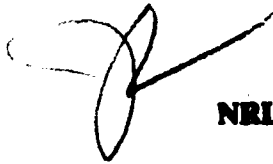


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NRL Memorandum Report 3314

Aviator's Breathing Oxygen Purity

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ii

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TABLE OF CONTENTS

INTRODUCTION 1

BACKGROUND 3

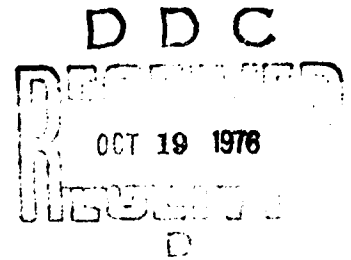
SPECIFIC CONTAMINANTS. 4

SUMMARY. 17

TABLE 1. 20

REFERENCES 22

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AVIATOR'S BREATHING OXYGEN PURITY

INTRODUCTION

The Procurement Specification Limits for Aviator's liquid (breathing) Oxygen (ABO) are set forth in MIL-O-27210 (1). These limits were established based on safety related reasons and what can be produced and the sensitivity of various analytical techniques. The Navy has established contaminant levels for ABO that are somewhat relaxed from MIL-O-27210, which dictate maximum contaminant levels for ABO use. These have been termed Use Limits (2). If the Use Limits could be increased without impairing the safety or capacity of naval installations and personnel, more efficient usage (lower cost) and less stringent testing (easier and lower cost) of ABO would result. This report reviews the Use Limits and makes some recommendations about contaminant levels.

The MIL-O Specifications as interpreted literally (3) are unrealistic since the inert gases krypton and xenon by default come under the limit for all compounds not specifically listed -- 0.1 part per million (ppm). Industrial standards (4) subtly do not include krypton or xenon, as it is not possible to detect these compounds by the currently used analytical tool for liquid oxygen (LOX) analysis, infrared (IR).

Krypton and xenon are concentrated in the LOX fraction upon air liquefaction since they have boiling points above that of oxygen and are present in the atmosphere at approximately 1 ppm. Even high purity cylinder oxygen of 99.99% purity contains up to 15 ppm krypton and 5 ppm xenon (5). As long as the oxygen concentration of ABO is above 99.5%, with nitrogen, argon, krypton and xenon total concentration less than 0.5%, the ABO should be satisfactory. These concentrations should not be a problem, but it does indicate that probably all LOX produced by or purchased for the Navy is technically in violation of MIL-O-27210. Standards are not sacred but should be employed with understanding.

While Use Limits are set higher than procurement specifications and this report suggests increases in some of these Use Limits, changes to MIL-O-27210 itself (excluding the exceptions of krypton and xenon, e.g., to 100 ppm) are not suggested.

A modern LOX production plant, utilizing relatively unpolluted air as intake and with adequate desiccant, can produce LOX meeting the specifications with the exception cited above. Concentration of impurities higher than MIL-O specifications indicate non-optimum conditions in LOX production or intake air contamination, which should be traced and eliminated before impurities increase to dangerous levels. Exceeding a specification concentration level on one or several contaminants

Note: Manuscript submitted June 17, 1976.

increases the possibility that some other contaminant - perhaps not analyzed for - also is above desirable limits due to existing non-optimum conditions.

The authors of this report, being analytical and physical chemists, do not consider themselves competent to independently suggest increases in Use Limits which may have physiological reactions. We have relied on TLV levels (6), OSHA standards (7), and allowed contaminant levels in submarines (8), which are in use and have not led to difficulties. However, these are levels which may be used safely without injury, not levels at which there are no noticeable effects. Bureau of Medicine and Surgery, or other suitable agencies, should review Use Limits suggested in this report and offer their evaluation.

