

Chapter 2

HAZARDS OF BULK LIQUIDS

In order to appreciate the reasons for the practices adopted to ensure safety in tanker and terminal operations, all personnel should be familiar with the flammable properties of products, the effects of the density of the gases and their toxic properties. These are described in this Chapter.

Specific issues, including the handling of high vapour pressure cargoes and the particular hazards associated with the handling, storage and carriage of residual fuel oils, are also discussed.

The Chapter also describes the principles, uses and limitations of gas detection equipment and addresses issues relating to gas evolution and dispersion.

2.1 Flammability

The volatility (i.e. the tendency of a product to produce gas) is characterised by the vapour pressure. When a product is transferred to a gas free tank or container, it starts to vaporise, that is it liberates gas into the space above it.

Flammability is a primary risk in the handling of petroleum; this creates an ever present hazard.

For detailed information on flammability, see Section 1.2.

2.2 Density

The gases from bulk liquids can be heavier than air and handling of cargoes should take account of the hazard that this property presents.

Information on the density of these gases is given in Section 1.3.

2.3 Toxicity

2.3.1 Introduction

Toxicity is the degree to which a substance or mixture of substances can harm humans. Toxic means the same as poisonous.

Toxic substances can harm humans in three main ways: by being swallowed (ingestion), through skin contact (absorption), and through the lungs (inhalation). Toxic substances can have local effects, such as skin or eye irritation, but can also affect other, more distant, parts of the body (systemic effects). The purpose of this Section is to describe the adverse effects associated with toxic substances to which personnel engaged in tanker operations are most likely to be exposed, to indicate the concentrations at which those adverse effects are expected to occur in humans through a single or repeated exposure, and to describe procedures for reducing the risks of such exposure. Although not strictly a matter of toxicity, the effects of oxygen deficiency are also described.

Products and product vapours can have various effects. They can be carcinogenic (causing cancer), reprotoxic (affecting reproduction), and can cause chemical burns, eczema, asthma, damage to organs, etc. These effects will be described in the Material Safety Data Sheet for the product.

2.3.2 Bulk Liquids

2.3.2.1 Ingestion

The oral toxicity of chemical products varies in a wide range and the Material Safety Data Sheet (MSDS) should be checked for the specific information on the product and for the measures that have to be taken when a person swallows it. The MSDS will also describe the required Personal Protective Equipment (PPE).

Petroleum has low oral toxicity, but when swallowed it causes acute discomfort and nausea. There is then a possibility that, during vomiting, liquid petroleum may be drawn into the lungs and this can have serious consequences, especially with higher volatility products, such as gasolines and kerosenes.

2.3.2.2 Absorption

For chemical products the effect of absorption can vary considerably. Products can have acute effects (unconsciousness, dizziness, chemical burns, organ failure, death) or chronic effects (cancer, organ damage, reprotoxic).

The Material Data Sheet should be checked for the specific information on the product and for the measures that have to be taken when a person has skin contact with it.

Many petroleum products, especially the more volatile ones, cause irritation and remove essential oils, possibly leading to dermatitis, when they come into contact with the skin. They can also cause irritation to the eyes. Certain heavier oils can cause serious skin disorders on repeated and prolonged contact. Direct contact with petroleum should always be avoided by wearing the appropriate protective equipment, especially impermeable gloves and goggles.

The MSDS should be consulted for information on the appropriate PPE to be worn.

2.3.3 Product Vapours

2.3.3.1 Inhalation

The effects of inhaling product gases can vary considerably. Gases can have acute (unconsciousness, dizziness, chemical burns, organ failure) or chronic (cancer, organ damage, reprotoxic) effects. Of importance is the risk of pulmonary oedema. Liquid in the lungs can cause serious shortness of breath and often may occur hours after the inhalation.

The Material Data Sheet should be checked for the specific information and for the measures that have to be taken when a person has inhaled the product vapour. The MSDS will also describe the required PPE.

The absence of smell should never be taken to indicate the absence of gas.

In general, the danger of the product increases when the vapour pressure is high and the Threshold Limit Value is low.

Comparatively small quantities of product gas, when inhaled, can cause symptoms of diminished responsibility and dizziness similar to intoxication, with headache and irritation of the eyes. The inhalation of an excessive quantity can be fatal. This depends mainly on the product, for which information should be sought from the MSDS.

These symptoms can occur at concentrations well below the Lower Explosive Limit. However, petroleum gases vary in their physiological effects and human tolerance to these effects also varies widely. It should not be assumed that, because conditions can be tolerated, the gas concentration is within safe limits.

The smell of product gas mixtures is very variable and in some cases the gases may dull the sense of smell. The impairment of smell is especially likely, and particularly serious, if the mixture contains hydrogen sulphide.

2.3.3.2 Exposure Limits

The exposure limits are always described in the MSDS.

Exposure limits set by international organisations, national administrations or by local regulatory standards should not be exceeded.

Industry bodies and oil companies often refer to the American Conference of Governmental Industrial Hygienists (ACGIH) which has established guidelines on limits that are expected to protect personnel against harmful vapours in the working environment. The values quoted are expressed as Threshold Limit Values (TLVs) in parts per million (ppm) by volume of gas in air.

Best practice is to maintain concentrations of all atmospheric contaminants as low as reasonably practicable (ALARP).

In the following text, the term TLV-TWA (Time Weighted Average) is used. Because they are averages, TWAs assume short-term exposures above the TLV-TWA that are not sufficiently high to cause injury to health and that are compensated by equivalent exposures below the TLV-TWA during the conventional 8 hour working day.

To avoid the damage to health, exposure peaks have to be limited (see MSDS or similar).

2.3.3.3 Effects

The effects of exposure to vapours can vary depending on the type of product and information should be obtained from MSDS for the product.

2.3.4 Material Safety Data Sheets (MSDS) / Safety Data Sheets (SDS)

To assist ship's crews in preparing for toxic cargoes, the IMO has urged governments to ensure that ships are supplied with, and carry, Material Safety Data Sheets (MSDS) for significant cargoes. The MSDS should indicate the type and probable concentrations of hazardous or toxic components in the cargo to be loaded, particularly H₂S and benzene. In UN ECE and EU regulation these documents are called Safety Data Sheets (SDS). The MSDS or SDS has to be based on the standard format required by the applicable legislation.

The supplier should provide the relevant MSDS to a tanker before it commences loading the products. The tanker should provide the receiver with an MSDS for the cargo to be discharged. The tanker should also advise the terminal and any tank inspectors or surveyors whether the previous cargo contained any toxic substances.

Provision of an MSDS does not guarantee that all of the hazardous or toxic components of the particular cargo or bunkers being loaded have been identified or documented. Absence of an MSDS should not be taken to indicate the absence of hazardous or toxic components. Operators should have procedures in place to determine whether any toxic components are present in cargoes that they anticipate may contain them.

UN ECE and EU regulations do not require that tankers carry (M)SDS. Instead, tankers need to be issued with 'Instructions in Writing'. However, as these instructions contain fewer and more general information, it is strongly recommended that (M)SDS are available for all products carried on board as they will be of assistance in case of cargo related emergencies.

2.3.5 Benzene, other CMR-Products and other Aromatic Hydrocarbons

2.3.5.1 Aromatic Hydrocarbons

The aromatic hydrocarbons include benzene, toluene and xylene. These substances are components, in varying amounts, in many petroleum cargoes such as gasolines, gasoline blending components, reformates, naphthas, special boiling point solvents, turpentine substitute, white spirits and crude oil.

The supplier should advise the tanker of the aromatic hydrocarbon content of the cargo to be loaded (see Section 2.3.4 above).

2.3.5.2 Benzene and other CMR-Products

Exposure to concentrations of benzene vapours of only a few parts per million in air may affect bone marrow and may cause anaemia and leukaemia.

Benzene primarily presents an inhalation hazard. It has poor warning qualities as its odour threshold is well above the TLV-TWA.

Exposure Limits

IMO gives the TLV-TWA for benzene as 1 ppm over a period of eight hours. However, working procedures should aim at ensuring the lowest possible gas concentrations are achieved in work locations.

Personal Protective Equipment (PPE)

Personnel should be required to wear respiratory protective equipment under the following circumstances:

- Whenever they are at risk of being exposed to benzene vapours in excess of the TLV-TWA.
- When TLV-TWAs specified by national or international authorities are likely to be exceeded.
- When monitoring cannot be carried out.

Tank Entry

Prior to entry into a tank that has recently carried products containing benzene and/or other CMR-products, the tank should be tested for these concentrations. This is in addition to the requirements for enclosed space entry detailed in Chapter 10.

2.3.6 Hydrogen Sulphide (H₂S)

Hydrogen Sulphide (H₂S) is a very toxic, corrosive and flammable gas. It has a very low odour threshold and a distinctive odour of rotten eggs. H₂S is colourless, is heavier than air, has a relative vapour density of 1.189, and is soluble in water.

2.3.6.1 Sources of Hydrogen Sulphide (H₂S)

Many crude oils come out of the well with high levels of H₂S, but a stabilisation process usually reduces this level before the crude oil is delivered to the tanker. However, the amount of stabilisation may be temporarily reduced at times and a tanker may receive a cargo with an H₂S content higher than usual or expected. In addition, some crude oils are never stabilised and always contain high levels of H₂S.

H₂S can also be encountered in refined products such as naphtha, fuel oil, bunker fuels, bitumens and gas oils.

Cargo and bunker fuels (as cargo) should not be treated as free of H₂S until after they have been loaded and the absence of H₂S has been confirmed by both the results of monitoring and the relevant MSDS information.

2.3.6.2 Expected Concentrations

It is important to distinguish between concentrations of H₂S in the atmosphere, expressed in ppm by volume, and concentrations in liquid, expressed in ppm by weight.

It is not possible to predict the likely vapour concentration from any given liquid concentration but, as an example, a crude oil containing 70 ppm (by weight) H₂S has been shown to produce a concentration of 7,000 ppm (by volume) in the gas stream leaving the tank vent.

During transit, the concentration of H₂S vapours may increase significantly and therefore has to be monitored.

Attention should be given to the possibility of previous cargoes containing H₂S with respect to the release of contaminated vapours during loading, particularly when heated cargoes are being loaded.

Attention should also be given to the potential deviation of H₂S analysers which may be in the order of 0 – 3 ppm by weight.

Precautions against high H₂S concentrations are normally considered necessary if the H₂S content in the vapour phase is 5 ppm by volume or above. However, (inter)national legislation may be more stringent than this level.

The effects of H₂S at various increasing concentrations in air are shown in Table 2.1.

The H₂S concentration in vapour will vary greatly and is dependent upon factors such as:

- Liquid H₂S content.
- Amount of air circulation.
- Temperature of air and liquid.
- Liquid level in the tank.
- Amount of agitation.

2.3.6.3 Exposure Limits

For many countries, the TLV-TWA for H₂S is 5 ppm over a period of eight hours. However, (inter)national legislation may be more stringent. Working procedures should aim at ensuring that the lowest possible gas concentrations are achieved in work locations.

