12

Report SAM-TR-76-44

AVIATOR'S BREATHING OXYGEN SPECIFICATIONS

December 1976

Final Report for Period March 1976-October 1976

USAF SCHOOL OF AEROSPACE MEDICINE
Aerospace Medical Division (AFSC)
Brooks Air Force Base, Texas 78235

NOTICES

This final report was submitted by personnel of the Crew Environments Branch, Crew Technology Division, USAF School of Aerospace Medicine, Aerospace Medical Division, AFSC, Brooks Air Force Base, Texas, under job order 7930-11-02.

When U.S. Government drawings, specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Robert M. Olson
ROBERT M. OLSON, Colonel, USAF, MC
Project Scientist

Billy Richardson
BILLY RICHARDSON, Ph.D.
Supervisor

Robert McIver
ROBERT G. MCIVER, Colonel, USAF, MC
Commander

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER (14) SAM-TR-76-44	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. ~~TITLE (and Subtitle)~~ (6) AVIATOR'S BREATHING OXYGEN SPECIFICATIONS,		5. ~~TYPE OF REPORT~~ & PERIOD COVERED (9) Final Rep[redacted]t. Mar[redacted] 76 — Oct 76,
		6. ~~PERFORMING ORG. REPORT NUMBER~~
7. AUTHOR(s) (10) Robert M. Olson, Colonel, USAF, MC		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS USAF School of Aerospace Medicine (VNT) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 62202F (16) 7930[redacted]02 (17) 11
11. CONTROLLING OFFICE NAME AND ADDRESS USAF School of Aerospace Medicine (VNT) Aerospace Medical Division (AFSC) Brooks Air Force Base, Texas 78235		12. REPORT DATE (11) Dec[redacted] 1976
		13. ~~NUMBER OF PAGES~~ ~~18~~ (12) 16p.
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *~~(of this report)~~* Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Oxygen purity
Aviator's breathing oxygen
Oxygen standards
Liquid oxygen specifications

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This document tabulates the specifications for aviator's breathing oxygen used by various military and commercial agencies both in this country and abroad. The basis on which these contaminant levels for oxygen are set is discussed; and from this information emergency use limits are postulated, to be used under interim conditions when justified by operational considerations.

317 [illegible]

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

AVIATOR'S BREATHING OXYGEN SPECIFICATIONS

INTRODUCTION

The purity of aviator's breathing oxygen (ABO) is of vital concern to the safety of many flying missions. Numerous military and civilian agencies both in this country and abroad have their own specifications for allowable contaminant levels. The primary purpose of this document is to tabulate contaminant specifications for quick reference and comparison. The contaminant limitations specified for ABO will be discussed with reference to the following agencies:

	Reference
American Conference of Governmental Industrial Hygienists (ACGIH)	15
Air Standardization Coordination Committee (ASCC)	10
Federal Aviation Administration (FAA)	none
North Atlantic Treaty Organization (NATO)	11
Occupational Safety and Health Administration (OSHA)	17
Society of Automotive Engineers (SAE)	7

It is anticipated that as new aircraft and oxygen-generating systems become operational, the bases on which present specifications are founded will have to be reevaluated as to their relevance. Therefore, the physiological, chemical, and physical bases on which ABO specifications were based are reviewed. Finally, using these bases, recommendations are made for standards to be used under emergency conditions when some interim relaxation of standards is operationally justified.

Civilian specifications (15, 17) generally cover fewer substances than do military documents (1, 12). For instance, the ACGIH sets a threshold limit value (TLV) for only carbon dioxide and some refrigerants and solvents (15). OSHA requires that oxygen meet the standards of the U.S. Pharmacopoeia; i.e., 99% purity, less than 300 ppm CO_2 and less than 10 ppm CO (17). In contrast, military specifications cover a wide variety of contaminants (1, 12). Specifications for gaseous oxygen are summarized in Table 1; those for liquid oxygen (LOX) appear in Table 2--where separate values are given for procurement and use, allowing for contaminant buildup during transfer between containers.

