

AMERICAN NATIONAL STANDARD

ANSI/ISA-92.00.02-2013

**Installation, Operation, and
Maintenance of Toxic
Gas-Detection Instruments**

Approved 30 September 2013



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ANSI/ISA-92.00.02-2013, Installation, Operation, and Maintenance of Toxic Gas-Detection Instruments

ISBN: 978-0-876640-45-6

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INTRODUCTION

Toxic gas detection equipment may be used whenever there is the possibility of a hazard to life or property caused by the accumulation of a toxic gas-air mixture. Such equipment can provide a means of reducing the hazard by detecting the presence of a toxic gas and issuing suitable audible or visual warnings. Gas detectors may also be used to initiate precautionary steps (for example plant shutdown, evacuation, and operation of fire extinguishing procedures).

Equipment may be used to monitor a gas atmosphere below the applicable level, (PEL, REL, TWA, STEL or IDLH), limit in circumstances where accumulation of toxic gas may result in a concentration of the gas/air mixture to potential risks to life and health. Performance requirements for gas detecting equipment for such purposes are set out in ANSI/ISA-92.00.01 and ISA-92.00.04. However performance capability alone cannot ensure that the use of such equipment will properly safeguard life or property where toxic gases may be present. The level of safety obtained depends heavily upon correct selection, installation, calibration and periodic maintenance of the equipment, combined with knowledge of the limitations of the detection technique required. This cannot be achieved without responsible informed management.

Portable equipment covered by the ANSI/ISA-92.00.01 and ISA-92.00.04 commonly have additional detectors for combustible gases and also for oxygen deficiency. Users are cautioned that even mild oxygen deficiency may be due to toxic concentrations of some other gas or vapor, which may not be detectable or adequately detected by the equipment in use. This concept must not be relied upon for detection of a non-monitored toxic gas because 0.1% oxygen reduction can mean 1,000 ppm or greater of the unknown toxic gas, which usually exceeds most toxic gas safety limits. All toxic gases suspected should be monitored by the proper equipment.

Minimum requirements for the instruction manual of any particular toxic gas detection equipment are specified in ANSI/ISA-92.00.01 and ISA-92.00.04. These standards provide some necessary background knowledge on the points mentioned above.

This standard has been specifically written to cover all the functions necessary from the need for gas detection all the way through ongoing maintenance of a successful gas detection operation. Different clauses are appropriate for different tasks within this range of operations. Each clause has been written as stand-alone as far as practicable. This means that some information is repeated in different clauses but with a different emphasis.

The following table gives a broad suggestion as to the most relevant clauses to the typical tasks to be performed.

	Definitions	Basic information properties of gas and vapors	Measuring principles	Selection of equipment	Behavior of gas releases	Design and installation of fixed gas detection systems	Use of portable and transportable toxic gas detection equipment	Training of operational personnel	Maintenance, routines-procedures, and general administrative control	Measuring principles (full detail) (normative)	Environmental parameters (informative)
Function (Clause)	3	4	5	6	7	8	9	10	11	Annex A	Annex B
Authorities	+	+++	+++	+	+	-	-	-	+	-	-
General management	+	+++	+++	+	+	-	-	+	+	-	+
Selection	+++	+++	+	+++	+++	+	++	-	+	+++	+++
Design engineering / management	+++	+++	+	+++	+++	+++	-	-	-	+++	+++
Installation engineering / management	+++	+++	+	++	+++	+++	-	-	-	+++	+++
Installation, technical	++	+++	++	++	++	++	-	-	-	+	++
Commissioning	+++	+++	++	+	++	+++	-	++	+	-	-
Operations management	++	+++	++	+	+	++	++	+++	+++	+	+++
Operation training	+++	+++	+	+	+	+++	+++	+++	+++	+++	+++
Servicing / Calibration	+++	+++	-	-	-	++	++	+	+++	++	++
Repair	++	+++	++	-	-	+	+	+	+++	++	-
"+++" Essential "++" Advisable "+" Useful "-" Not applicable NOTE It should be noted that Clause 5 is a simplified version of Annex A.											