Such evaluation should consider that aviators begin inhaling 100% pure oxygen at atmospheric pressure once in the aircraft. This is to outgas nitrogen from their bodies to avoid nitrogen narcosis when exposed to reduced pressures at high altitudes. Exposure to contaminants while in 100% oxygen at atmospheric pressure may last up to one-half hour due to the finite time necessary to carrier launch large numbers of aircraft. Once aloft, delivery pressure of ABO is reduced and, thus, while the relative concentration of impurities remains constant, their partial pressures decrease proportional to oxygen delivery pressure.

BACKGROUND

Primary factors which affect the Use Limits are safety related. First to be considered is adverse physiological reactions, the point where the aviator's operating ability is impaired, which may occur at concentration levels far below toxic levels. Odors and temporary irritations, even if not injurious, can affect the aviator's operating ability. Second is flammability or explosion hazards. (Flammability limit as used in this report refers to the lean or lower flammability limit.) Third is contaminant solubility in LOX. If frozen contaminant particles enter the LOX converter, the aviator will be exposed to a short duration, but greatly increased concentration of contaminant. Also compounds such as acetylene exceed their flammability limit upon solidification in LOX, and contaminants present at concentration levels below their solubility limits may still adsorb onto other particles. Fourth is mechanical problems caused by clogging of transfer lines and valves by frozen particulates (especially carbon dioxide and water).

There are secondary factors which affect the Use Limits. While LOX entering the converter will yield the same concentration of impurities in the gas phase as in the liquid phase, liquid loss by evaporation in storage will act to concentrate impurities which have lower vapor pressures than that of liquid oxygen.

Also a high Use Limit for a particular contaminant may be regarded as "safe" in accordance with the above factors, but such high

levels may make analysis for other contaminants difficult or impossible at their respective Use Limits (interferences).

SPECIFIC CONTAMINANTS

The Use Limits for specific contaminants are discussed in this section with the criteria for the levels that are recommended.

Methane (CH₄)

Methane is a non-toxic; at very high concentrations asphyxiation from oxygen depletion occurs, not intrinsic methane poisoning. The lower flammability limit is 5% in oxygen. Methane is also miscible in LOX, almost up to 100%. Thus, strictly according to the primary factors, methane is "safe" in LOX up to approximately 50,000 ppm. Atmospheres from closed environments such as submarines can contain easily up to 500 ppm methane. The limit for methane in nuclear submarines is set at 13,000 ppm, i.e., one-fourth the flammability limit. However, methane does concentrate upon LOX evaporation, and calibrations can be inaccurate. Such a very high concentration of methane would indicate faulty plant operation or storage and could mask other hydrocarbons that must be detectable at far lower levels depending on the analysis scheme. After nitrogen and argon, which can be present in LOX up to 0.5%, methane should be allowed the next highest contaminant level.

A limit of 500 ppm is a reasonable compromise for a Use Limit, but this high level must not be 'acceptable' for LOX production plant operation. Methane contamination at the production point should be held to within MIL-O-27210 limits.

Acetylene (C₂H₂)

Acetylene is by far the most dangerous contaminant commonly found in LOX production. While it is non-toxic (it is a weak anesthetic, but not below 9%) and its lower flammability limit is 2.5% (5), it has a very limited solubility in LOX, approximately 5 ppm at atmospheric pressure (9). Once in the solid form, the flammability and explosive limits are easily exceeded. Furthermore, this solubility decreases below 5 ppm on approaching the temperature of liquid nitrogen. Once solidified, acetylene does not quickly reach equilibrium conditions and go back into solution. Furthermore, acetylene, even if present in concentrations below 5 ppm, may crystallize out from evaporation on tank walls as the liquid oxygen level drops. A suitable safety factor is required.

The Use Limit for acetylene in LOX for ABO should remain at 0.1 ppm, its current value. This limit includes a safety factor of 50,

which involves the secondary factors. The Use Limit for acetylene in gaseous oxygen would be much greater, as there would not be a solubility problem.