CONTAMINANT SOURCES

Aviator's breathing oxygen may be contaminated in a number of ways. The air used to make liquid oxygen is 78.03% nitrogen, 20.99% oxygen, and 0.94% argon by volume. The composition of the remaining 0.04%

TABLE 1. CONTAMINANT LIMITATIONS FOR GASEOUS OXYGEN (ABO TYPE I)

	Purity (%)	Methane (ppm)	Ethane equivalents (ppm)	Acetylene (ppm)	Ethylene (ppm)	Nitrous oxide (ppm)	Refrigerants (ppm)	Solvents (ppm)	Moisture, mg/l @ 21°C 760 mmHg	Carbon dioxide (ppm)	Fibers, particles, & solids
<u>Military</u>											
Air Force (4)	99.5	50	6	.1	.4	2	2	.2	.005[a]	10	No requirement
Army (16)	99.5	50	6	.1	.4	2	2	.2	.005	10	No requirement
Navy (16)	99.5	50	6	.1	.4	2	2	.2	.005	10	No requirement
<u>Civilian</u>											
SAE Comm. A-10[b] (7)	99.5	-	6	.1	.4	-	-	.2	.005	10	100(P)/600(F) X40 μm 1 mg/m^3 (solids)
FAA (7)	(No standards)										
<u>International</u>											
ASCC (10)	-	25	3	.05	.2	1	1	.1	-	-	No requirement
NATO (11)	99.5	-	-	-	-	-	-	-	.005	-	No requirement

[a] 0.005 mg/liter moisture = 6.7 ppm

[b] Proposed limits

TABLE 2. CONTAMINANT LIMITATIONS[a] FOR LIQUID OXYGEN (ABO Type II)

	Purity (%)	Methane (ppm)	Ethane equivalents (ppm)	Acetylene (ppm)	Ethylene (ppm)	Nitrous oxide (ppm)	Refrigerants (ppm)	Solvents (ppm)	Moisture, mg/l @ 21°C 760 mmHg	Carbon dioxide (ppm)	Fibers, particles, and solids
Military Procurement											
MIL-O-27210D (16)	99.5	25	3	.05	.2	1	1	.1	.005	5	1,000(P)/6,000(F) X40 μm 1 mg/l (solids)
Military Use											
Air Force (3)	99.5	50	6	.1	.4	2	2	.2	-	10	Filter paper test[b]
Navy (14)	99.5	50	6	.1	.4	-	2	.2	.01	10	No requirement
Army		(No standards)									
Civilian Procurement											
SAE Comm A-10[c] (7)	99.5	-	3	.05	.2	-	-	.1	.005	5	1,000(P)/6,000(F) X50 μm 1 mg/l (solids)
FAA		(No standards)									
Civilian Use											
SAE Comm A-10 (6)	99.5	-	-	-	-	-	-	-	.02	-	No requirement
FAA (7)		(None at present)									
International Procurement											
ASCC (10)	-	25	3	.05	.2	1	1	.1	-	5	No requirement
NATO (9)	99.5	25	3	.05	.2	1	1	.1	.005	5	No requirement
International Use											
ASCC (9)	-	75	9	.15	.6	3	3	.3	-	15	No requirement
NATO (9)	-	75	9	.15	.6	3	3	.3	-	15	No requirement

[a] Use limits refer to measurements made at point of delivery to aircraft (trailer LOX).

[b] 200 cm^3 LOX allowed to evaporate in 400 cm^3 beaker which is then inspected.

[c] Proposed limits: Aeronautical Standard No. 8010.

(400 ppm) of air is shown in Table 3, which is based on composite values obtained by Bailey et al. (8) from the literature (5, 16, 18). Table 4 presents the boiling and freezing points of compounds frequently present in the atmosphere. Wear and tear on valves, pumps, and filters contribute fibers, particles, and solids. Additional contamination can occur from refrigerants and solvents used in the LOX production plant. Gaseous oxygen, being derived from liquid oxygen (2, 3), also is vulnerable to plant contamination. Solvent and refrigerant limits are therefore included for ABO types I and II in Tables 1 and 2 respectively.