Table 1 – Functional applicability

This standard makes recommendations how to establish maintenance and calibration intervals. In certain countries there are general or industry-specific regulations that are mandatory and those shall be followed as a minimum requirement.

1 Scope

This standard gives guidance on, and recommended practice for, the selection, installation, use and maintenance of electrically operated equipment intended for use in industrial and commercial safety applications for the detection and measurement of toxic gases complying with the requirements of ANSI/ISA-92.00.01 and ISA-92.00.04.

This standard is a compilation of practical knowledge to assist the user, and applies to equipment, instruments and systems that indicate the presence of a toxic mixture of gas or vapor with air by using an electrical signal from a gas sensor to produce a meter reading, to activate a visual or audible pre-set alarm or other device, or any combination of these.

Such equipment may be used as a means of reducing the risk whenever there is the possibility of a risk to life or health specifically due to the accumulation of a toxic gas-air mixture, by providing such warnings. It may also be used to initiate specific safety precautions (e.g. plant shutdown, evacuation, ventilation).

This can be applied to all new permanent installations and, where reasonably practicable, to existing permanent installations. It is also applicable to temporary installations, whether new or existing.

Similarly it is applicable to the safe use of portable or transportable equipment, irrespective of the age or complexity of such equipment. Since much modern equipment of this type also includes other types of gas detection, some additional guidance is given for these topics.

NOTE Equipment intended for use in hazardous (classified) areas should be Listed or Labeled for use within the intended area. For fixed equipment, installation should be in accordance with the National Electrical Code, ANSI/NFPA 70.

For the purposes of this standard, except where specifically stated otherwise, toxic gases shall include toxic vapors.

For the purposes of this standard, equipment includes

- a) fixed equipment;
- b) transportable equipment, and
- c) portable equipment.

This standard is not intended to cover, but may provide useful information, for the following:

- a) equipment of laboratory or scientific type intended only for analysis or measurement purposes;
- b) equipment intended for underground mining applications (group I equipment);
- c) equipment intended only for process control applications;
- d) equipment intended for applications in explosives processing and manufacture;

- e) equipment intended for the detection of a potentially toxic atmosphere resulting from dust or mist in air.

2 References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ANSI/ISA-12.13.01, Performance Requirements for Combustible Gas Detectors

ANSI/ISA-60079-29-2 (12.13.02), Explosive Atmospheres – Part 29-2: Gas detectors – Selection, installation, use and maintenance of detectors for flammable gases and oxygen

ANSI/ISA-12.13.04, Performance Requirements for Open Path Combustible Gas Detectors

ANSI/ISA-92.00.01, Performance Requirements for Toxic Gas Detectors

ANSI/ISA-92.04.01, Performance Requirements for Instruments Used to Detect Oxygen-Deficient/Oxygen-Enriched Atmospheres

National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards, Title 29, Part 1910.1000, Occupational Safety and Health Standards

Threshold Limit Values for Chemical Substances in the Work Environment Adopted by the American Conference of Governmental Industrial Hygienists (ACGIH)

Documentation for Immediately Dangerous to Life or Health Concentrations (IDLHs) (NIOSH Taft Laboratories)

OSHA 29 CFR1910, 1000 OSHA Regulation on Air Contamination

API RP55 Conducting Oil and Gas Producing and Gas Processing Plant Operations Involving Hydrogen Sulfide

MSDS sheets for all gases/vapors present and/or suspected in the site being monitored.

3 Terms and definitions

For the purposes of this document, the terms and definitions given in the standards referenced in Clause 2, as well as the following apply. Also, since this is intended as a stand-alone standard, certain definitions within ANSI/ISA-92.00.01 are repeated below for the convenience of the reader.

3.1

alarm

an audible, visual, or physical signal that alerts the instrument user of a dangerous gas concentration or instrument problem

3.1.1

false alarm

any alarm that is triggered by a condition other than the one(s) that the alarm function is set for (ex: high gas alarm caused by RF interference or gas alarm caused by temperature changes)

3.2

alarm-only equipment

equipment having an alarm, but not having a meter or other indicating device

3.3

alarm setpoint

the selected gas concentration level(s) at which an alarm is activated

3.4

ambient air

air to which the sensing element is normally exposed.