OPNAVINST 4790.2A, Volume II (2) is misleading in Figure II-7-4, page 7-74, "Contaminant Build-up in LOX Undergoing Evaporation." The figure shows acetylene, starting from its MIL-O limit, reaches a solubility limit of 5 ppm after 90% evaporation. If true, this would be serious indeed. However, initial acetylene level is shown as 0.5 ppm, instead of the correct value of 0.05 ppm. Thus, upon concentration by evaporation, acetylene reaches its solubility point of 5 ppm after 99% evaporation, a small but very significant difference.

Carbon Dioxide (CO₂)

The Threshold Limit Value (TLV), or concentration level that can be maintained for long duration exposures for carbon dioxide is 0.5% (6). Onset level of effects is probably around 1% - but this can vary with environmental stress. Hyperventilation occurs at 5%, and lower levels can be tolerated as long as there is adequate oxygen supply (which there should be with ABO). Submarine 90-day exposure value is 0.5% (8).

Carbon dioxide is non-flammable and is concentrated upon LOX evaporation. The primary danger with elevated carbon dioxide levels is its limited solubility. Solid particles can give an aviator short duration but high concentration exposure or interfere with ABO equipment by clogging system components.

Current Use Limit is 10 ppm, with local command discretion to allow up to 30 ppm. But solubility of carbon dioxide in LOX is 4 ppm at atmospheric pressure (10), and thus higher readings indicate the presence of solid contaminant that is measured upon vaporization. Concentrations found above the solubility limit should serve as a warning as the amount detected will vary with the degree of suspension, sample point, and number of transfers of LOX. Newer LOX production facilities with sufficient adsorbent can hold the CO₂ concentration near 4 ppm. Practically speaking, the current Use Limits should be retained for older plants and their supply tanks, but newer plants should attain lower levels. As with acetylene, the Use Limit of carbon dioxide in gaseous oxygen can be much greater.

Although solid acetylene floats on LOX, acetylene coprecipitates with carbon dioxide. With carbon dioxide concentrations greater than 40%, the coprecipitate does not float. However, the coprecipitate does not present an explosion hazard (11). There is the possibility that solid carbon dioxide performs a safety function by adsorbing acetylene even below the solubility limit of acetylene. However, there is also the possibility of adsorbing other contaminants which could then expose the aviator to short, but high exposure of those contaminants.

Total Hydrocarbons

This is a misnomer, better nomenclature is Total Organics, i.e., Hydrocarbons and Oxygenated Hydrocarbons, as Ethane equivalent. A more comprehensive definition is used with the Navy's Total Hydrocarbon Analyzer (THA) which measures Total Organics as it also detects oxygenated hydrocarbons. This instrument responds to any organic compound that produces ions in a flame (12).

MIL-O-27210 lists ethylene (ethane - C_2H_4) separate from Total Hydrocarbons (represented by ethane - C_2H_6 - equivalent) with Use Limits of 0.4 ppm and 6.0 ppm, respectively. However, ethylene is much 'safer' than some of the other possible organics. The "Commodity Specification for Oxygen" (4) lists specifications for Grade E Oxygen as containing a maximum of 3.0 ppm "ethane and higher saturated hydrocarbons" and a maximum of 0.2 ppm ethylene. Other grades in this reference specify "Total Hydrocarbon" limits. However, "Total Hydrocarbon" content is to be determined by (a) IR for the characteristic C-H bond stretch, (b) IR or chemical means for carbon dioxide following oxidation (c) flame ionization - total response. All these measure total organics, and (d) gas chromatography - impractical to distinguish hydrocarbons from organics. "Ethane and higher saturated hydrocarbons" are to be determined by (a) "appropriately calibrated" IR or (b) flame ionization-gas chromatography. Both of these methods can discriminate against methane, but they do not exclude many organics or unsaturated hydrocarbons unless done with extreme care. "Ethylene" is to be determined by (a) IR at 5.3 microns or (b) flame ionization-gas chromatograph. Ethylene, like methane, can be uniquely determined.

One reason to list ethylene separately appears to be that it can be differentiated by some test methods and, thus, split out of total organics. Another possible reason is ethylene had been used as a refrigerant. At least one explosion may have been due to ethylene leakage. This is not a consideration now since fluorocarbon refrigerants are used.