2.3.6.4 Procedures for Handling Cargo and Bunkers Containing H₂S

The following precautions should be taken when handling all cargoes and bunker fuels likely to contain hazardous concentrations of H₂S. They should also be taken when ballasting, cleaning or gas freeing tanks which previously contained a cargo with an H₂S content. Practical guidance on operational measures that can be taken to minimise the risks associated with loading cargoes containing H₂S is given in Section 11.1.9.

H ₂ S Concentration (ppm by volume in air)	Physiological Effects
0.1 - 0.5 ppm	First detectable by smell.
10 ppm	May cause some nausea, minimal eye irritation.
25 ppm	Eye and respiratory tract irritation. Strong odour.
50 - 100 ppm	Sense of smell starts to break down. Prolonged exposure to concentrations at 100 ppm induces a gradual increase in the severity of these symptoms and death may occur after 4-48 hours' exposure.
150 ppm	Loss of sense of smell in 2-5 minutes.
350 ppm	Could be fatal after 30 minutes' inhalation.
700 ppm	Rapidly induces unconsciousness (few minutes) and death. Causes seizures, loss of control of bowel and bladder. Breathing will stop and death will result if not rescued promptly.
700+ ppm	Immediately fatal.
<p>Note: Persons over-exposed to H₂S vapour should be removed to clean air as soon as possible.</p> <p>The adverse effects of H₂S can be reversed and the probability of saving the person's life improved if prompt action is taken.</p>	

Table 2.1 - Typical effects of exposure to hydrogen sulphide (H₂S)

Vapour Monitoring

Exposure levels in all work locations should be monitored by using suitable instrumentation for detecting and measuring the concentration of the gas.

High concentrations and the corrosive nature of the gas can have a damaging effect on many electronic instruments. Low concentrations of H₂S over time can also have a damaging effect on electronic instruments. Detector tubes should therefore be used if it becomes necessary to monitor a known high concentration.

The use of personal H₂S gas monitoring instruments for personnel engaged in cargo operations is strongly recommended. These instruments may provide either a warning alarm at a pre-set level or an H₂S reading and an alarm. It is further recommended that the alarms be set at a value of the maximum TLV – TWA. Personnel should always carry personal monitors when working in enclosed spaces, gauging, sampling, entering a pumphouse, connecting and disconnecting loading lines, cleaning filters, draining to open containments and mopping up spills if HS concentrations could exceed the TLV-TWA.

Passive sampling badges provide an immediate visual indication of when a specific chemical hazard is detected or when an established safe exposure level to such a chemical is exceeded. They should only be used for industrial hygiene purposes such as area sampling and for determining exposure of personnel over a period of time. They should never be used as an item of personal protective equipment.

Personal Protective Equipment (PPE)

Procedures should be defined for the use of respiratory protective equipment when concentrations of vapour may be expected to exceed the TLV-TWA.

Consideration should be given to providing Emergency Escape Breathing Devices (EEBD) to personnel working in hazardous areas. These are very portable and can be donned quickly should gas be detected.

Personnel should be required to wear respiratory equipment under the following circumstances:

- Whenever they are at risk of being exposed to H₂S vapours in excess of the TLV-TWA.
- When TLV-TWAs specified by national or international authorities are exceeded or are likely to be exceeded.
- When monitoring cannot be carried out.
- When closed operations cannot be conducted for any reason and H₂S concentrations could exceed the TLV-TWA.

Company and Terminal Procedures

The tanker's Safety Management System (SMS) and the terminal's Operations Manual should contain instructions and procedures to ensure safe operations when handling cargoes that are likely to contain H₂S. The functional requirements should include, but not be limited to, the following:

- Training of all crew members in the hazards associated with H₂S and the precautions to be taken to reduce the risks to acceptable levels.
- Safe operating procedures for all operations.

- Gas testing/atmosphere monitoring procedures.
- Maintenance procedures for cargo related systems.
- PPE requirements.
- Contingency planning.
- Emergency response measures.
- Measures to protect visitors from exposure.

2.3.6.5 Additional Procedures when Handling Cargoes with Very High Concentrations of H₂S

Companies and terminals should develop additional procedures for use when handling cargoes with very high levels of H₂S. (100 ppm in the vapour space is considered to be a reasonable threshold.)

To prevent exposure to high concentrations of hydrogen sulphide, crew members on deck should wear a personal hydrogen sulphide alarm meter. When this meter gives an alarm the following actions, as a minimum, should be taken immediately:

- Stop cargo operations.
- Inform other crew members.
- Inform jetty personnel.
- Inform other adjacent tankers (especially those at leeward side).
- Inform tanker's operator.
- Ask terminal to perform a measurement.
- Discuss, in close cooperation with terminal and operator, how to proceed with the transfer operation.

Try to stay at windward side and do not stay on deck unnecessarily.

2.3.6.6 Corrosion

H₂S is very corrosive and enhanced inspection and maintenance regimes should be put in place if H₂S is likely to be present in high concentrations.

Pressure/vacuum valve seats made of brass are more likely to fail than stainless steel seats.

Mechanical tank gauges are more likely to fail since H₂S has a damaging effect on stainless steel tension springs and metals such as brass and bronze. An increase in the spare parts inventory may be necessary.

Computer and instrument components made of silver and gold are highly affected by even low H₂S concentrations.

2.3.6.7 General Nuisances

In addition to being a health hazard, the H₂S odour is also considered a public nuisance. Most local environmental regulations limit or ban the release of H₂S concentrations to the atmosphere and this is, in any case, good practice. It is therefore necessary to maintain cargo tank pressures within acceptably low limits.

The tank vapour pressure will rapidly increase if the vapour space is exposed to heat or the product is agitated.

2.3.7 Mercaptans

Mercaptans are colourless, odorous gases generated naturally by the degradation of natural organisms. Their smell has been likened to rotting cabbage. They can also be found in water treatment plants and ballast treatment facilities.

Mercaptans are also present in the vapours of pentane plus cargoes and in some crude oils. They are also used as an odourising agent in natural gas.

Mercaptans can be detected by smell at concentrations below 0.5 ppm, although health effects are not experienced until the concentration is several times higher than this.

The initial effects of mercaptans on people are similar to those caused by H₂S exposure, i.e. irritation to the lungs, eyes, nose and throat. If the concentration is very high, unconsciousness may occur and it may be necessary to administer oxygen.

2.3.8 Gasolines Containing Tetraethyl Lead (TEL) or Tetramethyl Lead (TML)

The amounts of Tetraethyl Lead (TEL) or Tetramethyl Lead (TML) normally added to gasolines are insufficient to render the gases from these products significantly more toxic than those from unleaded gasolines. The effects of the gases from leaded gasolines are therefore similar to those described for product gases (see Section 2.3.3).

2.3.9 Inert Gas

2.3.9.1 General

Inert gas is principally used to control cargo tank atmospheres, thus preventing the formation of flammable mixtures. The primary requirement for an inert gas is low oxygen content. Its composition can, however, be variable. (Table 7.1 in Section 7.1.3 provides an indication of typical inert gas components expressed as a percentage by volume.)

2.3.9.2 Toxic Constituents

The main hazard associated with inert gas is its low oxygen content. However, some inert gases might contain trace amounts of various toxic gases that may increase the hazard to personnel exposed to them.

Precautions prior to tank entry do not include requirements for the direct measurement of the concentration of the trace constituents of inert gas. This is because the gas freeing activity required for tank entry is sufficient to reduce these toxic constituents to below their TLV-TWA.

2.3.9.3 N/A

2.3.9.4 N/A

2.3.9.5 N/A

2.3.10 Oxygen Deficiency

The oxygen content of the atmosphere in enclosed spaces may be low for several reasons. The most obvious one is if the space is in an inert condition, and the oxygen has been displaced by the inert gas. Oxygen may also be removed from an atmosphere by chemical reactions, such as rusting or the hardening of paints or coatings.

As the amount of available oxygen decreases below the normal 21% by volume, breathing tends to become faster and deeper. Symptoms indicating that an atmosphere is deficient in oxygen may give inadequate notice of danger. Most people would fail to recognise the danger until they were too weak to be able to escape without help. This is especially so when escape involves the exertion of climbing.

While individuals vary in susceptibility, all will suffer impairment if the oxygen level falls to 16% by volume.

Exposure to an atmosphere containing less than 10% oxygen content by volume inevitably causes unconsciousness. The rapidity of onset of unconsciousness increases as the availability of oxygen diminishes, and death will result unless the victim is removed to the open air and resuscitated.

An atmosphere containing less than 5% oxygen by volume causes immediate unconsciousness with no warning other than a gasp for air. If resuscitation is delayed for more than a few minutes, irreversible damage is done to the brain, even if life is subsequently saved.

2.3.11 FAME (Fatty Acid Methyl Ester)

FAME is used as a bio component to blend in middle distillate bio fuels. The molecules are primarily obtained from vegetable oils by transesterification (the process of exchanging the alcohol group of an ester compound with another alcohol). When shipped, care needs to be taken to avoid contamination with noxious materials that could affect the safety of the final product and effect the processing of the oleochemical itself. Methyl esters in the range C8 – C18 are practically non-toxic.

The resistance of cargo tank coatings and synthetic or rubber parts of cargo equipment to methyl esters should be considered.

2.3.12 MTBE/ETBE

Methyl-Tertiary-Butyl-Ether (MTBE) and Ethyl Tert-Butyl Ether (ETBE) are highly flammable liquids with a distinctive disagreeable odour. They are made from blending chemicals such as Isobutylene and Methanol, and have been used as an oxygenate gasoline additive in the production of gasoline. MTBE/ETBE quickly evaporates and small amounts may dissolve in water. MTBE/ETBE may stick to particles in water, which will cause it to eventually settle to the bottom sediment.

Consideration should be given to the environmental hazards associated with mixtures of water and MTBE/ETBE in cargo and slop tanks. It is recommended that MTBE/ETBE is only carried in tankers that have a segregated ballast system.

It is recommended that tankers carrying MTBE/ETBE are fitted with low-emission sampling points.

Ethyl Tert-Butyl Ether is commonly used as an oxygenate gasoline additive. MTBE and ETBE vapours are heavier than air so will naturally drift towards the river water surface. Thus in transit, ideally vapours should not be vented.

Ballasting should always be restricted to dedicated ballast tanks. Any cleaning of cargo tanks, as well as the disposal of any product residues and wash waters must be done in a controlled manner at authorised disposal facilities and according to the applicable local law.

2.3.13 Ethanol

Ethanol (ethyl alcohol, grain alcohol) denatured is a clear, colourless liquid with a characteristic, agreeable odour and is used as a blend component in bio fuels.

Ethanol is denatured to prevent its use as a beverage. Denatured ethanol can contain small amounts, 1 or 2% each, of several different unpleasant or poisonous substances.

Consideration should be given to mixtures of water and ethanol in cargo and slop tanks and related flammability. A separate ballast cargo tank system, as well as vapour return and efficient stripping facilities is preferred. Attention should be given to the wide flammable range (3.4 – 19% by volume in air) of product vapours and ballasting should always be restricted to dedicated ballast tanks. Any cleaning of cargo tanks, as well as the disposal of any product residues and wash waters, must be done in a controlled manner at authorised disposal facilities and according to the applicable local law.

