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Uncertainties with assessment of the safety atmosphere in vessel cargo tanks and enclosed spaces

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Abstract

This paper discusses the problem of atmosphere composition assessment related to entrance and inspection of a vessel cargo tank after washing, gas-freeing and ventilation. A correct assessment of the atmosphere before an entrance into the cargo tank or other enclosed spaces is a basic condition for the possibility of safe crew working. An assessment of the flammability hazard, presence of toxic or dangerous gases for human, and the oxygen concentration should be completed. In this regard, the ship-owner should prepare adequate procedures before an entrance, during work, and in emergency situations. The officers responsible should perform an assessment onboard the vessel their decisions are crucial for the safety of successive operations. A proper assessment of oxygen concentration in the air into the cargo tank or an enclosed space after the measurement is one of the primary problems which should be properly interpreted. This concerns such situations when the measured oxygen concentration into the tank reaches the value over 22% and below 20.6% of volume (mole) contribution (v/v). Air temperature in the 5–25°C range may create additional threats. This manuscript clarifies the controversial information included in manuals concerning the safety of entrance into enclosed spaces on vessels and the ship-owners procedures concerning the safety precautions for preparing, entrance, protection, and work inside the cargo tanks.

Introduction – washing process of the cargo tanks

Transport of crude oil by sea is important for the global economy. Oily tankers carry different types of crude oil and its products. Crude carriers are designed for carrying crude oil from one region of the world to another one (Mou et al., 2019). Oxygen concentration in the atmosphere and pressure of gases in cargo tanks should be controlled during laden and ballast voyages. Washing process of the cargo tanks should be done during and after unloading operation even in a case of the same vessel route with the same cargo. The atmosphere composition into the cargo tank or enclosed spaces depends on many different processes during vessel operation.

After the unloading and stripping operations the cargo tank should be washed. The washing process seems to be a very important procedure during vessel operation. It distinguishes two basic stages of washing: prewashing and essential washing. It allows the cargo tank to reach the proper purity enabling the loading of the next (another type) cargo. In a case of loading the same type of cargo in the next voyage, the washing should be done as well to remove residues and sediments which decrease the active volume of the tank capacity, and to reach the inert atmosphere inside cargo tank, considering the threat of explosion during the ballast voyage. In preparation, cargo tanks require proper aeration to reach the safe atmosphere for entrance of the vessel crew members (Standard Club, 2017; M&CA, 2018).

The prewashing process of oily tankers (crude oil washing method) should be performed in an inert atmosphere. Due to the unloading operation and a decrease in the level of liquid inside the tank, keeping the overpressure to about 4–8% over the ambient is obtained by filling in the inert gas and controlling the oxygen concentration (in the inert gas should be in the range of 0.5–5%, always below 8% into the cargo tank).

The final washing is done using fresh water (sometimes with additives of permitted washing agents) and pressure between 0.8 and 1.6 MPa in a washing machine. After completing the washing process, the slops are transferred to slop tanks for their treatment or pumped to port facilities. The tank atmosphere consists of mainly hydrocarbons, hydrogen sulfide, and other chemical substances from the transported cargo making it dangerous for people (Marine Online, 2017; EI, 2018).

The gas-freeing process (removing the gas residues from cargo) with the use of an inert gas is to reduce the concentration of dangerous gases (hydrocarbons) to below the required level (about 2–4%). To reduce it to 0% would be time-consuming and basically impossible to achieve. After this process, the cargo tanks should be gas free.

The next process step depends on the target to attain. The tank should be aerated till the atmosphere is suitable for entrance. Reaching this level (hydrocarbons concentration about 2–4% depending on the completed procedure) requires atmospheric ventilation of the vans inert gas system from a few to several dozen hours. It is possible to get the tank atmosphere's to approximately the same as the atmosphere. Before people enter into a tank, an assessment of the atmosphere composition should be carried out (CCNR/OCIMF, 2010; H&SA, 2012; PRS, 2016; CSBP, 2017; IHSA, 2019; Portal, 2019). The air composition should be similar to fresh air fulfilling all required precautions for safe entrance and work inside.

The proper procedures (required and approved by the ship-owner) should be performed checking that the tank atmosphere is safe for the crew members. The basic threats which may exist in cargo tank (enclosed space) after washing, gas-freeing, and aerating are as follows (CCNR/OCIMF, 2010; H&SA, 2012; Standard Club, 2017):

- hydrocarbon explosion – the hydrocarbons concentration is required to be below 10% (5% in some procedures) of the lower explosive concentration (LEL);
- human toxicity – toxic substances for people and their toxicity levels. The main threat comes from hydrogen sulfide (H_2S). The tank history operation should be assessed searching for other possible toxic substances for human;
- oxygen concentration in the range of 20.6–22% in dry air.

