore to use one detector to monitor a wide range of flammable gases and vapours.

Pellistor detectors consist of two coils of fine platinum wire each embedded in a bead of alumina, connected electrically in a bridge circuit. One of the beads is impregnated with a special catalyst which promotes oxidation whilst the other is treated to inhibit oxidation. Current is passed through the coils so that they reach a temperature at which oxidation of a gas readily occurs at the catalysed bead (about 500°C). This raises the temperature further which increases the resistance of the platinum coil in the catalysed bead, leading to an imbalance of the bridge. This output change is linear, for most gases, up to and beyond 100% LEL and response time is only a few seconds to detect alarm levels (typically 20% LEL).


CROWCON

Pellistor

Catalytic sensors can be 'poisoned' temporarily (e.g by compounds containing halogens, sulphur or chlorine) or permanently (e.g by substances containing lead or silicones). This has the effect of reducing sensitivity. Crowcon fit poison resisting pellistors to all fixed flammable gas detectors. Further protection against poisoning of fixed flammable gas detectors can be provided by using Crowcon's self adhesive carbon filter which is fitted on the outside of the sintered flame arrestor. It is suitable for hydrogen and methane monitoring but, unfortunately it reduces the sensitivity of the detector to propane (20% reduction), butane and pentane (50% reduction). The filter must always be replaced when a detector is re-calibrated and at no more than 6 months intervals.

If a pellistor is exposed to gas above the UEL for more that a few minutes, it may suffer reduction in sensitivity caused by "sooting". The degree of sensitivity reduction and whether the effect is permanent will depend on the gas. Aromatic compounds, having a high carbon content cause the worst problems.

In the absence of adverse factors pellistor sensors will last for many years. However they do lose performance continuously, typically by 20% per annum, therefore 6 monthly re-calibration of instruments employing pellistors is recommended. Pellistor based detectors work satisfactorily in ambient temperatures of -40 to +60°C.

Correction Factors

When an estimate of a particular gas concentration is required and where the gas being measured is known to differ from the gas for which the detector is calibrated a **"CORRECTION FACTOR"** may be applied.

Most equipment is calibrated for either 0 to 100% LEL methane or 0 to 100% LEL n-pentane. The lists of factors can be used for calculating the concentrations of other gases using either of these calibrations.

Example 1

If a detector is calibrated for n-pentane and the gas being measured is hydrogen, then from the appropriate list it will be seen that the factor to use is 0.6. Therefore for a meter reading of 65, the corrected reading for hydrogen is:

65 x 0.6 = 39% LEL hydrogen

As the reading is higher with hydrogen it follows that the alarm will operate at a lower level. For an alarm setting for n-pentane of 20% LEL, the level at which the alarm will operate in hydrogen is 20 x 0.6 = 12% LEL hydrogen. In some instances the correction factor is greater than one. In these cases the detector reads low and the reading has to be increased to bring it up to the proper value.

Example 2
If a methane calibrated detector is used to measure acetone, the correction factor is 1.6, therefore a reading of 65%
LEL would be corrected to 65 x 1.6 = 104% LEL acetone and an alarm setting of 20% LEL would actually operate at 20 x 1.6 = 32% LEL acetone.

CORRECTION FACTORS FOR PELLISTORS

To obtain an approximate LEL value for the gases/vapours below, multiply the meter reading on a pentane or, methane calibrated detector by the value shown.

	Detector Calibration	
	Pentane	Methane
Acetaldehyde	0.8	1.6
Acetic Acid	0.8	1.6
Acetic Anhydride	1.0	2.0
Acetone	0.9	1.6
Acetylene	0.8	1.7
Acrylonitrile	1.0	2.0
Alkyl Alcohol	0.9	1.9
Ammonia	0.35	0.6
N-Amyl Alcohol	1.4	2.8
Aniline	1.2	2.5
Benzene	1.1	1.9
1.3 Butadiene	0.8	1.3
N-Butane	0.8	1.6
Iso-Butane	0.9	1.8
Butene-1	1.0	2.0
N-Butanol	1.4	2.9
I-Butanol	0.9	1.9
Tert-Butanol	0.6	1.3
Butyl Acetate	1.5	3.0
N-Butyl Benzene	1.4	3.0
Iso-Butyl Benzene	1.4	3.0
Carbon Monoxide	0.6	1.2
Carbon Disulphide	4.0	8.0
Carbon Oxysulphide	0.5	1.0
Cyclohexane	0.9	2.0
Cyclopropane	0.8	1.6
N-Decane	1.4	2.8
Diethylamine	0.9	1.8
Dimethylamine	0.8	1.6
2.3 Dimethylpentane	1.1	2.2
2.2 Dimethylpropane	1.1	2.2
Dimethyl Sulphide	1.1	2.2
Dioxane	1.0	2.0
Ethane	0.7	1.4
Ethyl Acetate	0.9	1.8
Ethanol	0.6	1.85
Ethyl Benzene	1.3	2.6
Ethyl Bromide	0.5	1.0
Ethyl Chloride	0.8	1.6
Ethyl Cyclopentane	1.1	2.2
Ethyl Ether	1.0	2.1
Ethylene	0.7	1.2
Ethylene Dichloride	0.7	1.4
Ethylene Oxide	0.9	1.8
N-Heptane	1.3	2.3
N-Hexane	1.3	2.0
Hydrogen	0.6	1.2
Kerosene	1.4	2.8
LPG	1.1	2.1
Methane (LNG)	0.5	1.0
Methanol	0.5	1.2
Methyl Chloride	4.0	8.0
Methyl Cyclohexane	1.0	2.0
Methylene Dichloride	0.5	1.0
Dimethyl Ether	0.7	1.4
Methyl Ethyl Ether	1.0	2.0
Methyl Ethyl Ketone	1.1	2.2
Methyl-N-Propyl-Ketone	1.6	3.2
Naphthalene	1.3	2.8
N-Nonane	1.4	2.8
N-Octane	1.3	2.6
N-Pentane	1.0	1.9
Iso-Pentane	1.0	1.9
Petrol	1.0	1.9
Propane	0.65	1.3
N-Propanol	1.0	2.0
I-Propanol	0.9	1.8
Propylene	0.9	1.8
Propylene Oxide	1.0	2.0
Iso-Propyl Ether	1.0	2.0
Propyne	1.1	2.2
Styrene Monomer	4.0	8.0
Tetra Hydra Furan	1.0	2.1
Toluene	1.1	1.9
Trimethylbenzene	1.5	3.0
White Spirit	1.5	3.0
o-Xylene	1.2	2.8
m-Xylene	1.1	2.2
p-Xylene	1.1	2.2