2.4 Gas Measurement

2.4.1 Introduction

This Section describes the principles, uses and limitations of portable instruments for measuring concentrations of hydrocarbon gas (in inerted and non-inerted atmospheres), other toxic gases and oxygen. Certain fixed installations are also described. For detailed information on the use of all instruments, reference should always be made to the manufacturer's instructions and the product's MSDS.

It is essential that any instrument used is:

- Suitable for the test required.
- Sufficiently accurate for the test required.
- Of an approved type.
- Correctly maintained.
- Frequently checked against standard samples.

2.4.2 Measurement of Product Concentration

There are a number of different portable instruments available to detect product concentrations and hazardous atmospheres, toxic gases and oxygen. In the light of the differences in instrument sensitivity and limitations, reference should be made to guidance contained in manufacturer's literature and MSDSs when selecting an instrument for a particular task.

The measurement of hydrocarbon vapours on tankers and at terminals falls into two categories:

1. The measurement of hydrocarbon gas in air at concentrations below the Lower Explosive Limit (LEL).

This is to detect the presence of flammable (and potentially explosive) vapours and to detect concentrations of hydrocarbon vapour that may be harmful to personnel. These readings are expressed as a percentage of the Lower Explosive Limit (LEL) and are usually recorded as % LEL. The instruments used to measure % LEL are Catalytic Filament Combustible Gas (CFCG) Indicators, which are usually referred to as Flammable Gas Monitors or Explosimeters. A CFCG Indicator should not be used for measuring hydrocarbon gas in inert atmospheres.

2. The measurement of hydrocarbon gas as a percentage by volume of the total atmosphere being measured.

On board a tanker, this is usually carried out to measure the percentage of hydrocarbon vapour in an oxygen deficient (inerted) atmosphere. Instruments used to measure hydrocarbon vapours in an inert gas atmosphere are specially developed for this purpose. The readings obtained are expressed as the percentage of hydrocarbon vapour by volume and are recorded as % Vol.

The instruments used to measure percentage hydrocarbon vapours in inert gas are the Non-Catalytic Heated Filament Gas Indicators (usually referred to as Tanksopes) and Refractive Index Meters. Modern developments in gas detection technology have resulted in the introduction of electronic instruments using infra-red sensors that can perform the same function as the Tankscope.

2.4.3 Flammable Gas Monitors (Explosimeters)

Modern flammable gas monitors (Explosimeters) have a poison resistant flammable pellistor as the sensing element. Pellistors rely on the presence of oxygen (minimum 11% by volume) to operate efficiently and for this reason flammable gas monitors should not be used for measuring hydrocarbon gas in inert atmospheres.

2.4.3.1 Operating Principle

A simplified diagram of the electrical circuit incorporating a pellistor in a Wheatstone Bridge is shown in Figure 2.1.

Unlike early Explosimeters, the pellistor unit balances the voltage and zeros the display automatically when the instrument is switched on in fresh air. In general, it takes about 30 seconds for the pellistor to reach its operating temperature. However, the operator should always refer to the manufacturer's instructions for the start up procedure.

A gas sample may be taken in several ways:

- Diffusion.
- Hose and aspirator bulb (one squeeze equates to about 1 metre of hose length).
- Motorised pump (either internal or external).

Flammable vapours are drawn through a sintered filter (flashback arrestor) into the pellistor combustion chamber. Within the chamber are two elements, the Detector and the Compensator. This pair of elements is heated to between 400 and 600°C.

When no gas is present, the resistances of the two elements are balanced and the bridge will produce a stable baseline signal. When combustible gases are present, they will catalytically oxidise on the detector element causing its temperature to rise. This oxidation can only take place if there is sufficient oxygen present. The difference in temperature compared to the compensator element is shown as % LEL.

The reading is taken when the display is stable. Modern units will indicate on the display when the gas sample has exceeded the LEL.

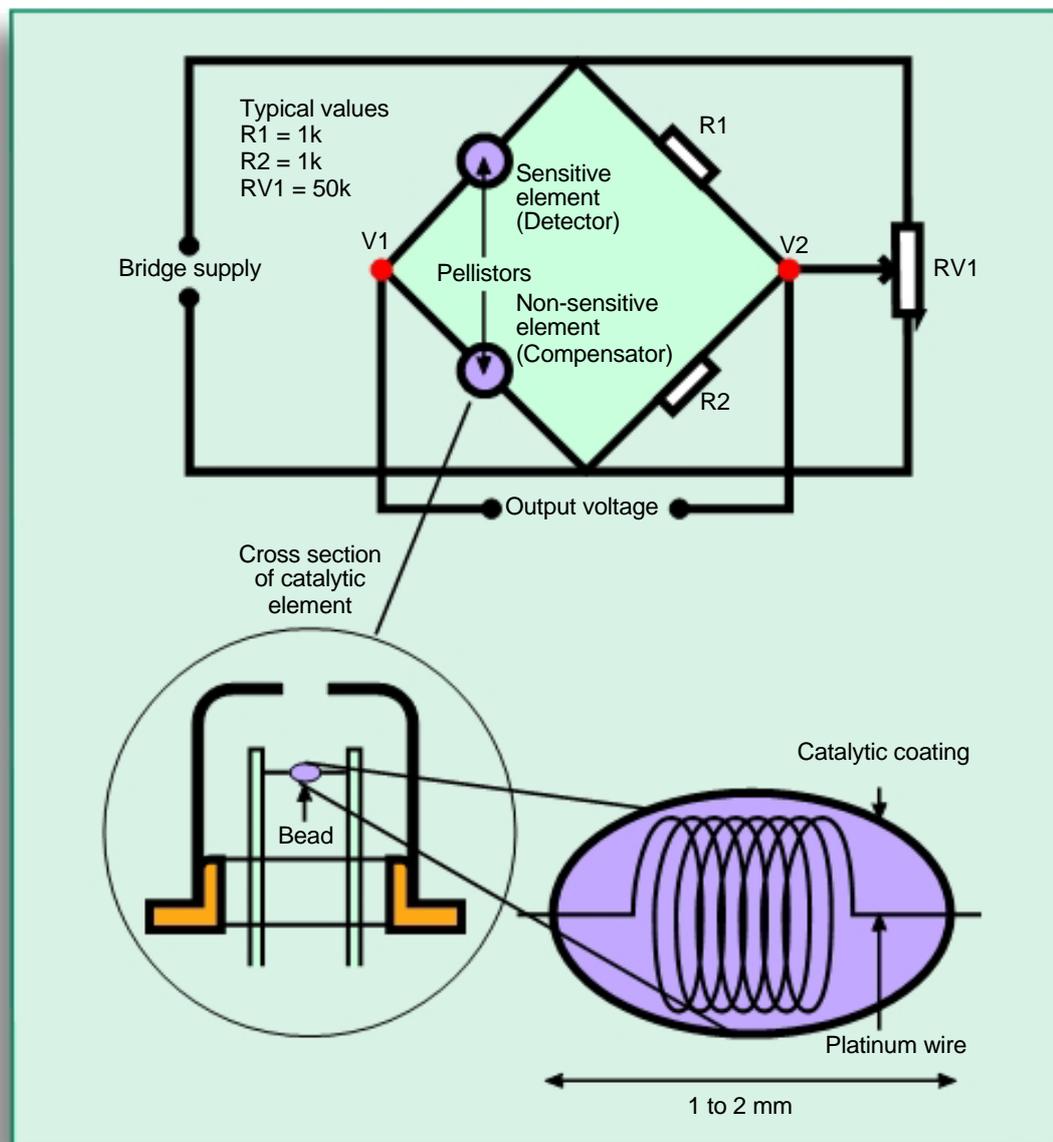


Figure 2.1 - Simplified diagram of a flammable gas monitor incorporating a pellistor

Care should be taken to ensure that liquid is not drawn into the instrument. The use of an in-line water trap and a float probe fitted to the end of the aspirator hose should prevent this occurrence. Most manufacturers offer these items as accessories.

Only cotton filters should be used to remove solid particles or liquid from the gas sample when hydrocarbons are being measured. Water traps may be used to protect the instrument where the sampled gas may be very wet. Guidelines on the use of filters and traps will be found in the operating manual for the instrument. (See also Section 2.4.13.3)

2.4.3.2 Cautions

Poisons and Inhibitors

Some compounds can reduce the sensitivity of the pellistor.

- Poisons - these are compounds that can permanently affect the performance of the pellistor and include silicone vapours and organic lead compounds.
- Inhibitors - these compounds act in a very similar way to poisons, except that the reaction is reversible. Inhibitors include hydrogen sulphide, freons and chlorinated hydrocarbons. If the presence of hydrogen sulphide is suspected, this should be tested for before any measurements of hydrocarbon vapours are carried out. (See Section 2.3.6.)

Pressure

Pellistor type instruments should not have their sensors subjected to pressure as this will damage the pellistor.

Such pressurisation may occur when testing for gas in the following conditions:

- Inert gas under high pressure or at high velocity, such as from a purge pipe or high velocity vent.
- Hydrocarbon gas mixtures at high velocity in vapour lines or from a high velocity vent.

The above is also relevant when using multi-gas instruments. For example, when an infra-red sensor is being utilised for taking a % Vol gas reading, any pellistor sensor in the instrument may suffer damage if the inlet gas stream into the instrument is at a pressure or has a high velocity.

Condensation

The performance of pellistors may be temporarily affected by condensation. This can occur when the instrument is taken into a humid atmosphere after it has been in an air conditioned environment. Time should be allowed for instruments to acclimatise to the operating temperature before they are used.

Combustible Mists

Pellistor instruments will not indicate the presence of combustible mists (such as lubricating oils) or dusts.

2.4.3.3 Instrument Calibration and Check Procedures

The instrument is set up in the factory to be calibrated using a specific hydrocarbon gas/air mixture. The hydrocarbon gas that should be used for calibration and testing should be indicated on a label fixed to the instrument.

Guidance on calibration and on operational testing and inspection of gas measuring instruments is given in Sections 8.2.6 and 8.2.7 respectively

2.4.3.4 Precision of Measurement

The response of the instrument depends upon the composition of the hydrocarbon gas being tested and, in practice, this composition is not known. By using propane or butane as the calibration gas for an instrument being used on tankers carrying stabilised crude oil or petroleum products, the readings provided may be slightly in error by giving a slightly high reading. This ensures that any reading indicated will be "on the safe side". (See also Section 8.2.6.)

Factors that can affect the measurements are large changes in ambient temperature and excessive pressure of the tank atmosphere being tested, leading to high flow rates which in turn affect the pellistor temperature.

The use of dilution tubes, which enable catalytic filament indicators to measure concentrations in over rich hydrocarbon gas/air mixtures, is not recommended.

2.4.3.5 Operational Features

Older instruments are fitted with flashback arresters in the inlet and outlet of the detector filament chamber. The arresters are essential to prevent the possibility of flame propagation from the combustible chamber and a check should always be made to ensure that they are in place and fitted properly. Modern pellistor type instruments have sintered filters usually built into the pellistor body.

Some authorities require, as a condition of their approval, that PVC covers be fitted around meters with aluminium cases to avoid the risk of incendive sparking if the case strikes rusty steel.

2.4.4 Non-Catalytic Heated Filament Gas Indicators (Tankscopes)

2.4.4.1 Operating Principle

The sensing element of this instrument is usually a non-catalytic hot filament. The composition of the surrounding gas determines the rate of loss of heat from the filament, and hence its temperature and resistance.