3.5

bump test

application of test gas or other means of obtaining a response from the sensor to check its function. This may include the generation of an alarm. This check is performed without adjustments of sensitivity.

NOTE This is also known as a "response check" or "functional check".

3.6

calibration

the procedure to adjust the equipment for proper response (e.g., zero level, span, alarm, and range)

3.7

calibration gas

the known concentration(s) of gas used to set the equipment span or alarm level(s)

3.8

clean air

air that is free of any substance that will adversely affect the operation of or cause a response from the equipment

3.9

consumables

materials or components that are depleted or require periodic replacement through normal use of the equipment

3.10

control unit

that portion of a gas detection equipment that is not directly responsive to the gas, but which responds to the electrical signal obtained from one or more detector heads. This unit is intended to provide meter indication, alarm functions, output contacts and/or alarm signal outputs when utilized with a detector head.

3.11

detector head

the gas responsive portion of a gas detection equipment located in the area where sensing the presence of gas is desired. It may be integral with or removed from its control unit.

NOTE The detector head may incorporate, in the same housing, circuitry such as signal processing or amplifying components or circuits in addition to the gas sensing element (sensor).

3.12**diffusion**

a process by which the atmosphere being monitored is transported by natural random molecular movement to and from the gas-sensing element

3.13**field check with gas (response check)**

application of test gas to the sensor to check the response signal or the generation of an alarm, without adjustments of zero, sensitivity, or alarm level

3.14**full-scale**

the maximum claimed operational level of the gas-detection equipment

3.15**gas-detection equipment**

an assembly of electrical and mechanical components (either a single integrated unit or a system comprised of two or more physically separate but interconnected component parts) which senses the presence of a gas and responds by providing an alarm, indication, or other output functions

3.16**gas-sensing element**

the particular subassembly or element in the gas-detection equipment that, in the presence of a gas, produces a change in its electrical, chemical, or physical characteristics

3.17**indication**

a discrete communication of a measured value or alarm condition

3.18**IDLH (Immediately Dangerous to Life and Health)**

the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without a respirator and without experiencing any escape-impairing (e.g., severe eye irritation) or irreversible health effects

3.19**mobile equipment**

a continuous-monitoring equipment mounted on a vehicle, such as, but not limited to, a mining machine or industrial truck

3.20**nominal voltage**

the voltage given by manufacturers as the recommended operating voltage of their gas detection equipment. If a range (versus a specific voltage) is given, the nominal voltage shall be considered as the midpoint of the range, unless otherwise specified

3.21**PEL (Permissible Exposure Limit)**

time-weighted average (TWA) concentration that must not be exceeded during any 8-hour work shift of a 40-hour work week, as defined by the Occupational Safety and Health Administration (OSHA)

3.22

portable equipment

spot-reading or continuous duty equipment that has been designed to be readily carried from place to place and to be used while it is being carried. A portable equipment is battery powered and includes, but is not limited to

- a) a hand-held equipment, typically less than 1 kg, suitable for single-handed operation;
- b) personal monitors, similar in size and mass to the hand-held equipment, that are continuously operating (but not necessarily continuously sensing) while they are attached to the user; and
- c) larger equipment that can be operated by the user while it is suspended by hand, by a shoulder strap or by a carrying harness; it may or may not have a hand directed probe.