SECTION 9

ELECTROCHEMICAL SENSORS

Any gas which can be oxidised or reduced electrochemically can be detected by means of a fuel cell based electrochemical sensor. Other gases may be detected by galvanic electrochemical sensors.

Fuel Cell Sensors

Fuel cells are electric batteries, which consume gas from outside rather than solid/liquid materials inside them. (Their main application is in space vehicles where hydrogen is consumed to provide electrical power). In addition to consuming the fuel gas they also consume oxygen. Crowcon fuel cell sensors are miniaturised fuel cells which react to low (parts per million) concentrations of gas. They consume minute amounts of gas, the absorption of gas and electrical output being controlled by a "diffusion barrier".

In most cases oxidation of the measured gas takes place and the sensing electrode becomes negative eg

$$CO + H_2O = CO_2 + 2H^+ + 2e$$
$$H_2S + 4H_2O = H_2S0_4 + 8H^+ + 8e$$

At the counter electrode, reduction of oxygen takes place:

$$O_2 + 2H^+ + 2e = 2H_2O$$

In a few cases reduction of the gas being measured takes place and the sensing electrode becomes positive eg

$$NO_2 + 2H^+ + 2e = NO + H_2O$$
$$Cl_2 + 2H^+ + 2e = 2HCl$$

In these cases oxygen is formed by oxidation of water at the counter electrode.

$$2H_2O = O_2 + 2H^+ + 2e$$

The electrochemical reactions produce current (uA) which is linearly proportional to the concentration of gas in air. In theory, because fuel cell sensors consume no internal ingredients, they should have an infinite life. In practice they last up to 3 or 4 years.

Galvanic Electrochemical Sensors

Galvanic sensors are not fuel cells because electrodes or electrolyte are used up. Crowcon's oxygen sensor is not a fuel cell but a metal oxygen cell. The metal is gradually consumed and this governs the sensor's life.

Acid gas sensors are more complex. The electrolyte is calcium bromate solution, any strong acid gas liberates bromine chemically from the electrolyte and this reacts electrochemically with a silver anode, which gradually dissolves.

Other gases such as ammonia and hydrogen cyanide are measured by consumable or galvanic sensors. The life of these sensors is governed by the amount of gas, which they absorb, so their life can be very short in continuous gas.

Cross Sensitivity

Electrochemical sensors are made as specific as possible to one gas but there is some degree of cross sensitivity. This usually is not a problem in environmental monitoring. The table below gives information on cross sensitivity.

Sensor	OX	CO	H_2S	SO_2	NO	NO_2	CL_2	H_2	HCN	HCl	C_2H_4
standard range ppm	(25%) 250000	250	25	10	100	10	5	1000	25	10	
maximum range	30%	2000	1000	500	500	100	20	2000	100	100	

Gas Sensor	OX	CO	H_2S	SO_2	NO	NO_2	CL_2	H_2	HCN	HCl	C_2H_4
CO		1.0	0.02	0	0.2	0	0	0.6	0.2	0	0.75
H_2S		0.02	1.0	0.2	0	-0.2	-0.2	0.015	0	0	0
SO_2		0.01	1.33	1.0	0	-1.2	-0.5	0	0.5	0.2	0
NO		0	0.33	0	1.0	0.3	0	0	0	0.2	0
NO_2		0	-0.1	0	0	1.0	1.0	0	0	0	0
CL_2		0	-0.1	0.01	0	1.0	1.0	0	0	0	0
H_2		0.01	0.2	0	0.28	0	0	1.0	0.3	0	0.8
HCN		0.001	4.67	1.6	-0.1	-2.0	-0.5	0	1.0	no data	0.001
HCl		0.01	1.5	0.7	0.08	0	-0.5	0.005	0.03	1.0	0.03
NH3		0	1.0	0.6	0.2	0	-0.5	0	0.05	0	0
O_3		0	-0.13	0	0	0.7	1.0	0	0	0	0