The sensor filament forms one arm of a Wheatstone Bridge. The initial zeroing operation balances the bridge and establishes the correct voltage across the filament, thus ensuring the correct operating temperature. During zeroing, the sensor filament is purged with air or inert gas that is free from hydrocarbons. As in the Explosimeter, there is a second identical filament in another arm of the bridge which is kept permanently in contact with air and which acts as a compensator filament.

The presence of hydrocarbon changes the resistance of the sensor filament and this is shown by a deflection on the bridge meter. The rate of heat loss from the filament is a non-linear function of hydrocarbon concentration and the meter scale reflects this non-linearity. The meter gives a direct reading of % volume hydrocarbons.

When using the instrument, the manufacturer's detailed instructions should always be followed. After the instrument has been initially set at zero with fresh air in contact with the sensor filament, a sample is drawn into the meter by means of a rubber aspirator bulb. The bulb should be operated until the meter pointer comes to rest on the scale (usually within 15-20 squeezes) then aspirating should be stopped and the final reading taken. It is important that the reading should be taken with no flow through the instrument and with the gas at normal atmospheric pressure.

The non-catalytic filament is not affected by gas concentrations in excess of its working scale. The instrument reading goes off the scale and remains in this position as long as the filament is exposed to the rich gas mixture.

2.4.4.2 Instrument Check Procedures

The checking of a non-catalytic heated filament instrument requires the provision of gas mixtures of a known total hydrocarbon concentration.

The carrier gas may be air, nitrogen or carbon dioxide or a mixture of these. Since this type of instrument may be required to measure accurately either low concentrations (1%-3% by volume) or high concentrations (greater than 10% by volume) it is desirable to have either two test mixtures, say 2% and 15% by volume, or one mixture between these two numbers, say 8% by volume. Test gas mixtures may be obtained in small aerosol type dispensers or small pressurised gas cylinders, or may be prepared in a special test kit.

2.4.4.3 Precision of Measurement

Correct response from these instruments is achieved only when measuring gas concentrations in mixtures for which the instrument has been calibrated and which remain gaseous at the temperature of the instrument.

Relatively small deviations from normal atmospheric pressure in the instrument produce significant differences in the indicated gas concentration. If a space that is under elevated pressure is sampled, it may be necessary to detach the sampling line from the instrument and allow the sample pressure to equalise with the atmosphere pressure.

2.4.4.4 Instruments with Infra-red Sensors

When selecting an instrument that uses an infra-red sensor for measuring the percentage by volume of hydrocarbon in an inert gas atmosphere, care should be taken to ensure that the sensor will provide accurate readings over the spectrum of gases likely to be present in the atmosphere to be measured. It may be prudent to make comparison readings with a Tankscope to verify the acceptability of the readings provided by the instrument under consideration.

2.4.5 Inferometer (Refractive Index Meter)

2.4.5.1 Operating Principle

An inferometer is an optical device that utilises the difference between the refractive indices of the gas sample and air.

In this type of instrument, a beam of light is divided into two and these are then recombined at the eyepiece. The recombined beams exhibit an interference pattern that appears to the observer as a number of dark lines in the eyepiece.

One light path is via chambers filled with air. The other path is via chambers through which the sample gas is pumped. Initially, the latter chambers are filled with air and the instrument is adjusted so that one of the dark lines coincides with the zero line on the instrument scale. If a gas mixture is then pumped into the sample chambers, the dark lines are displaced across the scale by an amount proportional to the change of refractive index.

The displacement is measured by noting the new position on the scale of the line that was used initially to zero the instrument. The scale may be calibrated in concentration units or it may be an arbitrary scale whose readings are converted to the required units by a table or graph.

The response of the instrument is linear and a one-point test with a standard mixture at a known concentration is sufficient for checking purposes.

The instrument is normally calibrated for a particular hydrocarbon gas mixture. As long as the use of the instrument is restricted to the calibration gas mixture, it provides accurate measurements of gas concentrations.

The measurement of the concentration of hydrocarbon gas in an inerted atmosphere is affected by the carbon dioxide present when flue gas is used for inerting. In this case, the use of soda lime as an absorbent for carbon dioxide is recommended, provided the reading is corrected appropriately.

The refractive index meter is not affected by gas concentrations in excess of its scale range. The instrument reading goes off the scale and remains in this position as long as the gas chambers are filled with the gas mixture.

2.4.5.2 Instrument Check Procedures

A mixture of known hydrocarbon, e.g. propane in nitrogen at a known concentration, should be used to check the instrument. If the hydrocarbon test gas differs from the original calibration gas, the indicated reading should be multiplied by the appropriate correction factor before judging the accuracy and stability of the instrument.

2.4.6 Infra-red (IR) Instruments

2.4.6.1 Operating Principle

The infra-red (IR) sensor is a transducer for the measurement of the concentration of hydrocarbons in the atmosphere, by the absorption of infra-red radiation.

The vapour to be monitored reaches the measuring chamber by diffusion or by means of a pump. Infra-red light radiation from the light source shines through a window into the chamber, is reflected and focused by the spherical mirror, and then passes through another window and hits the beam splitter. The portion of the radiation that passes through the beam splitter passes through a broadband interference filter (measuring filter) into the housing cover of the measuring detector, and is converted into an electric signal.

The portion of the radiation reflected by the beam splitter passes through the reference filter to reach the reference detector.

If the gas mixture in the chamber contains hydrocarbons, a part of the radiation is absorbed in the wavelength range of the measurement filter, and a reduced electric signal is given. At the same time, the signal of the reference detector remains unchanged. Gas concentration is determined by comparing the relative values of the reference detector and the measuring detector.

Differences in the output of the IR light source, dirt on mirrors and windows as well as dust of aerosols contained in the air have an identical effect on both detectors and are therefore compensated.

2.4.6.2 Instrument Check Procedures

This instrument should be checked using a check gas of a known mixture of hydrocarbons. The IR sensor does not require the presence of air or inert gas in the gas concentration, as it is reliant solely on the hydrocarbon molecules. In general, these instruments are very stable and require little maintenance. Calibration should be checked frequently in accordance with the manufacturer's instructions and ship's Safety Management System procedures. (See also Section 2.4.4.4.)

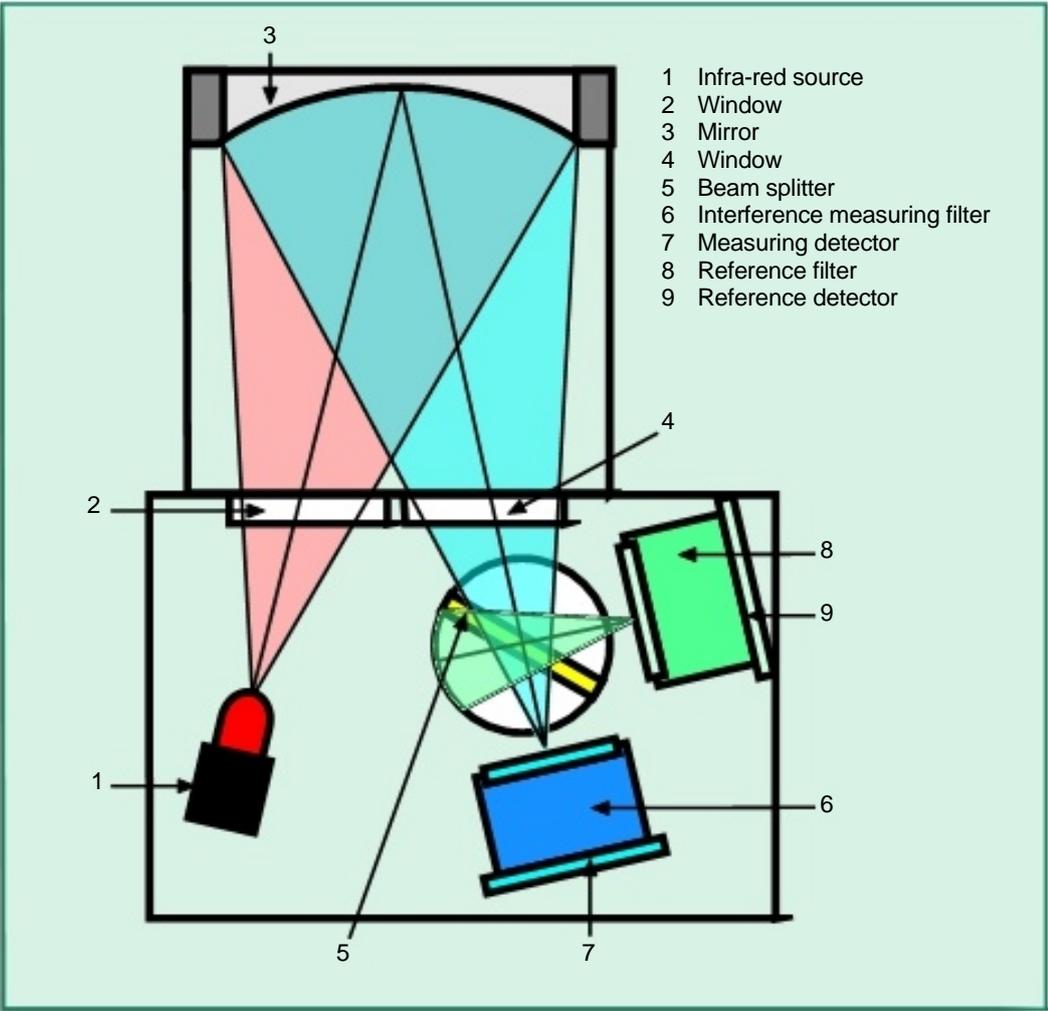


Figure 2.2 - Infra-red sensor

2.4.7 Measurement of Low Concentrations of Toxic Gases

2.4.7.1 Chemical Indicator Tubes

Probably the most convenient and suitable equipment for measuring very low concentrations of toxic gases on board tankers are chemical indicator tubes.

Measurement errors may occur if several gases are present at the same time, as one gas can interfere with the measurement of another. The instrument manufacturer's operating instructions should always be consulted prior to testing such atmospheres.

Chemical indicator tubes consist of a sealed glass tube containing a proprietary filling which is designed to react with a specific gas and to give a visible indication of the concentration of that gas. To use the device, the seals at each end of the glass tube are broken, the tube is inserted in a bellows-type fixed volume displacement hand pump, and a prescribed volume of gas mixture is drawn through the tube at a rate fixed by the rate of expansion of the bellows. A colour change occurs along the tube and the length of discoloration, which is a measure of the gas concentration, is read off a scale integral to the tube.

In some versions of these instruments, a hand operated injection syringe is used instead of a bellows pump.

It is important that all the components used for any measurement should be from the same manufacturer. It is not permissible to use a tube from one manufacturer with a hand pump from another manufacturer. It is also important that the manufacturer's operating instructions are carefully observed.

Since the measurement depends on passing a fixed volume of gas through the glass tube, any use of extension hoses should be in strict accordance with the manufacturer's instructions.

The tubes are designed and intended to measure concentrations of gas in the air. As a result, measurements made in a ventilated tank, in preparation for tank entry, should be reliable.