3.23

REL (Recommended Exposure Limit)

exposure levels that are safe for various periods of employment, including but not limited to the exposure levels at which no employee will suffer impaired health or functional capacities or diminished life expectancy as a result of that work experience

3.24

range

the values of concentrations of toxic gas over which accuracy is ensured by calibration

3.25

spot-reading equipment

equipment intended to be used for short periods of time as required (typically 5 min or less)

3.26

sample-draw

a method to cause deliberate flow of the atmosphere being monitored to a gas-sensing element

3.27

signal-processing detector head

an equipment intended to be incorporated with separate signal processing, data acquisition, central monitoring, or other similar systems in which the equipment provides a conditioned electronic signal or output indication to systems of the aforementioned type that typically process information from various locations and sources including, but not limited to, gas-detection equipment

3.28

span

the algebraic difference between the upper and lower values of a range

3.29

stabilization

state when three successive readings of an equipment, taken at intervals equal to the maximum $t(90)$ value defined in Annex A (Item 5), indicates no changes greater than the accuracy value defined in Annex A (Item 2)

3.30**stationary equipment**

a gas-detection equipment intended for permanent installation in a fixed location

3.31**(TLV-)STEL, (Threshold Limit Value-) Short-Term Exposure Limit**

a 15-minute Time-Weighted Average (TWA) exposure that should not be exceeded at any time during a workday, even if the 8-hour TWA is within the Threshold Limit Value - Time-Weighted Average (TLV-TWA)

3.32**test gas**

toxic gas diluted with clean air or inert gas to a known concentration within the test-gas tolerance stated in Annex A, Item 1

3.33**transportable equipment**

equipment not intended to be portable, but which can be moved readily from one place to another

3.34**(TLV-)TWA, (Threshold Limit Value-) Time-Weighted Average**

the time-weighted average concentration for a normal 8-hour work day in a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect

3.35**toxic gas**

toxic gases, for the purpose of this standard, are gases that may cause significant health effects at low concentrations. Health effects may include severe skin or eye irritation, pulmonary edema, neurotoxicity, or other potentially fatal conditions.

3.36**trouble signal**

information that alerts an equipment user to abnormal conditions

3.37**stand-alone gas detection equipment**

a detector which provides a conditioned electronic signal or output indication to a system. The stand-alone detector is intended to be interfaced to unspecified separate control unit, signal processing data acquisition, central monitoring, or other similar systems in which the equipment provides a conditioned electronic signal or output indication to systems.

3.38**stand-alone control unit**

fixed gas detection control units intended to provide meter indication, alarm functions, output contacts and/or alarm signal outputs when utilized with stand-alone detector head

4 Basic information on the properties, behavior, and detection of gases and vapors

For this clause, a distinction is drawn between gases, which remain gaseous at typical ambient pressures and temperatures, and vapors where liquid can also exist at any relevant pressure or temperature.

4.1 Detecting gases and vapors – General

Effective operation of toxic gas detection equipment depends not only on its performance but also on its correct usage.

Equipment capability, and its suitability for the intended application and the user's knowledge of its limitations, both generic relating to sensor technology, and individual relating to its other design features, cannot alone ensure that its use will properly safeguard personnel, areas, or locations where toxic gases or vapors may be or are present. The level of safety obtained also depends upon the user having a basic knowledge of gas and vapor properties and phenomena.

This knowledge should enable the user to determine whether the gases are heavier or lighter than air, and whether the vapors are heavier than air or of similar density, and therefore where they may accumulate. If the direction and velocity of air movement is known, it can be seen how they may propagate. Also there may be physical or chemical reasons imposing limitations on a particular application, such as calibration considerations.

Consideration has to be given not only to those gases and vapors that are required to be detected, but also to those gases and vapors that are not required to be detected, but may also be present.

The effects of humidity and temperature variations may need to be evaluated, particularly when sampling lines are used, and, more importantly, if vapors other than water are involved.

Small environmental changes, such as a rise or fall in temperature, which may be ignored for most purposes, can significantly modify conditions, particularly if liquids are present and produce increased amounts of vapors, or if vapors condense as fogs or inside the equipment itself.

Failure to take these properties of gases and vapors into account at any of the stages of selection, installation, commissioning, training, operation and on-going maintenance of even the simplest of equipment can result in the production of erroneous readings. These in turn can lead, on one hand to false alarms or incorrect action, and on the other hand failure to alarm or failure to take any appropriate action. Such factors can unnecessarily endanger lives and property.