NOTES

1. The figures shown below represent approximate response factors when the sensor is exposed to concentrations of the interfering gas at or around the 8 hour OEL (TLV). For example, if an H2S sensor is exposed to 50ppm CO, the sensor response will be equivalent to 50 x 0.02 = 1 ppm H2S.
2. Acid gases including carbon dioxide increase oxygen sensor output eg 1% CO2 increases the signal by 0.3% ie increases a 21 % reading to 21.06%. 25% CO2 or more reduces oxygen sensor life. '
3. Fuel cell sensors generally operate at temperatures of -55 to +55°C intermittently (eg. 8 hours in 24 hours) and at -20 to +45°C continuously (-40 to +45°C for hydrogen sulphide and -20 to +30°C for ammonia).
4. Relative humidity must be between 15 and 90% RH for satisfactory operation and there needs to be at least 1 % oxygen present.
5. Cross sensitivities should only be used for calibration after consultation with Crowcon.

Broad Range Electrochemical Sensor

The 7VO broad range sensor responds to a number of gases and vapours including several organic vapours. Instruments using it can therefore be used to provide warning in the event of these substances being encountered in the working area. It is not possible to calibrate instruments to the specific vapours; a 100 ppm CO calibration is used, the table below providing the approximate ranges of the substances at this sensitivity. The sensor output is linear so the range at the 100ppm CO calibration can be used as a factor to give a crude measurement. eg a reading of 50 in acetaldehyde means there is about 125ppm present.

Gas/Vapour	Formula	8 hour OEL	Approximate range at100ppm CO calibration ie reading of 100 =
Acetaldehyde	CH 3 CHO	20	250
Acetylene	C2H2	-	30
Acrylonitrile	CH2CHCN	2 (MEL)	135
Butadiene	CH2CHCHCH2	10 (MEL)	60
Carbon disulphide	CS2	10 (MEL)	70
Carbonyl sulphide	COS	-	75
Dimethyl sulphide	$(CH_3)_2S$	-	65
Ethanol	C_2H5OH	1000	55
Ethylene	C_2H4	-	45
Formaldehyde	HCHO	2 (MEL)	30
Methanol	CH3OH	200	25
Methyl mercaptan	CH 3SH	0.5	35
Toluene	C6H5CH3	50	500
Vinyl acetate	CH3COOCHCH2	10	50

Substances, which cannot be readily detected by the 7VO sensor, include acetone, benzene, ethyl acetate, methylamine, methyl ethyl ketone, tetrachloroethylene and vinyl chloride.

Continuous Exposure to Gas

Toxic gas sensors will only work continuously if the sample gas contains not less than 1 % oxygen. If the oxygen level is less that 1%, purging with fresh air is required for 30 minutes in every hour.

The level of gas to which sensors may be continuously exposed is dependent on the sensor type and the following table provides typical data.

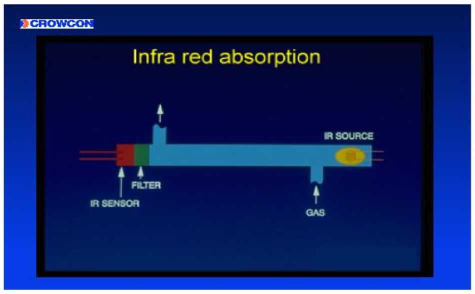
	Sensor type	Concentration
Carbon monoxide	3E	200ppm
Carbon monoxide	3F	500ppm
Hydrogen sulphide	3H	100ppm
Hydrogen sulphide	3M	1000ppm
Sulphur dioxide	3ST/F	200ppm
Nitric oxide	3NT	50ppm
Chlorine	3CLH	20ppm
Nitrogen dioxide	3NDH	20ppm
Hydrogen	3HYT	1000ppm

In these gas concentrations, a sensor life of 3 to 6 months is expected. If a longer life is required, the air purging method mentioned above would extend the sensor life to 1 year (and sensors should lose no more than 20% of their original sensitivity).

SECTION 10

INFRARED ABSORPTION

Gases, which contain more than one type of atom absorb IR radiation. Therefore gases such as carbon dioxide, carbon monoxide, methane, sulphur dioxide etc, can be detected by this means but gases such as oxygen, hydrogen, helium and chlorine cannot. Specific gases are detected by measuring their absorption at particular frequencies of IR which correspond to the resonance of the molecular bonding between dissimilar atoms. For example, the wavelength at which the carbon atom and each of the four hydrogen atoms resonate in a methane molecule is 3.3 microns. To detect methane, therefore, the infrared system will be filtered to emit radiation in a bandwidth centered on 3.3 microns.