For each type of tube, the manufacturers must guarantee the standards of accuracy laid down in national standards. Tanker operators should consult the ship's flag administration for guidance on acceptable equipment.

2.4.7.2 Electrochemical Sensors

Electrochemical sensors are based on the fact that cells can be constructed that react with the measured gas and generate an electric current. This current can be measured and the amount of gas determined. The sensors are low cost and are small enough to allow several to be incorporated into the same instrument, making them suitable for use in multi-gas detectors.

There are numerous electrochemical sensors available covering a number of gases which may be present in the shipboard environment, such as ammonia, hydrogen sulphide, carbon monoxide, carbon dioxide and sulphur dioxide.

Electrochemical sensors can be used in stand-alone instruments, which may provide a warning at a predetermined concentration of vapour, or they can be fitted in a multi-sensor instrument to provide a reading of the concentration of the vapour, usually in parts per million (ppm).

These sensors may give erroneous readings due to cross-sensitivity. This occurs, for example, when measuring toxic gases with hydrocarbon gases present, for example H₂S in the presence of nitric oxide and sulphur dioxide.

2.4.8 Fixed Gas Detection Installations

Fixed gas detection installations are used on some tankers to monitor the flammability of the atmosphere in spaces such as double hull spaces, pumprooms double bottoms, engine rooms, boiler rooms, wheel house and accommodation(s).

Three general arrangements have been developed for fixed monitoring installations, as follows:

- Sensing devices distributed throughout the spaces to be monitored. Signals are taken sequentially from each sensor by a central control.
- A gas measurement system installed in the central control panel.
- Infra-red sensors located in the space being monitored with the electronics necessary for processing the signals located in a safe location.

Fixed gas detection units are usually fitted as a means of detecting leakage and not for gas testing prior to entry. Gas testing for entry should only be carried out using equipment that has been calibrated and tested and that has appropriate indicator scales. Some fixed gas detection units do meet these criteria. (See Section 10.10.2.)

2.4.9 Measurement of Oxygen Concentrations

Portable oxygen analysers are normally used to determine whether the atmosphere inside an enclosed space (cargo tank for example) may be considered fully inerted or safe for entry. Fixed oxygen analysers are used for monitoring the oxygen content of the boiler uptakes and the inert gas main.

The following are the most common types of oxygen analysers in use:

- Paramagnetic sensors.
- Electrochemical sensors.

All analysers, regardless of type, should be used strictly in accordance with the manufacturer's instructions. If so used, and subject to the limitations listed below, the analysers may be regarded as reliable.

2.4.10 Use of Oxygen Analysers

2.4.10.1 Paramagnetic Sensors

Oxygen is strongly paramagnetic (i.e. it is attracted by the poles of a magnet but does not retain any permanent magnetism) whereas most other common gases are not. This property means that oxygen content can be measured in a wide variety of gas mixtures.

One commonly used oxygen analyser of the paramagnetic type has a sample cell in which a lightweight body is suspended in a magnetic field. When sample gas is drawn through the cell, the suspended body experiences a torque proportional to the magnetic susceptibility of the gas. An electric current passing through a coil wound around the suspended body produces an equal and opposing torque. The equalising current is a measure of the magnetic force and is thus a measure of the magnetic susceptibility of the sample, i.e. related to its oxygen content.

Before use, the analyser should be tested with air for a reference point of 21% oxygen and with nitrogen or carbon dioxide for a 0% oxygen reference point.

Releasing nitrogen or carbon dioxide in a confined or unventilated area can lower the concentration of oxygen to a level that is immediately dangerous to life or health. Calibration should therefore only be carried out in well ventilated areas.

The analyser readings are directly proportional to the pressure in the measuring cell. The unit is calibrated to a specific atmospheric pressure and the small error due to atmospheric pressure variations can be corrected if required. Continuous samples should be supplied to the instrument by positive pressure. They should not be drawn through the analyser by negative pressure as the measuring pressure then becomes uncertain.

The filter should be cleared or replaced when an increase in sample pressure is required to maintain a reasonable gas flow through the analyser. The same effect is produced if the filter becomes wet due to insufficient gas drying. The need for filter cleaning or replacement should be checked regularly.

2.4.10.2 Electrochemical Sensors

Analysers of this type determine the oxygen content of a gas mixture by measuring the output of an electrochemical cell. In one commonly used analyser, oxygen diffuses through a membrane into the cell, causing current to flow between two special electrodes separated by a liquid or gel electrolyte.

The current flow is related to the oxygen concentration in the sample and the scale is arranged to give a direct indication of oxygen content. The cell may be housed in a separate sensor head connected by cable to the read out unit.

The analyser readings are directly proportional to the pressure in the measuring cell, but only small errors are caused by normal variations in atmospheric pressure.

Certain gases may affect the sensor and give rise to false readings. Sulphur dioxide and oxides of nitrogen interfere if they are present in concentrations of more than 0.25% by volume. Mercaptans and hydrogen sulphide can poison the sensor if their levels are greater than 1% by volume. This poisoning does not occur immediately but over a period of time; a poisoned sensor drifts and cannot be calibrated in air. In such cases, reference should be made to the manufacturer's instructions.

2.4.10.3 Maintenance, Calibration and Test Procedures

As these oxygen analysers are of vital importance, they should have a valid calibration certificate and should be tested strictly in accordance with the manufacturer's instructions before use.

It is essential that, each time an instrument is to be used, a check is made of batteries (if fitted) and zero point (21% oxygen) setting. During use, frequent checks should be made to ensure accurate readings are obtained at all times.

Testing is simple on all analysers using atmospheric air to test the reference point (21% oxygen) and an inert gas to test the 0% oxygen reference point (nitrogen or carbon dioxide). (See also Sections 8.2.6 and 8.2.7.)

2.4.11 Multi-gas Instruments

Multi-gas instruments are now widely used and are usually capable of housing four different sensors. A typical configuration would comprise sensors for measuring:

- Hydrocarbon vapour as a % LEL (explosimeter function using a pellistor sensor).
- Hydrocarbon vapour in inert gas as a % Volume (tankscope function using an infra-red sensor).
- Oxygen (using an electrochemical sensor).
- Hydrogen Sulphide (using an electrochemical sensor).

Multi-gas instruments should be tested at regular intervals in accordance with the manufacturer's instructions.

Multi-gas instruments may be supplied for gas measurement use and be fitted with a data logging capability, but without an alarm function.

Care should be taken when using multi-gas instruments to check for hydrocarbons in an inerted atmosphere under pressure as the pellistor within the instrument could be damaged if subjected to pressure (see Section 2.4.3.2).

2.4.12 Personal Gas Monitors

Multi-gas instruments may be supplied as compact units fitted with an alarm function for personal protective use during tank entry. These personal monitors are capable of continuously measuring the content of the atmosphere by diffusion. They usually employ up to four electrochemical sensors and should automatically provide an audible and visual alarm when the atmosphere becomes unsafe, thereby giving the wearer adequate warning of unsafe conditions.

Disposable personal gas monitors are now available. They usually provide protection against a single gas and are available for low oxygen level, and high concentrations of hydrocarbons and other toxic vapours. The units should provide both audible and visual warning at specified levels of vapour concentration, which should be at or below the TLV-TWA for the monitored vapour. These monitors typically weigh less than 100 grams and have a life of about 2 years.

2.4.13 Gas Sample Lines and Sampling Procedures

2.4.13.1 Gas Sample Lines

The material and condition of sample lines can affect the accuracy of gas measurements.

Metal tubes are unsuited to most cargo tank gas measurements and flexible lines should be used.

The gases from crude oils and many petroleum products are composed essentially of paraffinic hydrocarbons and there are a number of suitable materials available for flexible sample tubing. The problem of material selection is more difficult for those gases containing substantial proportions of aromatic hydrocarbons, in particular xylene. It is recommended that in such cases suppliers of sample tubing should be asked to provide test data showing the suitability of their product for the purposes for which it will be employed.

Sample tubing should be resistant to hot wash water.

Sample tubing which is cracked or blocked, or which has become contaminated with cargo residues, greatly affects instrument readings. Users should check the condition of the tubing regularly and replace any found to be defective.

In order to prevent liquid from being drawn up the gas sampling line and causing contamination of the line, manufacturers provide a float termination or a probe termination to prevent the ingress of liquid. Operators should consider using these fittings, but should be aware of any limitations on their use to avoid static hazards.

2.4.13.2 Sampling Procedures

Every tank has 'dead spots' where the rate of change of gas concentration during ventilation or purging is less than the average in the bulk of the tank. The location of these dead spots depends on the positions of the inlet and outlet through which ventilating air or inert gas is admitted and expelled and also on the disposition of the structural members in the tank. Generally, but not invariably, the dead spots are to be found within the tank bottom structure. The sample line should be long enough to permit sampling in the bottom structure.

Differences in gas concentration between the bulk volume of the tank and the dead spots vary depending on the operating procedures in use. For example, the powerful water jets produced by fixed washing machines are excellent mixing devices which tend to eliminate major differences in gas concentration between one location in the tank and another. Similarly, the introduction of ventilating air or inert gas as powerful jets directed downwards from the deckhead produces good mixing and minimises variations in concentration.

Because of the hazards associated with these dead spots, it is important to refer to Chapter 10 before entering any cargo tank or other enclosed space.

2.4.13.3 Filters in Sample Lines

Cotton filters are used to remove water vapour in some hydrocarbon gas meters, of either the catalytic or non-catalytic filament types, and additional filters are not normally needed. In extremely wet conditions, e.g. during tank washing, excessive water can be removed from the gas sample using materials that retain water but do not affect the hydrocarbons. Suitable materials are granular anhydrous calcium chloride or sulphate. If required, soda asbestos selectively retains hydrogen sulphide without affecting the hydrocarbons. However, it also retains carbon dioxide and sulphur dioxide and should not be used in tanks inerted with scrubbed flue gas.

Water traps are often used in modern gas measurement instruments. These utilise a Polytetrafluoroethylene (PTFE) membrane that prevents liquid and moisture passing onto the sensors.

The use of water-retaining filters is essential with oxygen meters, particularly of the paramagnetic type, because the presence of water vapour in the sample can damage the measuring cell. Only manufacturer's recommended filters should be used.

2.5 Product Gas Evolution and Dispersion

2.5.1 Introduction

During many cargo handling and associated operations, gas is expelled from cargo tank vents in sufficient quantity to give rise to flammable gas mixtures in the atmosphere outside the tanks. In this Guide, a major objective is to avoid such a flammable gas mixture being exposed to a source of ignition. In many cases, this is achieved either by eliminating the source of ignition or by ensuring that there are barriers, such as closed doors and ports, between the gas and unavoidable potential sources of ignition.

However, it is impossible to cover every possibility of human error and every combination of circumstances. An additional safeguard is introduced if operations can be arranged so that gas issuing from vents is dispersed sufficiently well to prevent flammable gas mixtures reaching those areas where sources of ignition may exist.

If gases are denser than air, this has an important bearing on how they behave, both inside and outside the tanks (see Section 1.3).

The gas which is vented is formed within the tanks and the way in which it is formed affects both the concentration when vented and the length of time during which a high concentration is vented. Situations which lead to gas evolution include loading, standing of cargo in full or part filled tanks (including slop tanks) and evaporation of tank residues after discharge.