If the major components of total organics, that is, methane, ethylene and other selected compounds, can be split out, sensitivity for the remaining organics is increased.

Ethylene is non-toxic. It has been used as an anesthetic, but at concentrations above 75%. The flammability limit is 2.75%, and solubility in LOX is about 12,000 ppm. Thus, a Use Limit of 100 ppm represents a 'safe' limit with a safety factor of over 100. However, such an exaggerated presence of ethene means definite non-optimum LOX production conditions with its implications of other possible trouble points. A Use Limit of 20 ppm is reasonable for ethylene with the same restriction as that suggested for methane. ABO meeting this Use Limit should not be accepted with complacency. The causes of levels at LOX production plants above MIL-O of 0.2 ppm should be eliminated. Causes of elevated ethylene levels could be similar to those giving increased acetylene concentrations.

Ethane itself is also non-toxic, and an anesthetic (no noticeable effects below 5% ethane), has a flammability limit of 3.0% and a solubility in LOX of 200,000 ppm (22%). Thus, it should be similar to methane in terms of hazard. A Use Limit of 200 ppm includes a safety factor of over 100. However, as in the case of ethylene above, a Use Limit of 20 ppm is more reasonable. Effort must likewise be made to reduce such elevated contamination level as it is an indication of production plant problems. Similar reasoning would apply for propane to give a use limit of 20 ppm also.

Among other possible organic contaminants, flammability limits will be in the percent range. Some will be toxic or capable of being detected by odor or be an irritant at levels of 10 ppm or less. Also, several compounds could be hazardous due to their low solubilities including acetaldehyde (CH_3CHO) 0.4 ppm, acetone (CH_3COCH_3) 1.5 ppm, 1,3 butadiene ($\text{CH}_2=\text{CHCH}=\text{CH}_2$) 2.5 ppm, methylacetylene ($\text{CH}_3\text{C}\equiv\text{CH}$), and possibly formaldehyde (HCHO). Larger hydrocarbons, six carbon atom skeletons and higher, likewise have low solubilities but should be easily separated from ABO during production. The solubility for n-decane given as 12 ppm in reference (11) is wrong; it is much lower.

Fortunately, butadiene and methylacetylene should be separated from LOX due to their relatively high boiling points, and most oxygenated hydrocarbons should be separated both due to their boiling points and their affinity for water. Water miscible organics will be removed with moisture early in LOX production. Careful experimental examination of organic contaminants in LOX is warranted to determine if low solubility compounds including acetaldehyde, acetone, butadiene, pentadiene, formaldehyde and C-6 and above hydrocarbons are present at significant levels. These results could then give guidance on the philosophical decision of how to separate these compounds, if at all, from Total Organics, and the setting of realistic limits. Any practical decision will be a compromise between low limits for specific contaminants and their probable presence in ABO.

Since Total Organics is such a 'grab bag' of possible hazards, and many odorants and irritants will be oxygenated organics (formaldehyde odor sensitivity is 1 ppm (13)), the current Use Limits should be retained. If ethylene (and ethane and propane) can be determined separately, the Use Limit might even be able to be lowered. If not, the Use Limit should remain at 6 ppm, notwithstanding the relative safety of ethylene and ethane.

While the contaminant characterization ideal would be separate quantification of all significant organics, this is not possible outside of a research laboratory environment. Knowing when ethane, ethylene or propane concentrations become excessive are measures of LOX production problems. It is difficult to envision a simple and reliable shipboard analytical tool that will be able to determine ethane, ethylene or propane. Fortunately, as long as methane, acetylene, and total organics can be adequately monitored, it is not necessary to go to more complex and expensive devices to do so.

Halogenated Compounds: Refrigerants

Fluorinated hydrocarbons (tradenames - Freons, Halons, Genetrons, Isotrons, or Ucons) are used as refrigerants within LOX production plants and for general purpose solvents. Refrigerant leaks upon initial plant startup and leaks developing with time can contaminate LOX. A practical reason to maintain low limits is that presence of fluorocarbon is used to indicate refrigerant leaks.