Infra red absorption

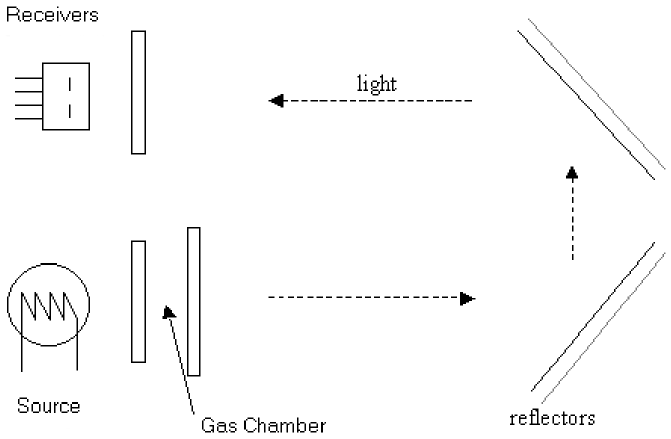
In-Line Measurement

In the simplest infrared gas detectors, the sample is drawn into an optical chamber by convection or by means of a pump. At one end of the chamber is an IR source, normally a filament lamp and at the other end is an IR sensor. The IR is tuned to the absorption frequency of the gas being measured by means of an optical filter. As the concentration of gas being measured increases, the output signal from the sensor reduces, in an approximately logarithmic fashion. This means that linearising circuitry needs to be built into the electronics.

Point Detectors

In a typical fixed point detector, the source (s) and receiver (s) are mounted in the main body of the housing, with the beam being reflected by a mirror at the far end of the housing. Parts of the beam are exposed to atmosphere so that, using natural or forced diffusion, gas can intersect the beam. As a gas concentration increases more infrared energy is absorbed by the gas and less reaches the receiver. In this way received energy is inversely proportional to gas concentration.

Infrared point detector



SECTION 11

SEMI-CONDUCTOR SENSORS

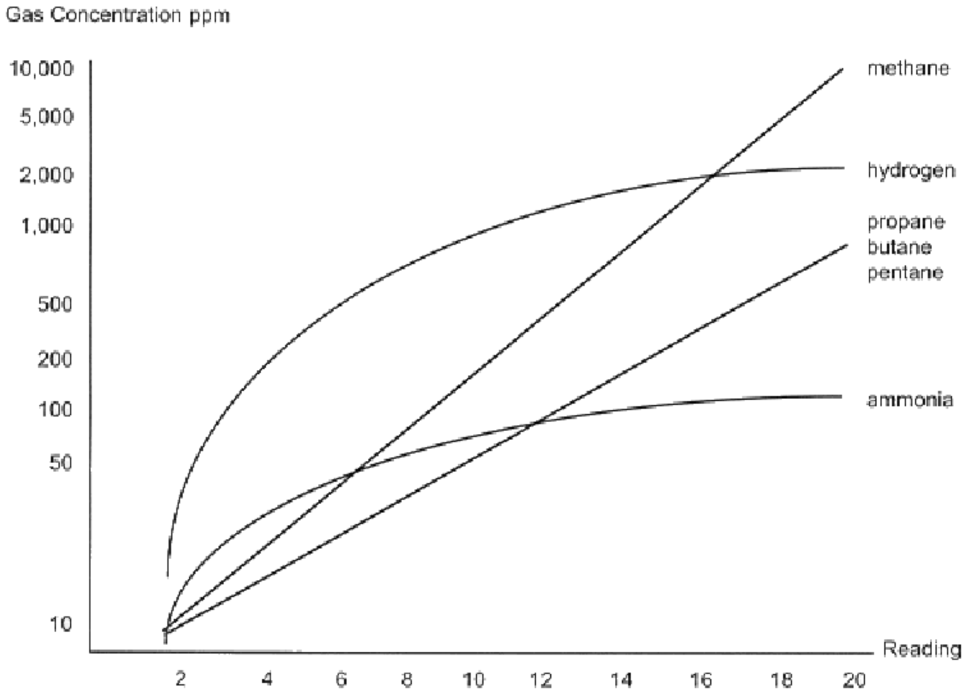
Considerable research is being carried out into semi-conductor gas sensors throughout the world. They are currently produced in large numbers for use in simple domestic gas detectors. Unfortunately, these devices are generally unsuitable for use in industrial gas detectors because they react to almost any gas, sometimes unpredictably and they are not very stable when in fresh air. Even water vapour causes a signal.

Operating Mechanism

Most semi-conductor gas sensors are based on a metal oxide (usually tin oxide) which is heated to 300 to 400°C by a heating coil. In air, oxygen is adsorbed onto the surface and the sensor has a resulting semi-conductivity. In the presence of other gases, the oxygen molecules are replaced with other gas molecules on the surface and the semi-conductivity of the metal oxide changes. The output signal is normally logarithmic to gas concentration.

Current sensors are not very specific and detectors using them are only really suitable for leak seeking.

The graph below shows some typical calibration curves for various gases.