TABLE 3. SOME GASES AND VAPORS WHICH MAY BE PRESENT IN THE AIR FEED TO LOX GENERATORS[a]

Gas or vapor	Concentration (ppm)
Carbon dioxide	200 to 500
Rare gases:	
Helium	4 to 5
Neon	12 to 18
Krypton	1.1
Xenon	0.08
Hydrocarbons:	
Methane	5 to 38
Acetylene	0.001 to 30
Others	<1 to 100
Organic compounds	1
Acidic gases:	
Carbon monoxide	1
Hydrogen sulfide	1
Hydrogen cyanide	1
Nitrogen oxides	1
Ammonia	1

[a] Taken from Bailey et al. (8).

Contaminants listed in Tables 3 and 4 for which no specifications are listed in Tables 1 and 2 consist mostly of rare or acidic gases. Specifications require that all such substances in liquid oxygen be less than 0.1 ppm, as determined by infrared spectroscopy. The acidic gas contamination occurs from production plants located in the vicinity of

TABLE 4. PROPERTIES OF POSSIBLE INGREDIENTS OF AIR[a]

Name	Normal boiling point °F (°C)	Freezing point °F (°C)
Helium	-452.0 (-268.9)	-455.8[b] (-271.0)
Hydrogen	-423.0 (-252.8)	-434.5 (-259.2)
Neon	-410.6 (-245.9)	-415.6 (-248.7)
Nitrogen	-320.4 (-195.8)	-345.7 (-209.7)
Carbon monoxide	-310.0 (-190.0)	-340.6 (-207.0)
Argon	-302.3 (-185.7)	-308.7 (-189.3)
Oxygen	-297.3 (-182.9)	-361.1 (-218.4)
Methane	-258.7 (-161.5)	-299.2 (-184.0)
Krypton	-243.2 (-152.9)	-249.2 (-156.2)
Nitric oxide	-241.2 (-151.8)	-262.5 (-163.6)
Ozone	-169.4 (-111.9)	-313.8 (-192.1)
Xenon	-160.8 (-107.1)	-169.6 (-112.0)
Ethylene	-155.0 (-103.9)	-272.9 (-169.4)
Ethane	-126.9 (- 88.3)	-277.6 (-172.0)
Nitrous oxide	-127.3 (- 88.5)	-152.3 (-102.4)
Acetylene	-188.5[c] (-122.5)	-115.2 (- 81.8)
Carbon dioxide	-109.3[c] (- 78.5)	- 69.9 (- 56.6) (5.2 atm)
Hydrogen sulfide	- 79.2 (- 61.8)	-117.2 (- 82.9)
Carbonyl sulfide	- 54.4 (- 48.0)	-216.4 (-138.0)
Propylene	- 52.6 (- 47.0)	-301.4 (-185.2)
Propane	- 43.9 (- 42.2)	-309.8 (-189.9)
Ammonia	- 28.0 (- 33.3)	-107.9 (- 77.7)
Formaldehyde	- 5.8 (- 21.0)	-133.6 (- 92.0)
iso-Butane	10.4 (- 12.0)	-229.0 (-145.0)
iso-Butylene	21.2 (- 6.0)	-220.5 (-140.3)
1-Butane	23.0 (- 5.0)	-202.0 (-130.0)
1,3-Butadiene	26.7 (- 2.8)	-164.0 (-109.0)
n-Butane	31.1 (- 0.5)	-211.0 (-135.0)
2-Butene	33.8 (cis)(1.0)	-218.0 (-139.0)
Ethylene oxide	51.3 (10.7)	-168.3 (-111.3)
Acetaldehyde	69.8 (21.0)	-190.3 (-123.5)
Nitrogen dioxide	70.3 (d) (21.3)	+ 15.3 (- 9.3)
N-Pentane	97.2 (36.2)	-204.7 (-131.5)
Acetone	133.7 (56.5)	-139.0 (- 95.0)
Methanol	148.4 (64.7)	-144.0 (-109.0)
Hexane	156.2 (69.0)	-137.7 (- 94.3)
Benzene	176.2 (80.1)	41.9 (5.5)
Water	212.0 (100.0)	32.0 (0.0)
N-Decane	345.2 (174.0)	- 23.8 (- 31.0)