The types of tank operations should be taken into consideration due to the possibility of other substances (gases) hazardous to humans occurring. Information present in the material safety data sheet (MSDS) should be used for the evaluation of detected substances (Standard Club, 2017, EI, 2018). The MSDS contain information about the required actions during emergency procedures.

The MSDS contains the following information (according to Commission Regulation of the European Union No. 2015/830 named REACH from 28th of May, 2015) (REACH, 2015):

- identification of the substance/mixture and of company/undertaking,
- hazards identification,
- composition/information on ingredients,
- first aid measures,
- firefighting measures,
- personal precautions, protective equipment, and emergency procedures,
- handling and storage,
- exposure controls/personal protection,
- physical and chemical properties,
- stability and reactivity,
- toxicological information,
- ecological information,
- disposal considerations,
- transport information (among others UN number),
- regulatory information,
- other information.

Procedures approved by the ship-owner (or charterer) are obligatory on vessels in accordance with state maritime administration which flag the vessel raising. Additionally, in accordance with classification society requirements, (every vessel should be in technical supervision) and in accordance with international shipping with the International Maritime Organization (IMO) (IMO, 2014).

The prevention of fire and explosion

The cargo tank is aerated using forced ventilation via the vans inert gas system without necessarily over pressuring the tank. It uses atmospheric air without any thermal-humid processing. The real state of the tank atmosphere is a derivative of the cargo, inert gases, and atmospheric air. After this process is completed and the vans are stopped, a minimum of 30 minutes is needed for homogenization of the atmosphere (full homogenization is achieved after a few days) before the tank atmosphere can be measured and assessed (Standard Club, 2017; EIGA, 2018). Assessment of hydrocarbons concentration should be done using the attested and checked explosimeters. The measurement is performed on three different heights in the tank: the upper, the middle and the bottom due to the tank atmosphere impurity and different gases density in comparison to air. Methane gas is lighter than air over the equilibrium temperature (about −112°C), ethane and ethylene gases have the specific density on the level about 1, hydrocarbons gases like: propane, butane, butadiene etc. are heavier than air. Two types of explosimeters are used – for the 0–10% range of the lower explosive limit (LEL) and for the 0–100% range of LEL (Draeger, 2019). It allows the level of explosion and flammability hazard to be assessed. After performing the measurements, the result recorded mean the following (M&CA, 2018):

- over 30% of LEL – an explosion or fire is possible due to tank impurity,
- in the range 10–30% of LEL – a potential existing hazard; hot work is prohibited,
- below 10% of LEL (some procedures require below 5%) in all measure points – no explosion hazard.

As a principle, people are not allowed to enter any enclosed spaces where the concentration of explosive gases in the atmosphere is over 1% of LEL. For crude oil and its products, the real volume concentration of hydrocarbon gases below 1% of LEL is outside the hazard of explosion in any case, but the toxicity hazard may still exist. A total hydrocarbons volume concentration (as a hydrocarbon mixture derived from crude oil gases) in the air below 0.1% (or 1000 ppm) of the LEL is outside the toxicity threshold hazard (in use are: TLV, MAC, NDS, PEL). The thresholds for Threshold Limit Value – Time Weighted Average (TLV-TWA) are as follows (IMO, 2017; Mathesongas, 2019):

- for methane 1000 ppm (0.1% v/v),
- for ethane 900 ppm,
- for propane 800 ppm,
- for butane 600 ppm,
- for ethene (ethylene) 200 ppm,
- for butadiene 10 ppm,
- for benzene 1 ppm,
- for carbon monoxide 50 ppm,
- for carbon dioxide 5000 ppm (0.5% v/v).

The data above concerns mentioned hydrocarbons performing independently. Of course, in the case of a gas mixture, the toxic action is a sum of components but the principles of summing their toxicity are not known. In dumbing down, it may be the arithmetic summing because the effects (for above mentioned hydrocarbons) confirming the synergic action are not known. Explosimeters essentially measure the explosive gases concentration as a sum without the indication on the type of hydrocarbon (Draeger, 2019).