SECTION 12

THERMAL CONDUCTIVITY SENSORS

Measuring the thermal conductivity of gases was one of the earliest forms of gas detection and it is suitable for volume levels of certain binary mixtures (two different gases, one of which can be air).

Method of Operation of Thermal Conductivity Gas Detectors

TC gas detectors, sometimes called Katharometers operate by comparing the thermal conductivity of the sample with that of a reference gas (usually air). A heated thermistor or platinum filament is mounted so that it is exposed to the sample and another, acting as a reference is enclosed in a sealed compartment.

If the sample has a higher thermal conductivity than the reference, heat is lost from the exposed element and its temperature decreases, whilst if the thermal conductivity is lower than that of the reference the temperature of the exposed element increases. These temperature changes cause electrical resistance changes, which are measured by means of a bridge circuit.

Because of the amount of power required to heat these sensors, they have to be mounted in a flameproof enclosure, in the same way as pellistors are. The precise mechanism, which occurs, is quite complex because the thermal conductivities of gases vary with temperature and convection as well as conductivity plays a role. Whilst most gases exhibit a linear output signal, this is not always the case.

Limitations in the use of Thermal Conductivity

Data on the thermal conductivities of gases is normally stated relative to that of air. The following gases are often measured by TC techniques and have a relative thermal conductivity to air of greater than one, so their presence leads to cooling of the exposed thermistor or filament.

Thermal Conductivity Relative to Air at 100°C

Helium	5.6
Hydrogen	6.9
Methane	1.4
Neon	1.8

The higher the thermal conductivity the lower the concentration which can be measured.

Gases with thermal conductivities of less than one are more difficult to measure, partly because water vapour may cause an interference problem.

Thermal Conductivity Relative to Air at 100°C

Argon	0.7
Butane	0.7
Carbon dioxide	0.7
Ethane	0.75
Freon/Halon	0.4
Hexane	0.5
Pentane	0.7
Propane	0.8
Water vapour	0.8
Xenon	0.2

Gases with thermal conductivities close to one cannot be measured by this technique. These include ammonia, carbon monoxide, nitric oxide, oxygen and nitrogen.

Binary Gas Mixtures

Mixtures of two gases in the absence of air can be measured by TC techniques. An example is methane in carbon dioxide mixtures found in sewage digester and coal gasification plants.

An instrument can be scaled 0 to 100% methane in carbon dioxide, and such equipment works well, as long as precautions are taken to separate water from the gas stream.

SECTION 13

THE SULPHISTOR SENSOR

The Sulphistor, is a hybrid device, patented by Detection Instruments, which combines the stability of the pellistor catalytic sensor with the sensitivity of the semi-conductor sensor. It is suitable for measuring hydrogen sulphide in air up to 100ppm, in the presence of high concentrations (LEL levels) of methane. It is useful for hot environments (more than 45°C) where electrochemical sensors may be unsuitable.

Performance of the Sulphistor

Trials have been carried out on the Sulphistor mounted in the DI 8 Detector by SIRA, whose report is available.

The tests were conducted in a 1 m^3 environmental chamber. The DI 8, fitted with a weatherproof cap, was supported in the middle of the chamber.

The overall results of this test were:-

Zero drift of less than 2.5ppm over the temperature range -38 to 60°C.

Sensitivity increases at low temperature (4.5ppm gas reads 7.5ppm at -20°C).

The effects of temperature are fully reversible.

Sensitivity not affected by humidity changes from 30 to 95% RH.

Cross Sensitivity

SIRA tested the Sulphistor in n-hexane, methane and ammonia and the results show that large concentrations of these gases are required to produce any significant response.

There is a reaction with alcohols and off-shore experience has suggested interference from mud oils, which contain alcohols.

Hydrogen sulphide in air must be used as the calibration gas.

SECTION 14

OTHER GAS SENSING TECHNOLOGIES

There are many physical properties of gas, which can be used as a method of detecting its presence. The more common sensing technologies have been described previously but other techniques include various means of ionising the gas sample so that its ability to conduct a small electric charge gives an indication of the presence or absence of certain gases. Photo-ionisation (PID) utilises an ultra-violet emitting lamp to ionise a wide range of volatile organic substances. Flame ionisation (FID) uses a pilot-light caused by burning a controlled jet of hydrogen in such a way as to be able to detect differences in the flame characteristics caused by the presence of very low concentrations of other flammable gases. This technique is particularly useful for leak detection of natural gas, and portable and vehicle mounted adaptations of this technology are relatively common-place.

Certain substances will absorb radiation in the ultra-violet part of the spectrum and it is possible to build gas detectors similar to the infrared absorption devices previously mentioned but using a UV emitting lamp and a UV sensitive detector.

Photo-acoustic detectors use a combination of infrared radiation and pressure pulse sensing, whereby a sample of gas is irradiated with a pulsed infrared source and the concentration of gas affects the amount of IR absorption, causing rapid expansion of the gas within a fixed cell. A Piezo-electric transducer (or other type) fitted in the wall of this cell will detect the transient pressure change and this can be used to determine the concentration very accurately.