The initial tank atmosphere, whether air or inert gas, has no bearing on gas evolution or venting.

2.5.2 Gas Evolution and Venting

2.5.2.1 Evolution During Loading

As a high vapour pressure cargo enters an empty gas free tank, there is a rapid evolution of gas. The gas forms a layer at the bottom of the tank that rises with the product surface as the tank is filled. Once it has been formed, the depth of the layer increases only slowly over the period of time normally required to fill a tank, although ultimately an equilibrium gas mixture is established throughout the ullage space.

The amount and concentration of gas forming this layer at the beginning of loading depend upon many factors, including:

- True Vapour Pressure (TVP) of the cargo.
- Amount of splashing as the product enters the tank.
- Time required to load the tank.
- Occurrence of a partial vacuum in the loading line.

The product gas concentration in the layer varies with distance above the liquid surface. Very close to the surface, it has a value close to that corresponding to the TVP of the adjoining liquid. For example, if the TVP is 0.75 bar, the product gas concentration just above the surface is about 75% by volume. Well above the surface, the hydrocarbon gas concentration is very small, assuming that the tank was originally gas free. In order to consider further the influence of gas layer depth, it is necessary to define this depth in some way.

When considering dispersion of gases outside cargo tanks, only high gas concentrations in the vented gas are relevant. For this purpose therefore, the gas layer depth will be taken as the distance from the liquid surface to the level above it where the gas concentration is 50% by volume. It should be remembered that product gas will be detectable at heights above the liquid surface several times the layer depth defined in this way.

Most high vapour pressure cargoes give rise to a gas layer with a depth in these terms of less than 1 metre. Its precise depth depends upon the factors listed above and most of the advice with respect to vented gas given in this Guide is intended for such cargoes. However, gas layers greater than 1 metre in depth may be encountered if the cargo TVP is great enough. Cargoes giving rise to these deeper gas layers may require special precautions (see Section 11.1.8).

2.5.2.2 Venting During the Loading of Cargo

Once the dense product gas layer has formed above the surface of the liquid, its depth, as defined in Section 2.5.2.1, increases only very slowly. As the liquid rises in the tank, the hydrocarbon gas layer rises with it. Above this layer, the atmosphere originally present in the tank persists almost unchanged and it is this gas that enters the venting system in the early stages of loading. In an initially gas free tank, the gas vented at first is therefore mainly air (or inert gas) with a product concentration below the LEL. As loading proceeds, the product content of the vented gas increases.

Concentrations in the range 30% - 50% by volume of product gas are quite usual in the vented gas towards the end of loading, although the very high concentration immediately above the liquid surface remains in the final ullage space on completion of loading.

Subsequently, evaporation continues until an equilibrium hydrocarbon gas concentration is established throughout the ullage space. This gas is only vented by breathing of the tank, and thus only intermittently. When the product is discharged, a very dense gas mixture travels to the bottom of the tank with the descending liquid surface and may contribute to the gas vented during the next operation in the tank.

If the tank is not initially gas free, the product gas concentration in the vented gas during loading depends upon the previous history of the tank. Before loading with a different product, the compatibility with the previous products must be checked to prevent any hazardous reactions.

The following provides examples of typical gas concentrations:

- Shortly after the discharge of a motor or aviation gasoline cargo, there is a layer at the bottom of the tank where concentrations of 30% - 40% by volume of hydrocarbons have been measured. If loaded at this stage, the gas enters the venting system immediately ahead of the concentrated layer formed by the next cargo.
- In motor or aviation gasoline tanks that have been battened down after discharge and not gas freed, uniform hydrocarbon gas concentrations as high as 40% by volume have been measured throughout the tanks. This concentration is expelled to the vent system throughout the next loading until the concentrated layer above the liquid surface approaches the top of the tank.

Note that in all loading operations, whether the tank is initially gas free or not, very high gas concentrations enter the venting system towards completion of loading.

2.5.2.3 Ballasting into a Cargo Tank

The atmosphere in cargo tanks before ballasting will be similar to that before the loading of the cargo, given a similar tank history. The gas concentration expected to enter the venting system during ballasting will therefore be comparable to that in the examples given above.

2.5.2.4 Inert Gas Purging

If inert gas purging is being carried out by the displacement method (see Section 7.1.4) any dense concentrated hydrocarbon layer at the bottom of the tank is expelled in the early stages, followed by the remainder of the tank atmosphere as it is pressed downwards by the inert gas. If there is a uniformly high concentration throughout the tank, for example after product washing, the product concentration of the vented gas remains high throughout the purging process until the inert gas reaches the bottom of the tank.

If inert gas purging is being carried out by the dilution method (see Section 7.1.4), the gas concentration at the outlet is highest at the beginning of the operation and falls continuously as it proceeds.

2.5.2.5 Gas Freeing

In a gas freeing operation, air is delivered into the tank where it mixes with the existing tank atmosphere and where it also tends to mix together any layers that may be present. The resultant mixture is expelled to the outside atmosphere. Because the process is one of continuous dilution with the air, the highest product concentration is vented at the beginning of gas freeing and decreases thereafter. For example, on a non-inerted tanker, gas freeing of a motor gasoline tank that has been battened down can give initial concentrations as high as 40% by volume, but in most circumstances the concentration in the vented gas is much lower, even at the start of the operations.

On inerted tankers, after purging to remove product vapour before gas freeing, the initial concentration will be low, 2% by volume or less.

In specific cases, gas freeing operations are regulated by legislation and require permits by competent authorities.

2.5.3 Gas Dispersion

Whether the product gas at the outlet is mixed with air or with inert gas will have no bearing on the dispersion of the gas after it has left the outlet.

As the product gas displaced during loading, ballasting, gas freeing or purging issues from the vent or vents on the tanker, it immediately starts to mix with the atmosphere.

The product concentration is progressively reduced until, at some distance from the vent, it passes below the LEL. At any point below the LEL, it ceases to be of concern as a flammability hazard because it cannot be ignited. However, there exists in the vicinity of any vent a flammable zone within which the gas concentration is above the LEL.

There is a potential danger of fire and explosion if this flammable zone reaches any location where there may be sources of ignition, such as:

- Accommodation blocks into which the gas can enter through doors, ports or ventilation intakes.
- The cargo deck which, although it is usually regarded as free of sources of ignition, is a work area and thoroughfare.
- An adjacent jetty which, although it is usually regarded as free of sources of ignition, is a work area and thoroughfare.
- Adjacent vessels.

2.5.4 Variables Affecting Dispersion

2.5.4.1 The Dispersion Process

A mixture of product gas and air (or inert gas), issuing vertically from an outlet, rises under its own momentum as a plume above the outlet. If there is no wind, the plume remains vertical, but otherwise it is bent over in the downwind direction. The rise of the plume due to its momentum is opposed by a tendency to sink if its density is greater than that of the surrounding air.

The flow velocity of the issuing gas is at its maximum as it passes through the outlet, and decreases as air is drawn into the plume. This air decreases the product gas concentration and hence the gas density in the plume. The progressive decreases in velocity, product concentration and density, together with the wind speed and other meteorological factors, determine the final shape of the plume and hence of the flammable zone.

The type of vent being used affects the dispersion of the gas plume. During normal loading operations, the venting will be either via:

- A high velocity vent installed at a minimum height of 2 m above the deck, which causes the vapour to be vented at a speed of 30 m/second irrespective of the loading rate of the cargo, or
- A vent riser with a minimum height of 6 m above the deck.

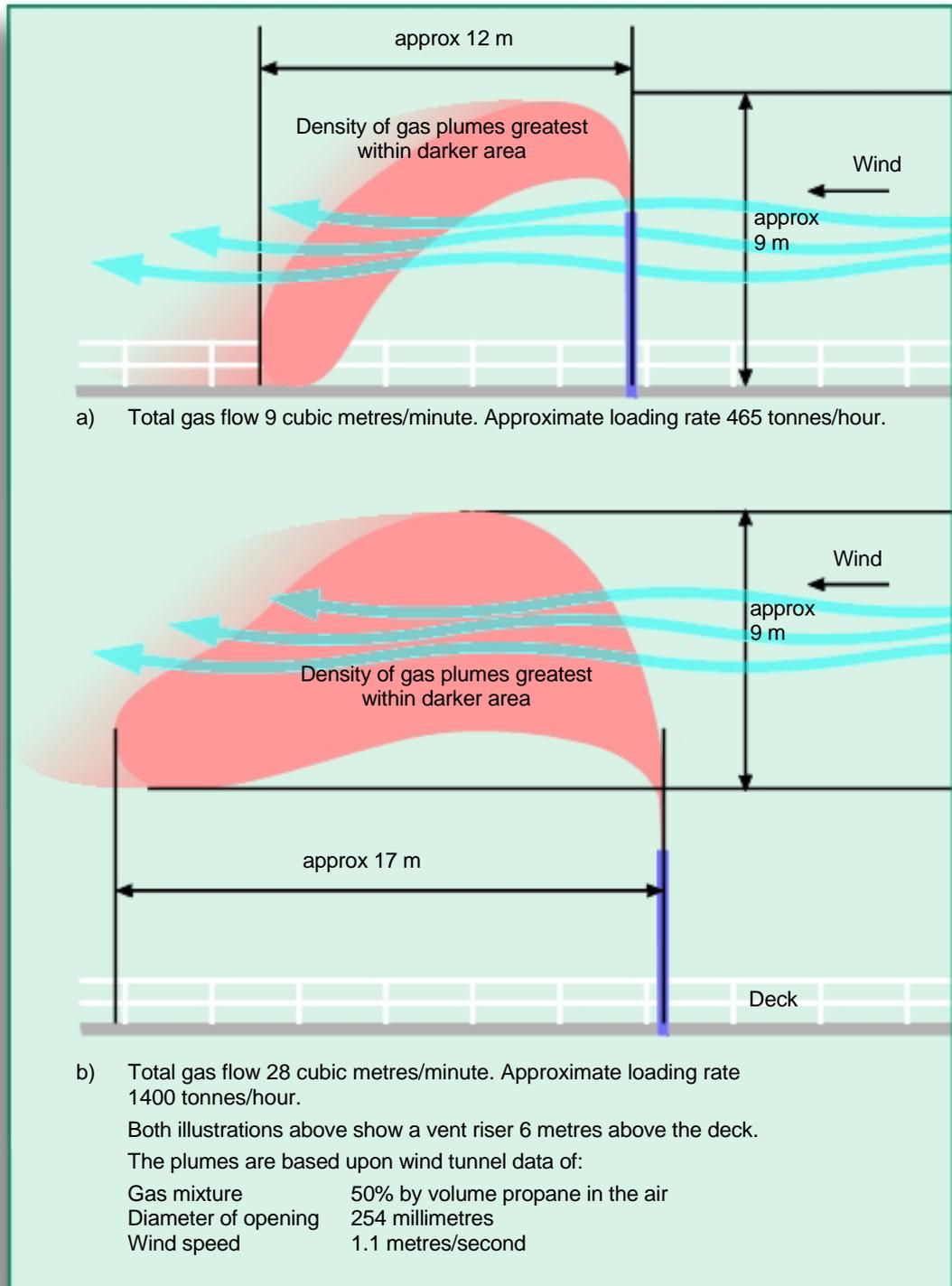
These high velocity vents and risers may not be placed closer than 10 m to any accommodation house vent, to ensure that cargo vapours will be safely dispersed before they reach these locations.