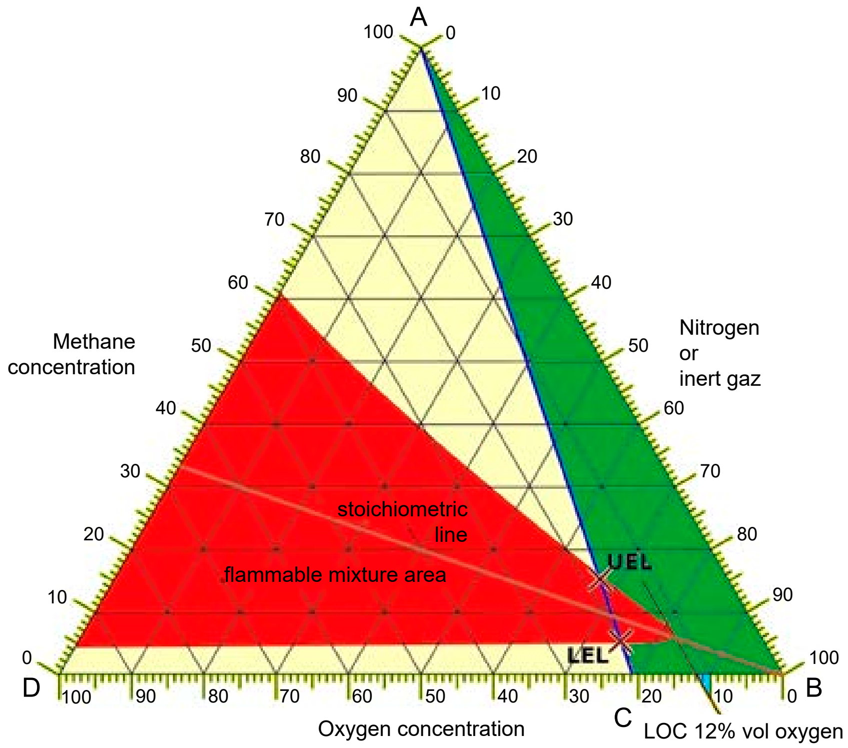

Figure 1. Diagram of methane-oxygen-inert gas mixtures

Reaching an oxygen volume concentration in the tested atmosphere in the range of 20.6–21.0%, is adequate for diluting the rested gases during the aerating process to the permissible range (below TLV-TWA it means for forty equivalent hours of working week).

Many gases (i.e., alkanes) are colorless and scentless. Depending on one's own senses (sight, smell) in assessing the possibility of safe work in enclosed spaces is not allowed. The Regulations of International Maritime Organization (IMO) MSC.1/Circ.1477 (IMO, 2014; Draeger, 2019) recommend the use of devices which allows for assessment of the atmosphere.

The threat of explosion may occur when the flammable gas, oxygen, and inert gases (mainly nitrogen, carbon dioxide, argon) mixtures are within the explosion limits. The range of explosion changes depending on the oxygen and inert gas concentration. Figure 1 presents the diagram (as an ABD triangle) for methane-oxygen and inert gases mixtures. Possibility of explosion exists only in the red area. An additional line of stoichiometric components has been drawn between methane and oxygen. In practical use, only the ABC triangle is essential. It means that by methane diluting the air, the explosive range is from 5.4% to 14% (for boil-off gas from liquefied natural gas, the range is from 5% to 15%) (TCF, 2017).

When the oxygen concentration decreases, the range narrows down and below the 12% concentration of oxygen, explosion (for methane-air mixtures) does not occur in the green area of the ABC triangle. For all types of cargo operations, the atmosphere in the tank, inside the green area, is safe but the procedures say that the oxygen concentration should be below 8% (due to measurement error and differences in composition of the atmosphere in different places of tank volume) to ensure safety.

Presence of toxic and dangerous gases – hydrogen sulfide concentration assessment

The presence of hydrogen sulfide (H_2S) in the cargo tank's atmosphere tank after the aerating process, is caused by the presence of the gas in crude oil and the next the process of its degassing. In spite of the degassing requirement for crude oil, the effect of the process declines during the cargo transport and may reach a level over a thousand ppm. The second phenomenon occurring at the same time, is the production of hydrogen sulfide during cargo transport. It is induced by the presence of sulfur compounds in cargo which in presence of water (steam or vapor as gas humidity) and the iron (iron alloys i.e., steels) as a catalyst react to form hydrogen sulfide. Crude oil as a natural product (feedstock) may include the strains of anaerobic bacterium which may produce hydrogen sulfide as a product of their metabolism.