Other spectroscopic means of gas detection such as microwave, optical or chromatographic are more widely used within the analysis field than safety instrumentation due to the relative cost and complexity of the technology employed.

Surface-acoustic-wave (SAW) technologies may have a part to play in future gas detectors. Certain gas molecules can be absorbed onto the surface of doped semiconductors and the change in the material's characteristics can be detected by the way that optical or acoustic radiation travels over the treated surface. Molecular absorption onto other materials, such as optical fibres, is another area of academic research that may form the basis of future generations of gas sensors.

SECTION 15

DETECTOR CALIBRATION

FLAMMABLE GASES AND VAPOURS

Most flammable gas detectors are calibrated 0-100% LEL methane or 0-100% LEL pentane and SECTION 4 describes the use of CORRECTION FACTORS for measuring other gases and vapours which are known to be present. Pellistor sensors are about twice as sensitive to methane as to pentane and these two calibrations are therefore convenient to use. Methane is readily available mixed with air at 25 or 50% LEL concentrations in aerosol cans which Crowcon supply or in larger pressurised cylinders. Other gases are available, although some (such as propane) are difficult to use.

Crowcon provide flammable gas detectors calibrated to particular gases or vapours using special gas mixing apparatus. For those users of Crowcon gas detection equipment with access to similar apparatus we provide the following notes on preparing dilute gas or vapour mixtures.

Preparing dilute gas mixtures

Mixing gases requires the use of special pumps and reference needs to be made to information on LEL concentration (some of the more common LELs are listed in Crowcon sales brochures).

To make a gas/air mixture of V% gas by volume, volume of pure gas required is:-

$\frac{V}{100}$ x 1000 = (100 V ml per litre)

Preparing dilute vapour mixtures

Pentane and other flammable liquids, which readily vaporise can be used to produce dilute mixtures with air by using plastic (Tedlar) bags available from Crowcon. These bags are of known volume or a flow of air can be measured into a bag. A bag is usually half filled with air and a carefully measured volume of the liquid is injected into the bag using a hypodermic syringe. There is usually a membrane for this purpose at the inlet to the bag. The liquid stream should be directed into the air in the bag rather than allowing it to settle on the inside surface of the bag. The bag should be kneaded to mix the vapour then more air is added to bring the volume up to the required level.

To calculate the volume of liquid required its molecular weight and specific gravity need to be known:-

The molecular weight of a gas or vapour will always occupy 22.4 litre at normal temperature and pressure (O°C, 760mm). This rule can be used to calculate the volume of a volatile liquid to make a vapour/air mixture of X% by volume as follows:-

$$\text{Volume of liquid required at } 0°\text{C, 760mm} = \frac{V}{100} \times \frac{M}{S \times 22.4} \text{ ml per litre of air}$$

Where M = molecular weight of liquid
S = specific gravity of liquid

To provide greater accuracy this liquid volume can be corrected by multiplying by a factor depending on ambient temperature and pressure as follows:-

Pressure	0°C	10°C	20°C	30°C
770mm (fine weather)	1.01	0.98	0.94	0.91
750mm (changeable)	0.99	0.95	0.92	0.89
730mm (stormy)	0.96	0.93	0.90	0.87

EXAMPLE

Volume of iso-butanol required to make a 50% LEL mixture in a 10 litre bag.

$$\text{Volume} = \frac{1.68}{100} \times \frac{74}{0.805 \times 22.4} \times \frac{50}{100} \text{ ml per litre}$$

= 0.034 ml per_litre i.e 0.34 ml for 10 litre bag.

(100% LEL iso-butanol is 1.68% v/v, specific gravity, S is 0.805, molecular weight M is 74).

If the dilution is carried out at 200C, 730mm more precision is provided by multiplying by the factor 0.90 to give a volume of 0.31 ml per litre (0.31 ml for 10 litre bag).

Below is information on LELs, specific gravities and molecular weight for some common volatile liquids.

LEL % by Volume		Specific Gravity (Water =1)	Molecular Weight
Acetone	2.6	0.8	58
Benzene	1.3	0.9	78
n-Butanol	1.4	0.8	74
iso-Butanol	1.7	0.8	74
Ethanol	4.3	0.8	46
Ethyl ether	1.9	0.7	74
n-Heptane	1.2	0.7	100
n-Hexane	1.1	0.7	86
Methanol	7.3	0.8	32
Methyl ethyl ketone	1.8	0.8	72
Pentane	1.5	0.6	72
iso-Pentane	1.4	0.6	72
n-Propanol	2.1	0.8	60
iso-Propanol	2.0	0.8	60
Toluene	1.2	0.9	92

Molecular weight can be calculated from the chemical formula using carbon C=12, oxygen 0=16 and hydrogen H=1.