Fluorocarbons are a broad class of compounds; prevalent ones include R-11 (CCl_3F), R-22 (CHClF_2), R-113 ($\text{CCl}_2\text{FCClF}_2$), and R-114 ($\text{CClF}_2\text{CClF}_2$). All these are non-flammable and have TLV's of 1000 ppm (1000 ppm is the highest TLV 'hazard limit' employed, except for CO_2). Unsaturated fluorocarbons have reduced TLV's and, like partially fluorinated hydrocarbons, are usually flammable. Such compounds should not be present.

Liquid oxygen generated on submarine tenders is used to charge submarine high pressure gaseous oxygen banks. Fluorocarbon contamination limits for submarine atmospheres are subject to the additional restraint that decomposition products generated in carbon monoxide hydrogen burners (CO/H_2), including HCl and HF, should not significantly deteriorate burner integrity or pass through scrubbers. Submarine limits for decomposition resistant R-12 and R-114 are set at 20 ppm for 90 days and 1000 ppm for 24 hours. R-11 does significantly degrade in the burner (14), and its limits are 5 ppm for 90 days and 20 ppm for 24 hours. Specific limits have not been set for other refrigerants, but data on extent of halocarbon decomposition over the Hopcalite catalyst used in the burners (14) can be used for guidance. R-21 decomposition susceptibility is similar to that of R-11; R-22 is slightly worse. R-113 decomposes but to a significantly lower degree than R-11. Use of decomposition-prone refrigerants should be discouraged. In all cases, fluorocarbon content in submarine atmospheres from trace contaminants in oxygen will be moderated by dilution by nitrogen and the on-board generation of oxygen.

In the absence of advice to the contrary from BUMED or low solubility data (R-22 had a reported solubility in LOX of 600 ppm, but that value is questionable), a Use Limit of 10 ppm is suggested, but values over 2 ppm should initiate searches for refrigerant leaks.

Halogenated Compounds: Solvents

The separation of halogenated compounds into refrigerants and solvents, though somewhat arbitrary, is useful. Refrigerants are typically low molecular weight fluorocarbons, whereas solvents are typically chlorocarbons. Recently, however, certain fluorocarbons are replacing some chlorocarbons as solvents. For example, R-113 is probably more widely used as a cleaning solvent than as a refrigerant. Many chlorocarbon solvents are specifically prohibited for use aboard

nuclear submarines. Most refrigerants are actually fluorochlorocarbons, i.e., they contain both fluorine and chlorine atoms. These compounds are referred to as fluorocarbons since fluorine has a more profound effect on their chemical and physical properties.

The practical distinctions between solvents and refrigerants are: (a) solvents would be present from high levels in the intake air stream, where refrigerants would be present from production plant leakage, and (b) chlorocarbons are more toxic than fluorocarbons or fluorochlorocarbons (e.g., carbon tetrachloride has a TLV of 10 ppm, whereas carbon tetrafluoride has a suggested TLV of 1000 ppm).

Brominated solvents without fluorine atoms on the same carbon atoms are much more dangerous than chlorocarbons, e.g., TLV of chloroform - CHCl_3 is 50 ppm, but TLV of bromoform - CHBr_3 is 0.5 ppm. A possible future source of bromocarbons is the fire suppression agent BFC_1 , CF_3Br . This compound is relatively inert.

Since 'solvents' are not intrinsic to LOX production, some have low TLV limits, and many are almost completely decomposed in submarine CC/B_2 burner, the current Use Limit of 0.2 ppm should be maintained.

Nitrous Oxide (N_2O)

Nitrous oxide is a naturally occurring component of the atmosphere at 0.5 ppm. It is used as an anesthetic (laughing gas) at relatively high concentrations - in the percent range. Presence of N_2O in the ppm range is not expected to cause physiological reactions.