The maximal hydrogen sulfide concentration for forty equivalent hours of work week is up to 5 ppm (over twenty years ago the limit was 10 ppm). Despite the strong odor of the gas (from concentration about 0.5 ppm), human smell is deactivated in a very short time and the gas gets impalpable. H_2S is again impalpable at a very high concentration and may be the reason that human senses do not react at all. It should be mentioned that the TLV-STEL (short time exposure limit) is 15 ppm for H_2S. This means that the maximum time for human work is up to 15 minutes every hour with the next 1-hour of rest. The TLV-C (ceiling threshold limit) is 30 ppm and the TLV-IDLH (threshold limit value immediately dangerous for human life and health) is only 300 ppm (at the most about 15 minutes for survival). The concentration of hydrogen sulfide over 700 ppm causes quick loss of consciousness and the loss of human life after a few minutes (PRS, 2016; CSBP, 2017; IMO, 2017). Hence the toxicity hazard from hydrogen sulfide is very serious for human. In all cases of doubtfulness, the measurement should be verified.

Oxygen concentration

The atmosphere composition of dry air is presented in the Table 1 (Mackenzie & Mackenzie, 1995; Bugbee & Blonquist, 2016; M&CA, 2018). In reality, the air composition may be different due to dilution of the main components through other gases (contaminated gases). Water vapor is the most shared gas which is not mentioned in Table 1.

Table 1. Dry air composition

Symbol	Name	Concentration [%] [v/v]
N_2	nitrogen	78.048
O_2	oxygen	20.947
Ar	argon	0.934
CO_2	carbon dioxide	0.041
Ne	neon	0.001818
He	helium	0.000524
CH_4	methane	0.00017
	other gases	the rest to 100%

Due to different concentration of water vapor depending on the air humidity, the air composition will still change and so it is in a reality. The air humidity is measured and indicated as absolute or relative. The quantity of water vapor depends on the air temperature and its relative humidity. In case of saturated air (100% relative humidity, the reaching of dew point) at +40°C of air temperature it is 50.5 g H_2O/m^3 but at −40°C it is only about 0.5 g H_2O/m^3(TCF, 2017). The difference between two mentioned points is a factor of approximately 100. The presence of water vapor dilutes the concentration of all atmospheric gases including oxygen.

At high air temperature (over +30°C) and high relative humidity, oxygen dilution may be essential. The influence of oxygen concentration on human health and a possibility of one's work in enclosed spaces is presented in Table 2 (CCNR/OCIMF, 2010; Draeger, 2019).

Oxygen insufficiency leads to the loss of consciousness and the threat of life loss (human death). In the cargo tank, the reasons for oxygen deficiency may be different: oxidation processes which use the oxygen from air (i.e., tank corrosion), biochemical processes in transported cargo, work carried out inside the cargo tank (i.e., welding), improper aerating process (pockets in the tank volume where the ventilating air did not reach, gases of bigger density than air, improper direction of ventilation etc.).

In manuals concerning the safety of work in enclosed spaces (H&SA, 2012; Bugbee & Blonquist, 2016; PRS, 2016; TCF, 2017; IHSA, 2019; Portal, 2019) a different oxygen concentration is noted (in the range 18.5–22%) which allows the possibility of human work but why is there a difference?

Table 2. Oxygen concentration in cargo tank atmosphere versus human health

Oxygen concentration [%] [v/v]	The hazards for human health depending on oxygen concentration in the atmosphere
>22	**prohibition of entrance**, enriched atmosphere in oxygen, increased the fire hazard, the human reaction – state of excitation and euphoria
20.6–22 or 20.6–21	**the possibility of human entrance** to enclosed space if no any additional hazards exist, human reaction – natural
19.5	**prohibition of entrance**, decreased oxygen concentration of the atmospheric air in tank, human reaction – speeding up the breathing, little difficulties in breathing, threat of loss the conscious during the work of high intensity
16	**prohibition of entrance**, significantly worsened the ability of stocktaking, difficulties in breathing, human reaction – the possibility of quick conscious loss without extortion prohibition of entrance, breathing with strong difficulties
<11	**human reaction – a loss of live in a few minutes**

The proper oxygen concentration should be in the range 20.6–21% (PRS, 2016) but this does not give the guarantee that the atmosphere is safe in reality due to the possibility of other hazards (see Table 2). On other hand, the concentration in the range 18–20.6% O_2 may be adequate for safe working in some situations.