Some common calibrations are given below:-

Calibration Required	Calibration Gas	Meter Reading (LEL)
Acetone	50% LEL Acetone	50%
Ammonia	50% LEL Methane	30%
Benzene	50% LEL Pentane	55%
n-Butane	50% LEL n-Butane	50%
Ethanol	50% LEL Pentane	30%
n-Hexane	50% LEL Pentane	65%
Hydrogen	50% LEL Hydrogen	50%
Kerosene	50% LEL Pentane	70%
Methane	50% LEL Methane	50%
Methanol	50% LEL Methanol	50%
Pentane	50% LEL Pentane	50%
Petrol	50% LEL Pentane	50%
Propane	50% LEL Propane	50%
	or 50% LEL Pentane	32%
Toluene	50% LEL Toluene	50%
White Spirit	50% LEL Pentane	75%
o-Xylene	50% LEL o-Xylene	50%

TOXIC GASES

Toxic gas detectors are normally calibrated to measure around the Occupational Exposure Level, which for most toxic gases will be less than 50ppm, an extremely low level. Because of the difficulty in preparing gas/air mixtures at this dilution, Crowcon use precision gas mixtures obtained from specialist gas suppliers and these mixtures are also available in disposable cans.

Unfortunately some toxic gases such as hydrogen sulphide and sulphur dioxide are readily absorbed by the materials used to make the cans or cylinders and stability of these mixtures can be a problem. These gases therefore have a limited shelf life. Nitrogen dioxide is available in pressurised cylinders but not in cans and chlorine is available in neither so we provide chlorine generators.

For certain gases, calibration can be done using another gas to which an electrochemical sensor is cross-sensitive but care is necessary.

Some examples are:-

Sensor	Calibration Gas	Equivalent to
0-10ppm acid gas	10ppm chlorine	10ppm acid gas
0-10ppm nitrogen dioxide	10ppm chlorine	9ppm nitrogen dioxide
0-25ppm hydrogen cyanide	10ppm sulphur dioxide	28ppm hydrogen cyanide
0-10ppm chlorine dioxide	10ppm chlorine	4ppm chlorine dioxide
0-2.5ppm phosphine	10ppm sulphur dioxide	2ppm phosphine
0-1 ppm ozone	2ppm chlorine	1 ppm ozone
0-10ppm hydrogen fluoride	5ppm hydrogen chloride	10ppm hydrogen fluoride

ppm - mg/m3 CONVERSION

ppm is a volume measurement (eg. 10ppm in air is 10 parts by volume of gas per 1 million parts by volume of air). mg/m^3 is weight per unit volume and is often used in emissions monitoring. Conversion from one to the other requires knowledge of the molecular weight of the gas and the fact that 1m^3 (1 cubic metre) is 1000 litres.

eg. 1mg/m^3 of CO= $\frac{1x10^{-3}}{1000}$ = $1x10^{-6}$g/litre
at 20°C, 1013 mbar

The molecular weight of any gas (28g for CO) occupies 24 litres at 20°C, 1013 mbar (22.4 litres at 0°C, 1013 mbar).

1 mg/m^3 of CO $\frac{1x10^{-6}x24\times1\times10^{6}}{28}$

= 0.86 ppm

So, formula for mg/m^3 to ppm at 20°C, 1013 mbar

is $\frac{\text{mg of gas}}{\text{molecular weight of gas (g)}}$ x 24 =ppm of gas

Formula for ppm to mg/m^3 at 20°C, 1013 mbar

is $\frac{\text{ppm of gas x molecular weight of gas (g)}}{24}$ = mg/m^3 of gas

EXAMPLES

	Formula	1 mg/m^3 =ppm	1 ppm =mg/m^3	Molecular Weight
Carbon monoxide	CO	0.86	1.17	28.01
Carbon dioxide	CO_2	0.55	1.83	44.01
Sulphur dioxide	SO_2	0.37	2.67	64.06
Nitric Oxide	NO	0.80	1.25	30.01
Ammonia	NH_3	1.41	0.71	17.03
Methane	CH_4	1.50	0.67	16.04

Automatic Calibration

Calibration can be time consuming, so for users with more than one portable gas detector, an automatic calibration unit solves the problem. For use with most portable instruments, Crowcon's AutocalibratorI is used in conjunction with a PC and provides a fully automatic calibration routine. The Autocalibrator can be connected to up to five gas cylinders and has an inlet for an air cylinder if the normal room air cannot be used. The PC will control all the pumps and solenoid valves and within a few minutes, the gas detector will be calibrated. The PC screen will show details of the routine and if any sensors failed. A report can be generated and printed after the routine of each instrument. The calibration information is stored in a file unique to that instrument and can provide an ongoing database of calibration history.

SECTION 16

SELECTION OF CALIBRATION RANGES AND ALARM LEVELS

Environmental Monitoring

For environmental monitoring applications, the concentrations of gases, which need to be measured, are determined by these concentrations which are hazardous. Flammable gas detectors are normally calibrated 0 to 100% LEL and toxic gas detectors are normally calibrated in a range in excess of, but around, the 15 minute occupational exposure level (OEL) of the gas. Both pellistor sensors and electrochemical toxic gas sensors used in environmental monitoring gas detectors are designed to operate at optimum efficiency at these levels.