Nitrous oxide does have a limited solubility of 70 ppm in LOX. It can cocrystallize with acetylene. While solid acetylene will float on LOX, cocrystals with over 50% nitrous oxide can form a suspension in LOX, and cocrystals with over 60% nitrous oxide will sink. Cocrystals with over 25% acetylene can detonate (11). Thus, the simultaneous presence of acetylene and nitrous oxide above their respective solubility limits can cause a new danger, accumulation of solid explodable acetylene on tank bottoms. (Pure nitrous oxide solid will not detonate in LOX.)

MIL-O-27210 limits nitrous oxide concentration to 1.0 ppm. There is no Navy Use Limit. The Air Force has a Use Limit of 2.0 ppm (T. O. 4876-1-1 [November 1966]), and Dr. Kenneth Ikels (15) has recommended this be increased to 4.0 ppm. The increased danger of nitrous oxide and acetylene coprecipitation contraindicates a Use Limit of 4.0 ppm. A Use Limit of 2.0 ppm gives a larger safety factor which is desirable for plant operation.

Nitrogen Oxides (NO_x): Nitric Oxide (NO) and Nitrogen Dioxide (NO₂)

Nitric oxide has a TLV of 25 ppm and a solubility in LOX of 6 ppm. It will spontaneously oxidize to nitrogen dioxide which has the lower TLV of 5.0 ppm (Russia uses 2.0 ppm) (6) and a solubility in LOX of 15 ppm. While NO oxidation is slow at low concentrations, there is the increased danger from probable synergistic effects of these two nitrogen oxides with each other and with carbon monoxide (6). Fortunately, NO₂, which is an odoriferous irritant and is the more dangerous of these two oxides, is removed from the intake airstream more efficiently than NO, because of its higher melting and boiling points.

Nitrogen oxides can sensitize explosions, and nitric oxide can react with dienes violently. While diene concentration should be low (dienes are a class of olefinic hydrocarbons), this hazard may occur if large amounts of dienes are present in the intake air.

Nitric oxide and nitrogen dioxide are not specifically mentioned in MIL-O-27210 and, thus, they come under the general limit of 0.1 ppm, each. This limit should be retained. The Environmental Sciences Division, USAF School of Aerospace Medicine (15) recently acquired a sensitive chemiluminescent NO_x detector. Their future studies on concentration levels of NO and NO₂ in ABO should provide needed information on the potential hazards of NO or NO₂. If found to be present, analysis for these compounds should be performed regularly.

Carbon Monoxide (CO)

The flammability limit of CO is approximately 15%. Carbon monoxide is soluble in LOX. Since CO boils at a lower temperature than LOX, it is not concentrated by evaporation. It is poisonous in high concentrations and causes headache, fatigue and dizziness. Low concentrations can degrade aviator abilities including judgment, coordination, and visual acuity.

Carbon monoxide poisoning acts primarily by combination with red blood cells, forming carbon monoxide hemoglobin (HbCO), thus depriving the body of the oxygen carrying capacity of such blood cells. Onset of ability impairment occurs at 2% HbCO and is serious at 5% HbCO. Cigarette smokers frequently show HbCO levels of above 5% but seem to have become accustomed to its effects and, thus, seemingly 'tolerate' higher ambient CO levels.

Typical nonsmoker HbCO concentration is 1%. Thus, reduction of CO concentration below 5-10 ppm is not significant. The submarine exposure limit is 25 ppm for 90-day exposure and the TLV is 50 ppm. Since carbon monoxide does not solidify in LOX nor concentrate upon LOX evaporation, a CO concentration of 2 ppm is a reasonable Use Limit.

Ozone (O_3)

Ozone is a very reactive oxygen molecule formed from three atoms, O_3 , rather than two, O_2 . It is commonly formed in photochemical smog, by electrical discharges, and by some electrical transformers. The OSHA limit for safe, long-term exposure is 0.1 ppm, but ozone can be detected by odor from 0.01-0.02 ppm. At low concentrations ozone is an irritant to the eyes and mucous membranes. More severe exposure results in headache, shortness of breath, drowsiness and ultimately pulmonary edema and hemorrhage (5).