The oxygen concentration below 20.6% means that an oxygen insufficiency exists and the reason for

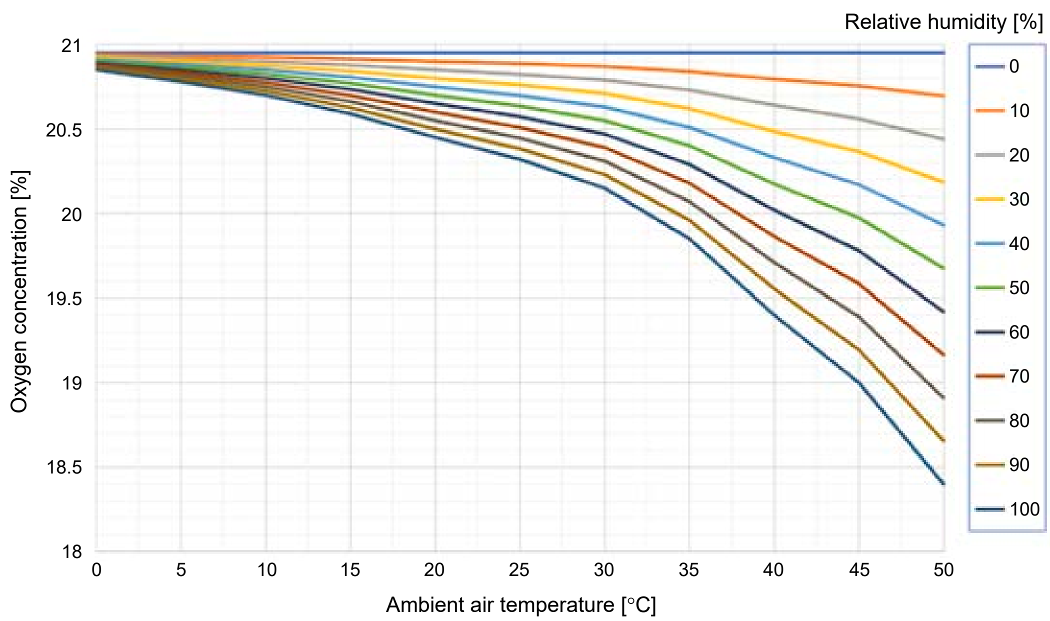

Figure 2. The influence of air humidity on the volume (mole) concentration of oxygen depending on ambient temperature at air pressure 101,325 Pa

such a situation needs to be recognized. An oxygen concentration correction should be done when the oxygen measurement was done at air temperature over +30°C and at high air relative humidity. In such conditions the range of 20.6–21% O_2 (v/v) may be impossible to reach. The oxygen concentration has reached the maximum possible value and the atmosphere is safe under conditions from Table 2.

The dilution effect of oxygen concentration through water vapor is presented in Figure 2.

Figure 3 presents the correction factor of oxygen concentration dependent on air temperature and humidity (for relative humidity of air the dependency is linear – it results from the definition of relative humidity).

At relative humidity 0%, the volume (mole) concentration of air components is identical to that of dry air (Table 1). The air temperature has no influence on oxygen concentration and the amount is 20.947% (also the correction factor for oxygen concentration is zero).

The situation is different for humid air especially when the air temperature is above +20°C and relative humidity over 70%. From that point the oxygen concentration is below the level 20.6%. For example, at +35°C and relative humidity 80%, the maximum oxygen concentration possible during aerating process is 20.07% and the correction factor 0.87%. It means that after a measurement in such conditions, the result should be corrected by adding the value 0.87% (such oxygen concentration will be for dry air). In extreme case at +45°C and air humidity 80% will be maximum at 19.39%. This is why the lower acceptable oxygen content is on the level of 19% in some procedures. The human reaction in humid hot air that the air is damp. The increased temperature and its humidity over the thermal comfort condition for human limits one's work productivity (M&CA, 2018; Portal, 2019).

Also, the ambient air pressure has essential influence on human oxygen concentration feeling and the productivity of work (especially the rapidity of change the air pressure). A change in atmospheric air pressure at the same temperature causes the change of air density and consequently the absolute amount of oxygen. According to Clapeyron's equation at isothermal change, the gas density (air and oxygen) is directly proportional to the gas absolute pressure.

In the case of work on vessels, it should be considered that the atmospheric air pressure is as on the sea level. There is no problem with the elevation (the air pressure decreases with the increasing altitude – this might mean that during work in the mountains there is an increase in the cases of depression).

A phenomenon may occur that inside high-pressure zone, humans feel better (easier to breathe) and on the other hand inside the low-pressure zone the breathing is more difficult (as oxygen deficiency). People particularly sensitive (meteoropathics) may feel heavy discomfort although the atmospheric conditions should be considered as being standard for the others.