Some gases or vapors can cause corrosion or other deterioration to certain types of sensors. Some types of sensors have specific lifetimes. The sensitivity can change over time. This applies to certain types of sensors for toxic gases and oxygen deficiency as well as for toxic gases and vapors. This is the major reason for requiring frequent response checking. It is usually done using a test gas or calibration gas applied in a specified way. The correct test/calibration equipment for one type of gas detection equipment may not be appropriate to another type, and some training will usually be needed.

4.1.1 Safety when monitoring for toxic gases where personnel could be present

Personnel should frequently observe the reading on any gas detection equipment when entering a potentially hazardous area. The area may already be dangerous and the personnel may need expedient warning of this danger. It is recommended that if methods of pre-testing an area to be entered prior to entry are available that these methods be used.

The equipment will only give a reading for the location where the reading is being taken, or the location of the end of the sampling line if a sampling line is being used. A toxic atmosphere may be building up a few meters from the sampling point. Therefore, many gas tests must be done all around the intended area of work to ensure that no pockets of hazardous gas or vapor are present in the work area. Checking all corners of the location and all entry/exit passages where gas may enter, even if continuous portable/transportable gas monitoring equipment is being utilized.

If vapors are likely to be present, some of the tests should be done one or two centimeters from the floor. This might detect a small problem (e.g. a minor liquid leak) at an early stage. All nearby low spots should be tested.

The readings are only valid for the time they are taken. Circumstances change. Frequent readings are recommended, particularly if vapors (see 4.3.2) could be involved and the temperature is rising.

Where a wide range of gases and vapors could be encountered in the work area there will be a range of potential sensitivities. A low "alarm point" or "action point" will therefore be required.

If the equipment being utilized detects combustible gases in addition to toxic gases and there is a chance of sensor "poisons" (such as silicones, leaded petrol, acids, etc.) being present then the sensitivity of equipment using catalytic combustion or semiconductor sensors should be checked at frequent intervals.

While the atmosphere is being monitored for concentrations of toxic gases and vapors, consideration should also be given to the fact that many of these, including all vapors except water, are also toxic to personnel. Additional detectors for the specific gases and vapors and additional precautions may be needed.

If a toxic gas or vapor detection equipment is also equipped with high sensitivity sensors for specific toxic gases it should be realized that they may only detect these specific gases. They will not usually detect other toxic materials.

Closely allied to toxic gas monitoring is monitoring for oxygen deficiency. Frequently this feature is added to the equipment. There are several possible reasons for an oxygen deficiency. Some of them are due to situations where a toxic substance, in high concentrations, is part of the cause of the deficiency, and these are of far greater concern. Again, additional detectors and precautions may be needed.

Therefore, when about to work in a hazardous area, it is advisable to specifically check on the potential toxicity of the atmosphere with the plant safety officer, industrial hygienist, or equivalent.

NOTE Different countries have different systems, and may use different values, for describing maximum safe levels of potentially toxic substances. For typical details, consult the USA's ACGIH book of TLV's (Threshold Limiting Values) and Biological Exposure Indices (BEIs), or the European Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area who publish a list of recommended TLV's. Both organizations update these publications annually. Other countries usually employ one or the other of these sets of data as basis of their national documents, which also may be referred to.

4.2 Some common properties of gases and vapors

All gases and vapors will fully mix with all others by diffusion over time or if stirred. They will not separate out. However, some gases and vapors may react chemically with each other on mixing.

If a gas or vapor concentration is increasing in an area it is because more of that substance is arriving. It is not due to settling out.

Once gases and vapors have been mixed, they will stay mixed, unless a component is removed chemically, or is absorbed (for instance on a charcoal filter). Additionally, in the case of vapors, removal can be by condensation due to increased pressure and/or falling temperature.

The density of pure gases and the effective density of vapors is proportional to their molecular mass. There is no significant change of volume on mixing gases and vapors. Therefore the density of mixtures of gases and vapors may be simply calculated from the volume fractions and molecular masses of their components. If relative density data is available, the relative density can be similarly calculated from the volume fractions and relative densities of the components.