Ozone is miscible with LOX up to 17.6% and will not explode until present above that concentration. However, a trace of ozone (below 0.1 ppm) can act as a sensitizer and initiator for detonations; e.g., ozone will cause the explosion of acetylene - LOX slurry. Ozone has not been known as a problem in the past (11).

Water (H_2O)

The presence of water is a problem because of the potential clogging of equipment by ice particles, as well as possible complications of some analytical techniques. The current Use Limit is 14 ppm. This is equivalent to a dew point of approximately minus 58°C at atmosphere pressure, whereas LOX boils at -183°C at atmosphere pressure. This Use Limit value should be reduced to avoid clogging of lines and valves, but such a reduction may not be practical. The problem of maintaining very low water concentration (and carbon dioxide as well) is compounded by back-diffusion of contaminant through vent lines and during LOX transfers.

Other Contaminants

All contaminants not specifically considered above are assigned a maximum concentration limit of 0.1 ppm by MIL-O-27210. This low value is adopted since the hazards involved are unknown as are detection limits. However, this catch-all category limit does not have much practical value. Impurity detection requires that one knows 'where to look' to achieve such low concentration sensitivity.

Particulates and Fibers

The industry specification for Grade E liquid oxygen (4) sets contamination limits on permanent particulates at 1.0 milligram per liter (mg/l) with none larger than 1 millimeter diameter and limits presence of fibers to none larger than 6 mm in length. There are no corresponding limiting characteristic categories specified in MIL-O-27210. Such 'permanent' solids (i.e., not including substances that

would not be solids at normal conditions, 20°C and atmospheric pressure) can be present in intake air or generated in LOX production, such as from fines from silica gel adsorbent, and contribute to clogging problems.

Investigation of the seriousness of 'solids' contamination of ABO should be performed, and if found to be significant, an appropriate Use Limit should be set. At a minimum, the industry limits for these categories should be employed with MIL-O-27210 for commercial procurement of ABO.

SUMMARY

Use Limits proposed in this report for ABO contaminant levels are summarized in the Table. Current limits for procurement and Use Limits are also given for comparison. All suggested changes are tentative and subject to review for medical hazards. High contaminant levels, even if acceptable for ABO use, do not imply 'laissez faire' for oxygen production and handling techniques, just that such use should not result in explosion or be detrimental to aviator performance.

Some contaminant limits for ABO usage are based on limited solubility properties in liquid oxygen. Thus, for some of the compounds given in the Table, presence of contaminants in gaseous oxygen above Use Limits suggested in this report may not be hazardous. Individual consideration of higher limits would have to be performed under their specific operating conditions.

All significant contaminants, except nitrogen, argon and carbon monoxide, are concentrated upon liquid oxygen evaporation. ABO satisfying Use Limits can thus become hazardous if proper insulation, transfer, and purging techniques are not employed.

It is not practical, nor is it necessary, to monitor all contaminants. The main emphasis should be on acetylene - explosive hazard; carbon dioxide - component clogging hazard and indicator of desiccant operation; and total organics - possible odoriferous, toxic or explosive hazards and indicator of plant conditions.

Methane, the highest concentration flammable contaminant, should not be a hazard at expected concentrations. However, it may be used as an indicator of intake air purity, proper plant operation, and LOX storage facility safety. Also, it may be needed to allow correction due to interferences and is easy to determine (16).

Halogenated solvents can be quite toxic or odoriferous and should be monitored. However, this may be difficult to do at low levels due to the variety of possible compounds. Also, the importance of chlorocarbons is decreasing as fluorocarbons replace solvents for many shipboard uses. Refrigerants should be monitored as an indicator of LOX plant refrigerant leakage.