The essential problem to be solved is to find the correction factor for the oxygen concentration in

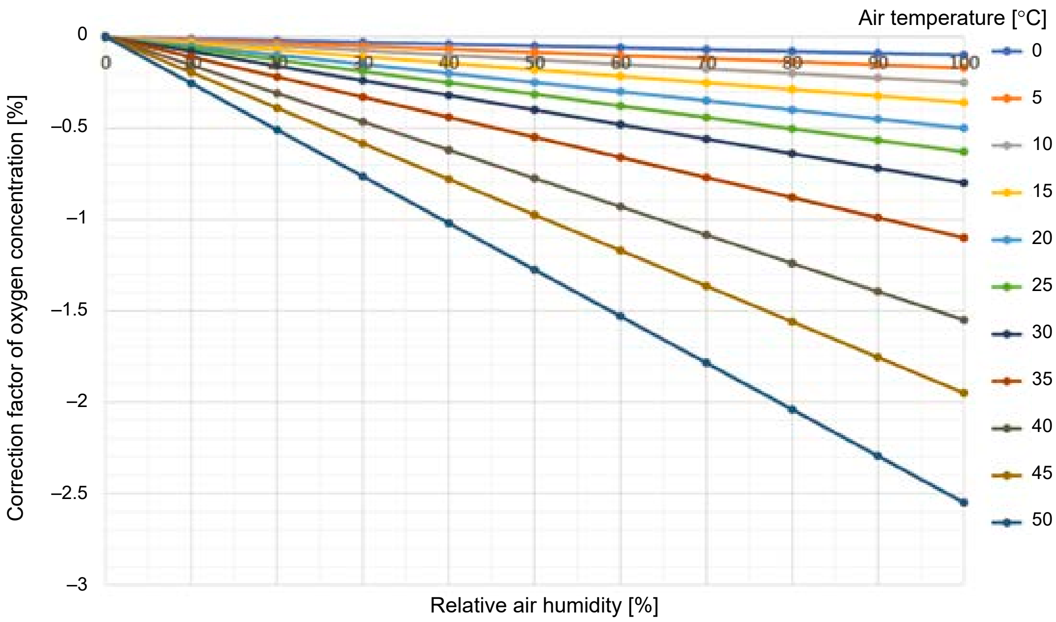

Figure 3. The influence of air temperature on the volume (mole) concentration of oxygen depending on humidity at air pressure 101,325 Pa

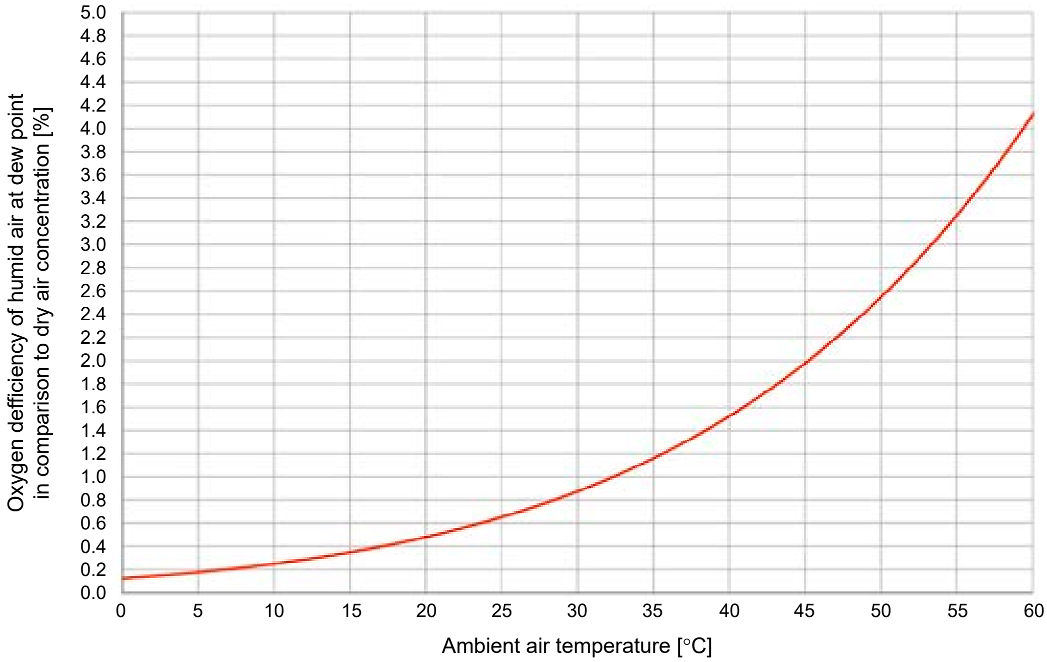

Figure 4. The oxygen deficiency in saturated air (at dew point) at pressure 101,325 Pa depending on ambient air temperature