Air has an equivalent molecular mass of approximately 29, corresponding to a relative density of 1. For instance, gases with lower molecular masses than 29 will have a relative density less than 1 and will be lighter than air and as a result, rise to the upper portion of the space being entered.

Mixtures of fresh air with pure or mixed gases that are lighter than air, will still be lighter than air, but less so. They will tend to rise until they become so diluted with fresh air that the effect may become negligible.

Mixtures of fresh air with gases or vapors that are heavier than air, will still be heavier than air, but less so. They will tend to flow into low spots; pits, trenches etc., where they may become so diluted with fresh air that the effect becomes negligible.

If a source of release and its surrounding air is substantially hotter than the ambient air the released mixture can rise initially, even if the relative density is greater than 1. As a rule of thumb, a temperature rise of 30 K will overcome what by calculation would be 10 % greater relative density than air. The converse applies where the release is colder than the ambient temperature.

Because of temperature differences at release and normal turbulence, gases and mixtures with relative density between 0.8 and 1.2 generally can be considered as having a similar relative density to air, and therefore are capable of propagating in all directions.

All vapors except water vapor are toxic to varying degrees. All flammable vapors are toxic at levels well below 25% LFL and most are toxic below 1% of LFL. All gases (except air or oxygen) are asphyxiants (i.e. their effect on personnel is due to dilution of the oxygen content of the air and may also vary from mild to extreme toxicity).

When detecting specific gases or vapors, it is necessary to be aware of the potential toxicity of other gases or vapors that might be present, but are not being detected.

4.3 The differences between detecting gases and vapors

The major practical differences between the detection of gases and the detection of vapors are outlined below.

4.3.1 Detection of gases

Substances that remain gaseous under the range of temperatures and pressures relevant to the gas detection application will closely follow the Gas Laws and behave predictably. Basically, simple training may be adequate.

Gases may be pure, or any mixture of gases can be made, unless they react chemically. The composition of non-reacting gas mixtures does not change with temperature or pressure.

4.3.1.1 Calibration considerations

It is possible to make and store under high pressure, calibration and other test gas mixtures fully representative of the intended gas detection application. Many can be made with a dry or synthetic air background. However the more-reactive gases tend to have longer storage life if the background is specially dried nitrogen, and this is normally chosen unless it is incompatible with the sensor.

Where more than one toxic gas (or vapor) may need to be detected, it is normally necessary to use separate calibration gas for each toxic gas intended to be detected. For further details see 4.3.2.1.

4.3.1.2 Propagation and sampling considerations

Gases can have a density that is lighter than air, such as hydrogen and methane. They can have approximately the same density as air, such as carbon monoxide, hydrogen sulphide, hydrogen cyanide, ethane, ethylene and acetylene; or they can have a density heavier than air such as chlorine, carbon dioxide, sulphur dioxide, LPG, propane, propylene and butane.

When sampling, at least some tests or readings should be taken in locations with the density of the gas in mind. This may also help to detect the source of release.

4.3.1.3 Water vapor

Although this subclause relates only to detecting gases, it is not normally possible to ignore water vapor. This can produce problems in cold equipment that have been suddenly exposed to a hotter and humid atmosphere. Examples of this situation are in leaving a cold store and entering a normal atmosphere, or in leaving an air-conditioned situation and entering into a humid tropical or sub-tropical atmosphere. Water can condense in or on a sensor, causing a temporary loss of sensitivity or some other problem, until the equipment warms up and the water re-evaporates. This is particularly the case with electrochemical sensors: A very rapid drop in an oxygen reading can occur from a normal 20.8 % or 20.9 % reading to 16 % or lower, due only to a coating of water condensing onto the cold sensor membrane. The sensitivity may then only recover slowly over some minutes as the sensor warms up to ambient, and the film evaporates. This is why most gas detector manufacturer's manuals indicate that performance of the equipment is based on non-condensing atmospheres.

Water vapor may also cause significant deviations of the reading of several types of sensors (see Clause 5 and Annex A).