Nitrous oxide is present in air. It is dangerous primarily in combination with acetylene, which is assumed to be monitored. Carbon monoxide is hazardous, but it has not been observed as a significant species in the past. Ethylene, and ethane and propane, are significant compounds in the total organics category. They are relatively inert, and it is desirable to measure their concentrations to allow for more sensitivity of the remaining more hazardous components of total organics. However, this should be done on field instruments, only if there is no significant deterioration of system reliability, ease of operation and economy.

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14. "Catalytic Decomposition of Halogenated Hydrocarbons Over Hopsalite Catalyst," J. K. Musick and F. W. Williams, I & EC Product Research and Development, Volume 13, p 175 (1974).

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TABLE 1
 ABO CONTAMINANT CONCENTRATION LIMITS¹

<u>Substance</u>	<u>Procurement Specification Limit MIL-0-27210</u>	<u>Use Limit OPNAVINGT 4790.2A Vol. II</u>	<u>Suggested Use Limit²</u>
Oxygen (O ₂)	99.5% min	99.5% min	99.5% min
Methane (CH ₄)	25 ppm	50 ppm	500 ppm ³
Acetylene (C ₂ H ₂)	0.05	0.10	0.10
Carbon Dioxide (CO ₂)	5.0	10.0(30.0) ⁴	10.0(30.0) ^{4,5}
Total Organics ⁶ (ethane equivalent)	2.0	6.0	6.0 ⁷
Ethane ⁸ (C ₂ H ₆)	-	-	20 ³
Propane ⁸ (C ₃ H ₈)	-	-	20 ³
Ethylene ⁹ (Ethene C ₂ H ₄)	0.2	0.4	20 ³
Halogenated Compounds Refrigerants (Fluoro- carbons)	1.0	2.0(6.0) ⁴	10.0 ³
Halogenated Compounds Solvents (not included above)	0.1	0.2(0.6) ⁴	0.2 ¹⁰
Nitrous Oxide (N ₂ O)	1.0	-	2.0 ^{3,11}
Nitric Oxide (NO)	0.1 ¹²	-	0.1
Nitrogen Dioxide (NO ₂)	0.1 ¹²	-	0.1
Carbon Monoxide (CO)	0.1 ¹²	-	2.0 ³
Ozone (O ₂)	0.1 ¹²	-	0.1
Water (H ₂ O)	7	14	14
Other	0.1	-	0.1

Odor: Due to the possible presence of odoriferous compounds that may not be analyzed for, or are undetectable due to lack of sensitivity or masking by other compounds, the current Odor Test requirements MIL-0-21749, should be retained as an additional Use Limit test.

(Notes are on next page)

TABLE 1 (Continued)

NOTES:

1. Concentration in parts per million by volume (ppm), except for oxygen, given in percent by volume.
2. Use Limit proposed in this report. Limits should be reviewed by BUMED or other suitable agency to evaluate toxic and irritant hazards.
3. Change in Use Limit proposed in this report. While such increased contaminant levels may be 'safe', they are undesirable, and corrective measures should be initiated.
4. Higher Use Limit allowed at local command discretion.
5. These limits are too high, but reduction at older production plants may not be practical.
6. Total organics, which includes oxygenated hydrocarbons, is a more inclusive compound classification than total hydrocarbons.
7. If ethane and propane (and ethylene - see note 9) are listed separately, this Use Limit should be reduced. Many odoriferous, irritant, or low solubility compounds are included in this category.
8. Ethane and propane are both included in "Ethane" under MIL-O-27210, which actually means total organics expressed as ethane equivalent.
9. While ethylene is specifically listed in MIL-O-27210, there does not seem to be a reason it should be treated differently than other hydrocarbons such as propane, unless it is taken to mean Total Unsaturated Hydrocarbons.
10. Due to the inclusion of odoriferous and hazardous compounds in this category, the higher discretionary Use Limit should be eliminated.
11. This limit would be higher were it not for the possibility of coprecipitation with acetylene.
12. Limit not specifically given in MIL-O-27210 and, therefore, the general limit of 0.1 ppm applies.