case of high air temperature or high relative humidity. In Figure 4 it may read the correction factor between the oxygen concentration for dry air and humid air at dew point (100% relative humidity). In case of partial humidity, the correction factor will be partial also. For example, for 50% of air humidity the correction factor (CF) will be half (0.5) of the CF read from Figure 3. For air temperature below +30°C, the CF is low (below 1%) but important to consider during performing in enclosed space (PRS, 2016; Standard Club, 2017; IHSA, 2019).

In order to constrain the necessity of applying the correction factor, the air temperature should be decreased efficiently through decreasing the air humidity. It can done using a thermal-humidity processing of ventilating air. It is possible in inert gas systems where there is such processing available. Before cargo operations on chemical tankers especially on gas tankers, the atmosphere inside the cargo tank must be inert and below the required dew point. The dew point constricts the maximum possible amount of water vapor. This has a crucial significance on the safety of carried cargo considering possible water-cargo reactions (creation of hydrates) and the risk of water freezing when the temperature of cargo will be below 0°C.

Thermal-humidity processing does not occur in inert gas systems on oily tankers. There is no technical possibility for decreasing the dew point. The practical possibility that remains is ventilating the cargo tank in such time of a day when the ambient air conditions are the best for such process.

An influence of ambient temperature on work conditions into cargo tanks

In ambient air temperature in the range 5–20°C, work is permissible when the crew member is dressed in proper overall and when appropriate work conditions (i.e., continuous ventilation, accessory of workplace, anti-falling precaution) and assuring human thermal comfort are fulfilled. Air temperature outside the mentioned range may create additional threats such as frostbites. Frostbites are dangerous especially to protruding parts of human body (nose, ears, fingers, and toes) (IHSA, 2019; Portal, 2019).

When the ambient air temperature is below +5°C and the ventilation system works (air flow), the worker may feel cold and experience hypothermia. At temperatures below 0°C, it happens earlier. The basic solution is the use of hot air ventilation which improves the work conditions without the necessity of work breaks to get warm. The other ones are the limitation of work time, using better work overalls, work breaks for warming, using hot drinks or meals etc.

Spending a long time dwelling in an environment where the temperature is extremely low may result in hypothermia occurring which is a conceived threat to human life. The symptoms of hypothermia are – nausea, quick extortion, headache and head giddiness, tendency for aggravation or euphoria. The first symptoms are shivers which is the reaction of the human organism as the compensation from body temperature decreases. This probes the creation of additional amount of heat from energy stock in human body. Frostbites are dangerous especially to protruding parts of human body (nose, ears, fingers, and toes) (IHSA, 2019; Portal, 2019).

More often, the case is working at too high ambient temperature over +30°C (sometimes over +40°C e.g., in fuel centrifuges room on vessels). The self-regulation of human body through perspiration has a limited impact. Basically, the cooling effect through perspiration decreases with ambient air temperatures over the human body temperature about and over +36.6°C. A person working at high ambient air temperatures loses water with sweat and mineral salts. Loss of water and mineral salts should be leveled out by drinking water and ingesting salt. Drinking about one liter of water in one hour is the highest function of a healthy human being. It should be done by drinking a small amount of water in short time intervals. The solution is taking special drinks (isotonic) which recompense the loss of mineral salts. The threat to human is the disturbance of the electrolyte balance which conditions the proper state of the heart. If an imbalance occurs, it risks the heart twitching, threaten seizures, disturbs the heart rhythm, changes blood pressure, causes confusion etc. Salts in tablet form should not be ingested, it is necessary to dissolve tablets in water. Do not drink any alcohol because they increase water excretion from human organism. It is important the work planning is carried out in the most suitable atmosphere conditions for humans (e.g., during nights) or with time limitation, often breaks in work and no work at midday hours etc.

Discussion – maritime regulations and their applicability in practice

Fulfilling the requirements for proper and safe air composition for human work is the preliminary condition for preparing for human entrance to enclosed spaces. The possibility for safe work depending on the type of work should be ensured and other requirements of procedures like:

- the assurance of other human supervision (including connection means between the worker and supervisor) and the reassurance of person working in enclosed space;
- the equipment preparation in case of emergency situations (breathing apparatus, lifeline, evacuation line etc.) – emergency procedures;
- continuous gas detection required the concentration control (including portable personal oxygen concentration detector and/or explosimeter);
- continuous ventilation of tank volume, at some works (e.g., welding) the application of extractor fans (welding fumes and dusts);
- other requirements according to the procedures being in force.