Alarm levels are selected to provide rapid warning of increasing gas levels, well before an atmosphere has become either flammable or toxic. For flammable gases, first alarms are normally set at 20% LEL (sometimes 10% LEL) and second alarms are set at 40% LEL. On some instruments where three alarm levels are available a visual prealarm can be set below the first alarm level.

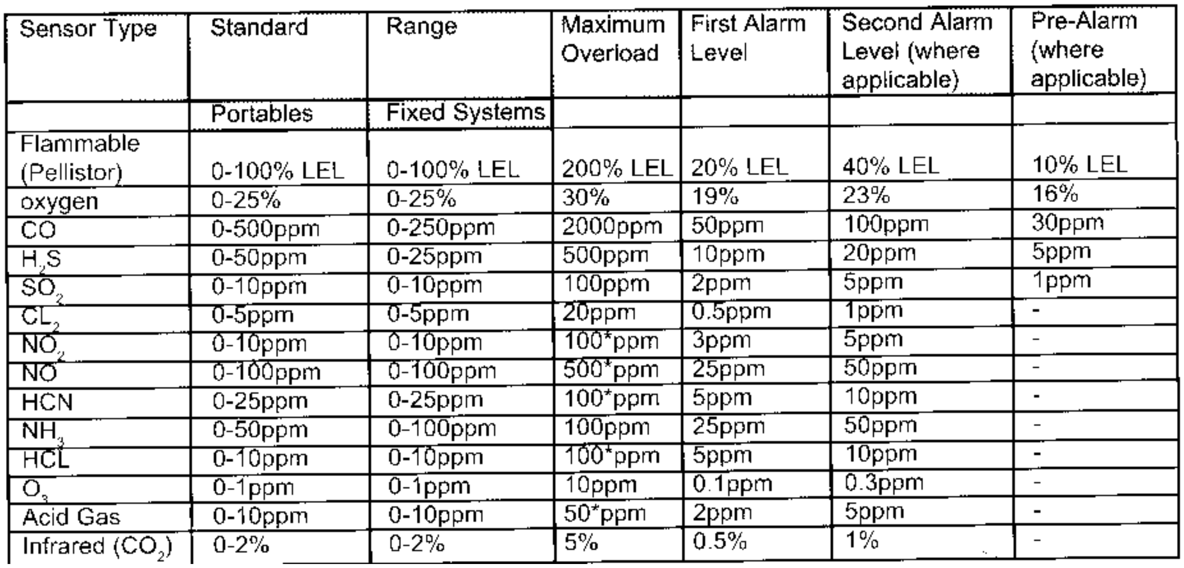
For toxic gases the first alarm is normally set to give an instantaneous alarm when the concentration limit for the 8 hour OEL is exceeded (although some users prefer a level below this). The second alarm point is set according to both the 15 minute OEL and the range of the sensor. (In the case of certain portable instruments the alarms may be timeweighted average (TWA) levels).

Oxygen detectors are usually set to provide alarms in deficient and enriched atmospheres (although Crowcon equipment can usually be set to operate at two levels of deficiency or enrichment).

Process Monitoring

Pellistor detectors should not be exposed for more than a few minutes to flammable gas concentrations above the upper exposure level (UEL) because incomplete combustion on the sensor surface will lead to sooting up and its sensitivity will be reduced. (Thermal conductivity or infrared detection techniques should be used in these circumstances).

Electrochemical sensors can sometimes be used in gas concentrations in excess of their standard ranges, providing it is possible to calibrate the detector, bearing in mind the availability and toxicity of the required calibration gas mixture.



Sensor Type	Standard	Range	Maximum Overload	First Alarm Level	Second Alarm Level (where applicable)	Pre-Alarm (where applicable)
	Portables	Fixed Systems				
Flammable (Pellistor)	0-100% LEL	0-100% LEL	200% LEL	20% LEL	40% LEL	10% LEL
oxygen	0-25%	0-25%	30%	19%	23%	16%
CO	0-500ppm	0-250ppm	2000ppm	50ppm	100ppm	30ppm
H_2S	0-50ppm	0-25ppm	500ppm	10ppm	20ppm	5ppm
SO_2	0-10ppm	0-10ppm	100ppm	2ppm	5ppm	1ppm
CL_2	0-5ppm	0-5ppm	20ppm	0.5ppm	1ppm	-
NO_2	0-10ppm	0-10ppm	100*ppm	3ppm	5ppm	-
NO	0-100ppm	0-100ppm	500*ppm	25ppm	50ppm	-
HCN	0-25ppm	0-25ppm	100*ppm	5ppm	10ppm	-
NH_3	0-50ppm	0-100ppm	100ppm	25ppm	50ppm	-
HCL	0-10ppm	0-10ppm	100*ppm	5ppm	10ppm	-
O_3	0-1ppm	0-1ppm	10ppm	0.1ppm	0.3ppm	-
Acid Gas	0-10ppm	0-10ppm	50*ppm	2ppm	5ppm	-
Infrared (CO_2)	0-2%	0-2%	5%	0.5%	1%	-