2.5.4.2 Wind Speed

For many years, it has been recognised that the dispersion of product gas/air mixtures is inhibited by low wind speeds. This recognition is based upon experience on tankers and little experimental work has been done to obtain quantitative information on the effect of wind speed. Much depends upon the quantity of gas being vented and how it is vented, but experience at terminals seems to suggest that, at wind speeds above about 5 metres/sec (10 knots), dispersion is sufficient to avoid any flammability risk.

2.5.4.3 Rate of Flow of Gas

As the rate of flow of a product gas/air mixture of fixed composition is increased through a given opening, several effects come into play. In the first place, the rate of emission of the product constituent increases in proportion to the total gas flow rate and therefore the distance the plume travels before it is diluted to the LEL should be greater. On the other hand, the higher the velocity, the more efficient is the mixing of the initially product-rich gas with the air and this tends to counterbalance the first effect.



Figures 2.3 (a) and (b) - Indicative effect of gas flow rate on flammable zone

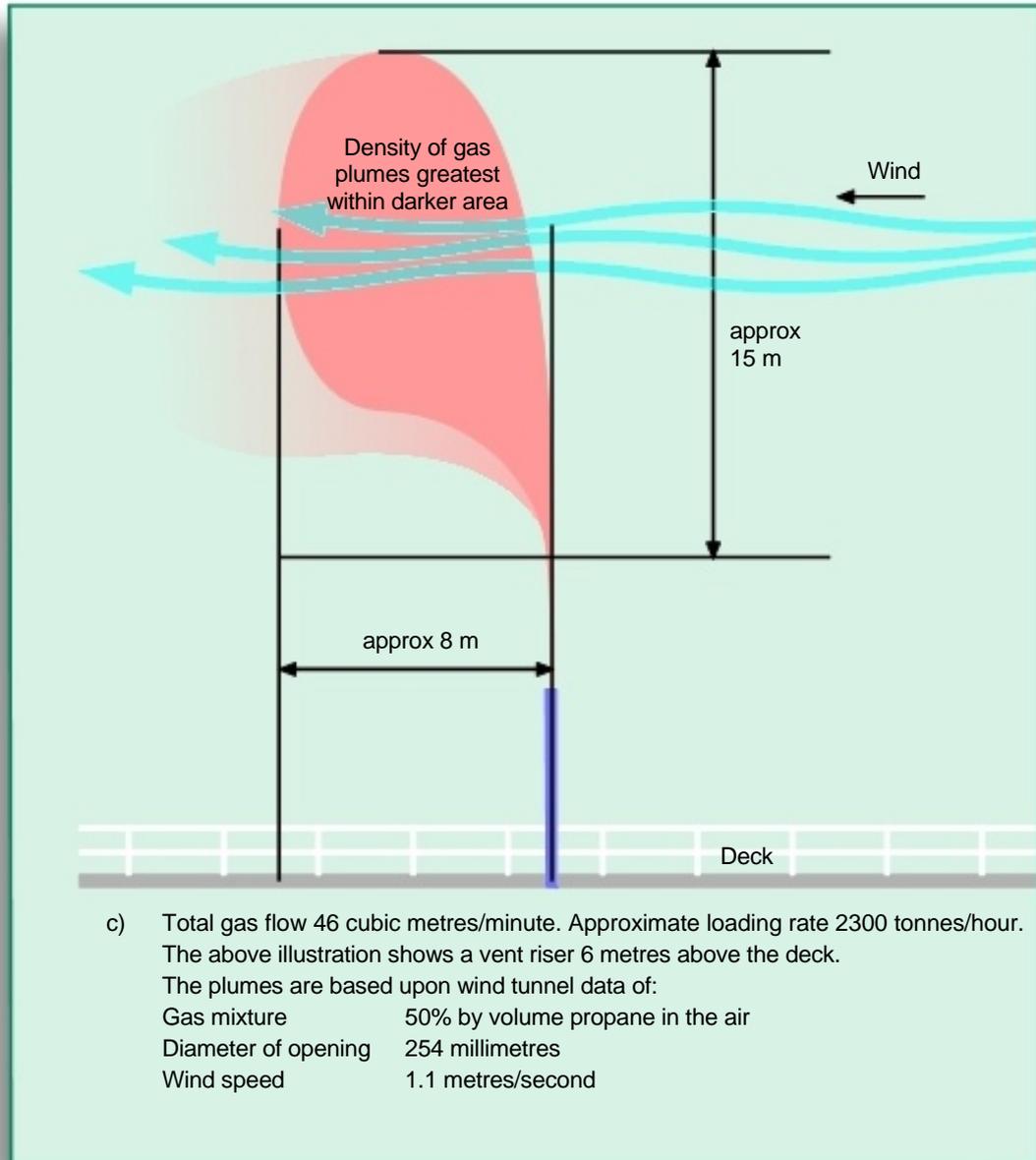


Figure 2.3 (c) - Indicative effect of gas flow rate on flammable zone

In addition, at low rates of total gas flow, the initial momentum of the plume may not be enough to counteract the tendency of the plume to sink if it has a high density.

The results of the interaction of these different processes at low wind speed are illustrated in Figure 2.3. The gas mixture used in obtaining these diagrams was 50% by volume propane and 50% by volume air. At the lowest flow rate (Figure 2.3 (a)) the density effect predominates and the gas sinks back towards the deck. At the highest flow rate (Figure 2.3 (c)) mixing is far more efficient and there is no tendency for the plume to sink.

2.5.4.4 Concentration of Product Gas

With a constant total rate of flow of gas, changes in product concentration have two effects. The rate of emission of hydrocarbon gas increases in proportion to the concentration so that, other things being equal, the extent of the flammable zone increases. Also, the initial density of the gas mixture as it issues from the opening becomes greater so that there is a greater tendency for the plume to sink.

At low concentrations, therefore, a flammable zone similar in outline to that shown in Figure 2.3 (c) is to be expected, but it is likely to be small because of the relatively small amount of hydrocarbon gas. As the concentration increases, the flammable zone tends to assume such shapes as depicted in Figures 2.3 (b) and 2.3 (a) as the increasing density exerts its influence. In addition, the overall size of the zone becomes greater due to the greater rate of emission of hydrocarbon gas.

2.5.4.5 Cross-Sectional Area of the Opening

The area of the opening through which the product gas/air mixture issues determines, for a given volumetric rate of flow, the linear flow velocity and hence the efficiency of the mixing of the plume with the atmosphere. Effects of this kind occur, for example, in gas freeing. If fixed turbo-blower fans are used, the mixture is usually vented through a standpipe with a cross-sectional area small enough to give a high velocity and to encourage dispersion in the atmosphere. When using small portable blowers, which normally have to be operated against a low back pressure, it is usual to exhaust the gas through an open tank hatch. The outflow velocity is then very low with the outlet close to the deck; circumstances that encourage the gas to remain close to the deck.

2.5.4.6 The Design of the Vent Outlet

The design and position of a vent outlet must comply with current applicable (inter)national legislation.

In certain operations, such as gas freeing, vapour may be vented from the tank through apertures other than these designated tank vents.

2.5.4.7 Position of the Vent Outlet

If vent outlets are situated near structures such as accommodation blocks, the shape of the flammable zone is influenced by turbulence produced in the air as it passes over the superstructure. A diagram illustrating the kind of eddies formed is given in Figure 2.4. This shows how, on the upwind side, there are downward eddies below a level indicated by the line X-X and how, above and in the lee of the structure, there is a tendency for turbulent air to form eddies close to the structure.

These movements can adversely affect the efficient dispersion of product gas.

If the exit velocity from an opening near a structure is high, it can overcome the influence of eddies.

For example, Figure 2.5 (a) shows the flammable zone from a tank opening situated only about 1.5 metres upwind of an accommodation block; the plume is almost vertical and only just touches the accommodation block. However, a somewhat lower rate of venting would have resulted in serious impingement of the zone upon the accommodation block.

Figure 2.5 (b) illustrates the effect of an additional opening which doubles the amount of gas released. Partly as the result of eddies and partly due to the denser combined plume, the flammable zone is in close contact with the top of the accommodation block.

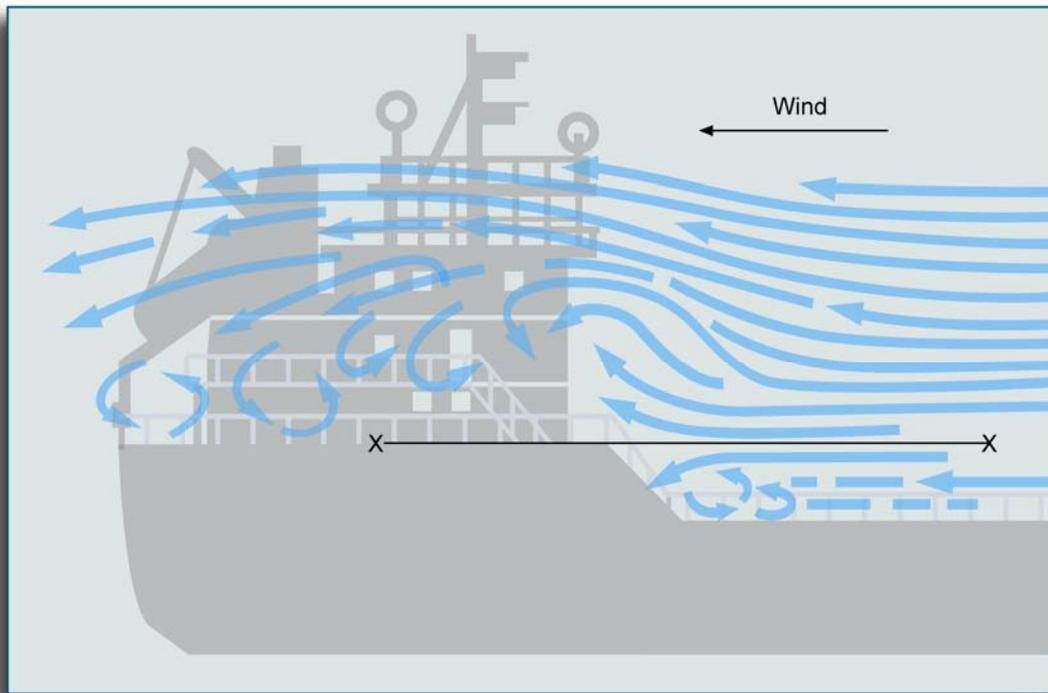


Figure 2.4 - Typical pattern of airflow around an accommodation block

2.5.5 Minimising Hazards from Vented Gas

The objective of venting arrangements and their operational control is to minimise the possibilities of flammable gas concentrations entering enclosed spaces containing sources of ignition, or reaching deck areas where, notwithstanding all other precautions, there might be a source of ignition. In previous Sections, means have been described of promoting rapid dispersion of gas and minimising its tendency to sink to the deck. Although this Section is concerned with flammability, the same principles apply to dispersion of gas down to concentrations that are safe to personnel.