An example of proper preparation in the workplace during the inspection process in the tank is presented in Figure 5.

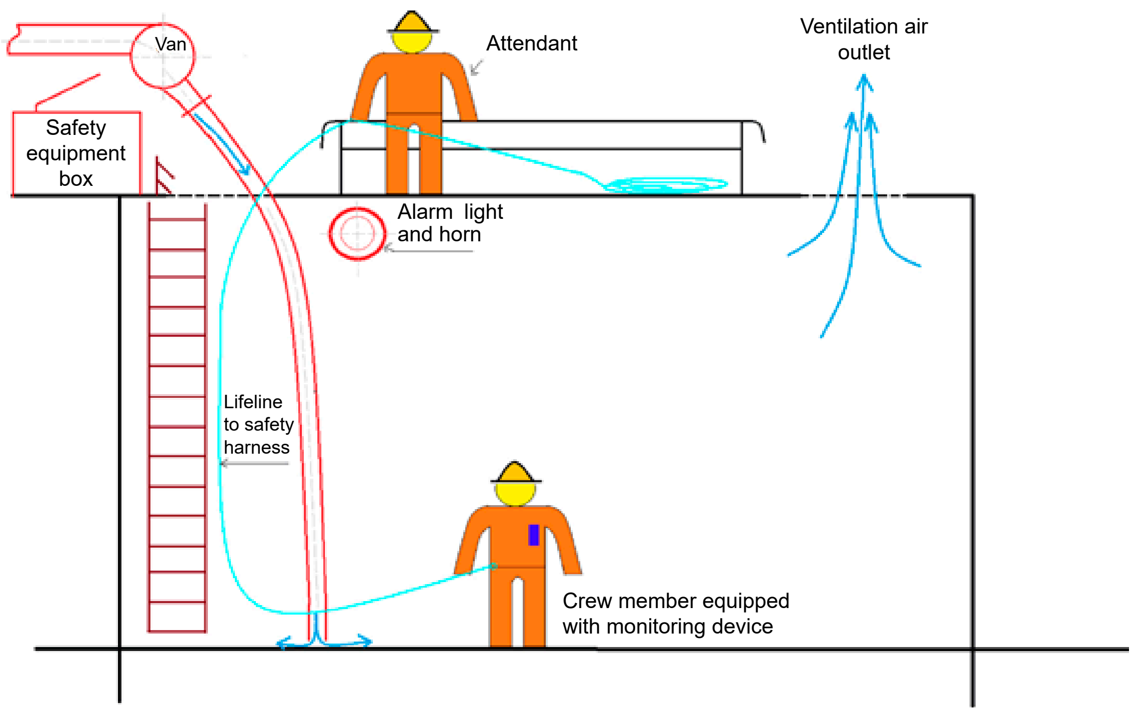

Figure 5. Essential conditions for allowing the work into enclosed spaces – the safety system

The measurement of dangerous gases concentration is clear for experienced responsibility officers and is done properly (a fault causes the necessity of performing an emergency procedure and it is important for all that it rarely happens).

The essential question is, how to interpret the result of the oxygen concentration measurements in cargo tanks giving the guarantee of safe work. The information that the oxygen concentration in the range 18.5–19% still gives the conditions for safe work and there is no mention about the upper limit. In other manuals, there is the interpretation that safe oxygen concentration should be in the range 20.6–22% (presented in Table 2).

The assessment of the atmosphere composition in cargo tank, after many different processes during preparing, loading, laden voyage, discharging, gas-freeing, aerating and others, is a complicated problem and sometimes difficult for a clear-cut answer. The verification and analysis of all processes dropped in is a necessity. Even after fulfilling all necessary precautions in cargo tank, the human factors – health state, age, time of rest, mood etc. still exist which influence human productivity. The final decision about the permission for work in enclosed spaces depends on the decision of responsibility officer (competent person). It must be remembered that the atmosphere composition still changes (human presence, prosecuted work, ventilation efficiency, moment of a daytime, external atmospheric conditions, change position of a vessel and others). Also, the condition for safe work may change, and it must still be monitored carefully with an alarm or sensor to notify when it is inappropriate. After determined intervals of time (often 4–12 hours) the atmosphere assessment and new procedure should be performed again.

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