4.3.2 Detection of vapors

Vapors are more difficult to understand than gases. Substances, where the liquid or solid can coexist with their gaseous state at normal or slightly abnormal temperatures and pressures are said to have vapors. Vapors behave differently than gases, and can present

more problems. Where vapors are likely to be found, additional training in their properties is required.

Where a liquid is present, the rate of evaporation will increase with temperature. Similarly the maximum volume fraction of the vapor that can be achieved in a closed system (saturated vapor) will increase with temperature. This is dependent on the temperature and pressure and is independent of the quantity of liquid, provided there is some liquid remaining. The maximum volume fraction of the vapor is also independent of the background gas provided it is at the same temperature and pressure, and is not soluble in the liquid.

The volume fraction that can be reached by the vapor at any temperature is inversely proportional to the absolute pressure. So an increase in pressure can cause condensation.

As a rule of thumb, at constant pressure, the maximum (saturated) volume fraction of any vapor will increase by a factor between 1.5 and 2.0 for each 10 K rise in liquid temperature, and will fall by a factor of 1.5 to 2.0 for every 10 K reduction.

The effect of doubling the absolute pressure has an equivalent effect to a decrease in temperature of 10 to 17 K at constant pressure. Halving the pressure has an effect equivalent to a similar rise in temperature.

The temperature at which the saturated volume fraction can reach 100 % at the prevailing pressure is the boiling point.

It is only possible to have 100 % volume fraction of a vapor at or above the boiling point at that atmospheric pressure. Below the boiling point of the liquid, the maximum possible concentration of vapor in air or other gases must be less than 100 % volume fraction.

The actual amount of vapor will be less than the amounts predicted above if fresh atmosphere is being continually passed over the liquid surface, or if there has not been enough time for equilibration to be established. However this maximum amount can be achieved in an enclosed space, particularly if it has been closed for some time and the air space is slowly stirred by convection or mechanical means.

Toxic liquids have flashpoints, which are determined in a different way from LFL, but are essentially the temperatures at which their vapors can reach their LFL volume fractions in the air above their liquid surfaces, again provided that the vapor is not continuously removed by air currents. Toxic vapors can be present when the vapor is well below a flammable level.

All of these points impose limits on mixtures of vapors with gases. For any particular volume fraction of a vapor in a mixture with gas, a fall in temperature or increase in pressure will, at a certain stage, reach the saturation point, below which liquid will start to condense as a fog or liquid. When applied to water vapor this is known as the "dew point". This term is frequently applied to other vapors. Below the dew point the composition of any vapor-gas mixture must therefore change.

4.3.2.1 Calibration considerations

Real restrictions on what calibration or test vapors are practical for field use are imposed by the minimum temperature at which they will be used, and the required pressure in a calibration gas or test gas cylinder.

Whenever test or calibration gases other than the gas or vapor of interest are used, it is recommended that additional safety margins, lower alarm settings etc. are employed in order to compensate for the added uncertainty of relative response data due to the factors mentioned above.

4.3.2.2 Propagation and sampling considerations

Only the vapor of water is lighter than air. There are only four vapors, three of which are toxic, with a similar density to air (methanol, hydroxylamine, hydrazine and hydrogen peroxide, the last three being uncommon).

All other vapors are more dense than air. Most are considerably more dense than air. At a point of release, unless heated, they will initially flow downwards or across level surfaces, and until they are well mixed with air they will stay close to the ground, possibly only a few centimeters deep, which is where they will present the greatest flammability problems. A severe instance of this is in the case of pits, trenches and tunnels which will tend to fill from the bottom upwards and can permit extensive propagation over hundreds of meters. This can also cause the most serious toxicity problems for personnel entering pits and tunnels.

When sampling for toxic vapors in relatively undisturbed atmospheres, some tests must be performed at very low levels, ideally within a centimeter of the floor or ground.

Once mixed with an excess of air, all vapors will be found at all levels, possibly at volume fractions well below their LFL but still presenting major toxicity problems

The vapor of a high flashpoint toxic liquid may not be detectable if the ambient temperature is well below the flashpoint. As an example, using the rule of thumb at the beginning of 4.3.2, if the ambient is 60 K below the flashpoint, it can be estimated that the vapor can only reach between 1 % and 8 % of LFL as a maximum, and then only slowly, close to the liquid, and if the vapor is not being blown away.