The following conditions should be taken into account for any operation where flammable mixtures are displaced to the atmosphere or where mixtures are displaced which could become flammable on dilution with air, such as on inerted tankers:

- An unimpeded vertical discharge at a high efflux velocity.
- Positioning the outlet sufficiently high above the deck.
- Placing the outlet at an adequate distance from the superstructure and other enclosed spaces.

When using a vent outlet of fixed diameter, usually designed for 125% of the maximum cargo loading rate, the efflux velocity will drop at lower loading rates. Vent outlets with automatically variable areas (high velocity vent valves) may be fitted to maintain a high efflux velocity under all loading conditions.

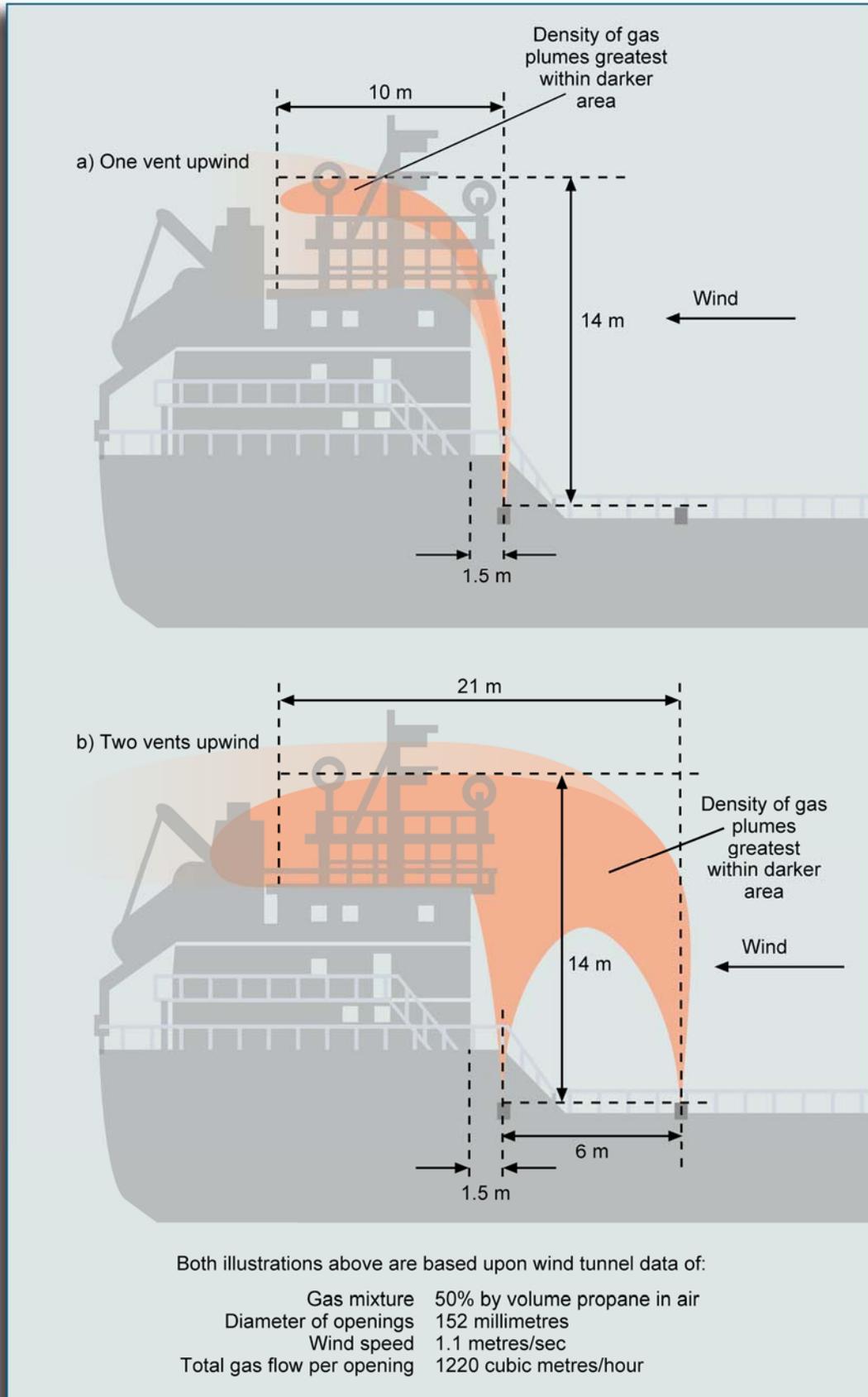


Figure 2.5 - Flammable zone from apertures near an accommodation block

The venting arrangements should always be used during cargo loading operations and during any ballasting into non-gas free cargo tanks.

When gas freeing by fixed mechanical blower, or purging with inert gas either by displacement or dilution through designated outlets, sufficiently high efflux velocities should be maintained to ensure rapid gas dispersion in any conditions.

When gas freeing by portable blowers, it may be necessary to open a tank hatch lid to act as a gas outlet, with a resulting low gas outlet velocity. Vigilance is then required to ensure that gas does not accumulate on deck. If an inerted tank is being gas freed through the open hatch, there may be localised areas where the atmosphere is deficient in oxygen. If practicable, it is preferable to gas free through a small diameter opening, such as a tank cleaning opening, with a temporary standpipe rigged.

In all operations where gas is being vented, great vigilance should be exercised, especially under adverse conditions (e.g. if there is little or no wind). Under such conditions, it may be prudent to stop operations until conditions improve.

2.5.6 N/A

2.6 N/A

2.7 **The Hazards Associated with the Handling, Storage and Carriage of Residual Products**

2.7.1 General

The first part of this Section deals with the flammability hazards associated with residual fuel oils and provides information on flashpoint and vapour composition measurement, together with recommended precautionary procedures to be adopted when handling, storing or carrying residual fuel oils.

It should be noted that this guidance refers only to residual fuel oils and not to distillate fuels.

Reference should be made to Section 11.8.2 for precautions to be taken when measuring and sampling in non-inerted tanks when there is any possibility that a flammable gas/air mixture may be present.

The last part of this Section refers to the hydrogen sulphide hazard associated with fuel oil (see also Section 2.3.6).

2.7.2 Nature of Hazard

Residual fuel oils are capable of producing light hydrocarbons in the tank headspace, such that the vapour composition may be near to or within the flammable range. This can occur even when the storage temperature is well below the measured flashpoint. This is not normally a function of the origin or manufacturing process of the fuel, although fuels containing cracked residues may show a greater tendency to generate light hydrocarbons.

Although light hydrocarbons may be present in the headspaces of residual fuel oil tanks, the risk associated with them is small unless the atmosphere is within the flammable range and an ignition source is present. In such a case, an incident could result. It is therefore recommended that residual fuel oil headspaces be regarded as being potentially flammable.

2.7.3 Flashpoint and Headspace Flammability Measurement

2.7.3.1 Flashpoint

Fuel oils are classified for their safety in storage, handling and transportation by reference to their closed cup flashpoint (see also Section 1.2.5). However, information on the relationship between the calculated flammability of a headspace atmosphere and the measured flashpoint of the residual fuel oil has shown that there is no fixed correlation. A flammable atmosphere can therefore be produced in a tank headspace even when a residual fuel oil is stored at a temperature below its flashpoint.

2.7.3.2 Headspace Flammability

Traditionally, gas detectors such as explosimeters have been used to check that enclosed spaces are gas free, and they are entirely suited to this purpose (see Section 2.4.3). They have also been used to measure the “flammability” of headspaces in terms of percentage of the Lower Explosive Limit (LEL). Such detectors rely on a calibration carried out normally on a single hydrocarbon, such as methane, which may have LEL characteristics that are far removed from the hydrocarbons actually present in the headspace. When using an explosimeter to assess the degree of hazard in non-inerted residual fuel oil tank headspaces, it is recommended that the instrument is calibrated with a pentane/air or hexane/air mixture. This will result in a more conservative estimate of the flammability, but the readings should still not be regarded as providing a precise measurement of the vapour space condition.

When taking measurements, the manufacturer’s operating instructions for the instrument should be closely followed and the instrument’s calibration should be checked frequently as oxidation catalyst detectors (pellistors) are likely to be susceptible to poisoning when exposed to residual fuel oil vapours. For information on poisoning of pellistors, see Section 2.4.3.2.

In view of the problems associated with obtaining accurate measurements of the flammability of residual fuel tank headspaces using readily available portable equipment, the measured % LEL only ranks fuels broadly in terms of relative hazard. Care should be exercised therefore in interpretation of the figures obtained by such gas detectors.

2.7.4 Precautionary Measures

2.7.4.1 Storage and Handling Temperatures

When carried as fuel, temperatures of the residual fuel oil in the fuel system should conform to relevant codes of practice at all times and excessive local heating should be avoided.

2.7.4.2 Filling and Venting

When tanks are being filled, tank headspace gas will be displaced through vent pipes. Particular care should be taken to ensure that flame screens or traps are in good condition and that there are no ignition sources in the area immediately surrounding the venting system.

When filling empty or near empty tanks, the heating coils should be shut down and cool. Fuel oil contacting hot, exposed heating coils could possibly lead to the rapid generation of a flammable atmosphere.

2.7.4.3 Headspace Classification

All residual fuel oil tank headspaces should be classified as hazardous and suitable precautions taken. Electrical equipment within the space must meet the appropriate safety standards.

2.7.4.4 Hazard Reduction

The flammability of the headspace of residual fuel oil tanks should be monitored regularly.

If a measured value in excess of recommended levels is detected (IMO Resolution A.565(14) refers to a level in excess of 50% LEL), action should be taken to reduce the vapour concentration by purging the headspace with low pressure air. Gases should be vented to a safe area with no ignition sources in the vicinity of the outlet. On completion of venting, gas concentrations within the tank should continue to be monitored and further venting undertaken if necessary.

When residual fuel oil is carried as cargo on board tankers fitted with inert gas, it is recommended that the inert gas is utilised and that the headspace is maintained in an inert condition.

2.7.4.5 Ullaging and Sampling

All operations should be conducted such as to take due care to avoid the hazards associated with static electrical charges (see Section 11.8.2).

2.7.5 Hydrogen Sulphide Hazard in Residual Fuel Oils

Bunker fuels containing high H₂S concentrations may be supplied without advice being passed to the tanker beforehand. Tanker's personnel should always be alert to the possible presence of H₂S in bunker fuel and be prepared to take suitable precautions if it is present.

Before loading bunkers, the tanker should communicate with the supplier to ascertain whether the fuel to be loaded is likely to have any H₂S content.

The design of bunker tank vents and their location makes managing the exposure to personnel more difficult, as closed loading and venting cannot usually be implemented.

If bunkering with fuel containing H₂S above the TLV-TWA cannot be avoided, procedures should be in place to monitor and control the access of personnel to exposure areas.

Ventilation to lower the concentration of vapour in the ullage space and in specific areas where vapours may accumulate should be carried out as soon as practicable.

Even after the tank has been ventilated to reduce the concentration to an acceptable level, subsequent transfer, heating and agitation of the fuel within a tank may cause the concentration to reappear.

Periodic monitoring of the concentration of H₂S should be continued until the bunker tank is refilled with a fuel oil not containing H₂S.