Conversely, if the temperature rises, and particularly in an enclosed area, the concentration can change dramatically. Again, using the rule of thumb, the vapor concentration in an enclosed space could increase by a factor up to eight for a 30 K rise in temperature, caused, for instance, by the sun on an external tank. A previously undetected amount of vapor while the tank was cold could become very significant when it heated up. When temperatures are rising, frequent vapor testing is necessary.

Other problems can arise with substances of high molecular mass. The higher the molecular mass is, the lower the rate of diffusion will be. This applies to non-pumped equipment where diffusion screens are used to prevent external ignition, and also within certain sensors. In particular this can adversely affect both the speed of response and the sensitivity in catalytic combustion sensors, particularly the "poison-resistant" varieties.

Major problems also arise in vapor testing due to the possible condensation of the sample itself in the detector or its accessories: Gas detectors will only detect the gases or vapors present. They will not detect mists or condensed liquids caused as a result of the equipment, or a sample line, being markedly colder than the atmosphere being sampled.

If the equipment or its sampling line gets contaminated by condensed vapor because it was too cold, or worse still if it gets contaminated by drawing up the toxic liquid, spurious, and possibly dangerously misleading, readings will occur until such contamination is totally removed.

4.3.2.3 Toxicity and other considerations

All vapors except water are toxic to some degree. All toxic vapors are toxic at concentrations well below LFL. Most vapors, including many commonly found in industry, are of toxic concern well below 20 % of LFL. So they may be undetectable at concentrations where they are already a toxic problem if only using a toxic gas detector with a normal LFL range. Additional precautions are needed.

NOTE For example, 5 % LFL of n-Hexane is 500ppm which is also the TLV of n-Hexane.

4.4 Oxygen deficiency

Oxygen deficiency detectors are frequently incorporated with combustible gas equipment, with or without toxic sensors as well. Such oxygen detectors are essential for work in confined spaces conforming with the requirements of ANSI/ISA-92.04.01.

Some varieties of oxygen sensors respond to changes in pressure, and so need checking in fresh air, and possibly adjusting, each time they are used and/or if there is a significant change of altitude.

The volume fraction of oxygen in dry air is about 20.9 % v/v. A typical oxygen deficiency alarm setting is between 19.0 % to 19.5 % v/v.

Taking as an example a setting of 19.0 % v/v, the alarm should operate on a 1.9 % v/v deficiency or, put another way, a deficiency of 9.1 % of the original concentration. In certain circumstances this may not be adequate for personnel protection.

Similarly, with a setting of 19.5 % v/v, the alarm should operate on a 1.4 % v/v deficiency or, put another way, a deficiency of 6.7 % of the original concentration. In certain circumstances this also may not be adequate for personnel protection on its own.

It is not commonly appreciated that if an operator is relying on equipment to detect a toxic gas or vapor and a deficiency of oxygen, it is also necessary to know what could be the cause of any oxygen deficiency found.

There are three basic physical and chemical mechanisms by which oxygen deficiency can occur, described in the next three subclauses with reference to the 19.5 % v/v alarm setting example above.

4.4.1 Chemical reaction of oxygen, with solid products

The main examples are the rusting of steel or the corrosion of other metals. Oxygen has simply been subtracted from the air, and a solid oxide is left. This can typically happen in confined spaces constructed of metal.

When the alarm operates at 19.5 % v/v, the atmosphere is equivalent, in physiological terms, to working at an altitude about 650 m higher than the current altitude. Normally this will not cause any health problem to personnel.

4.4.2 Chemical reaction of oxygen, with gaseous products

In the simplest case this could be the result of respiration, aerobic bacterial action (but not anaerobic action), or clean combustion. The 1.4 % reduction in oxygen content needed to set off the alarm would be accompanied by an increase in carbon dioxide level of about 0.8 %, which is fairly safe in the short term, and there would be no short-term or long-term effects on a 'normal person'.