[a] Taken from Bailey et al. (8).
[b] Lambda point
[c] Sublimes

metallurgical and other industrial sites. The TLV for some of these contaminants is rather low. For example, the TLV for hydrogen cyanide and for hydrogen sulfide is 10 ppm (15). Fortunately, IR spectroscopy detects these contaminants as long as they are not masked by other contaminants. The analyst is responsible for identifying all contaminants; and if an unlisted contaminant is identified, its concentration must be below 0.1 ppm, the level set by MIL-0-27210D. It should be noted that the presence of maximum allowable concentrations of several contaminants may hinder detection of other substances. The more contaminants that are present in a sample, the more chance there is for error in analysis. Hydrogen sulfide, for example, has bands which overlap acetylene in the lower frequencies (600-800, 1100-1400 cm^{-1}). Masking effects would be one reason not to relax existing procurement standards.

Contamination may occur in any LOX transfer. When transfer lines are first connected, atmospheric contaminants or dirt may be trapped and carried into the system by the moving liquid. At the time of disconnection, atmospheric contamination may deposit inside the cold transfer equipment, ready to enter the rest of the system during the next transfer operation.

For contaminant levels of ABO, types I (gas) and II (liquid), the principles adopted by the ASCC subcommittee on gas sampling and analysis (10) seem reasonable. They state that limits should be (a) within existing analytical capability, (b) easily met by production plants, and (c) no greater than the least of the following:

(1) 1/10 TLV,
(2) 1/10 odor threshold, or
(3) 1/10 flash or explosion point (presumably applies only to type II ABO).

SETTING ABO SPECIFICATIONS

In this section, the rationale used in setting ABO specifications is discussed, and a set of emergency use limits is proposed for type II aviator's breathing oxygen.

In general, the contaminants of ABO can be divided into five types, the first two applying to type II only: (a) Solid inert contaminants which may contribute to mechanical malfunctioning; (b) dissolved inert contaminants; (c) toxic substances; (d) odor-producing contaminants; (e) combustible contaminants, solid or dissolved, which may constitute a fire or explosion hazard to both general safety and equipment.

Solid inert contaminants are small particles, generally in the range of 1 to 100 μm in average diameter, essentially insoluble and unreactive with liquid oxygen. These contaminants are divided into two categories: grossly insoluble material, such as rust and metal fragments derived from the equipment; and slightly soluble contaminants, particularly carbon dioxide and water, which are associated with the production and handling of liquid oxygen.

Dissolved inert contaminants, such as nitrogen or argon, are unreactive and quite soluble in liquid oxygen.

Toxic substances in ABO are almost always of low concentration and do not pose a problem. Documented cases of toxicity specifically due to contaminated oxygen stores are extremely rare. A computer search for such information from data stored at the Air Force Safety and Inspection Center (AFSIC), Norton AFB, California, turned up no instances of illness that could be positively attributed to toxic substances in the oxygen stores.

Odor-causing contaminants in breathing oxygen must be kept at a minimum. Once detected, an odor can have serious psychological effects and, even when nontoxic, can lead to vomiting, anxiety, and decreased performance.

Combustible contaminants include compounds which combine with oxygen upon suitable ignition, producing sufficient heat of reaction to raise the temperature of the reaction products. Typical combustible contaminants are methane, acetylene, ethane, and ethylene. The hazards of combustible contaminants are obvious and of special importance. Much of the following discussion regarding combustibles is from the report of Bailey et al. (8) and applies to LOX only.

"In order to support ignition in liquid oxygen, dissolved combustibles, such as methane, must be present in concentrations sufficiently high that the heat of reaction raises not only the reaction products but also the excess liquid oxygen to the ignition temperature. Thus, a limiting concentration called the 'lower explosive limit' or 'lower flammability limit' (LFL) is associated with the presence of excess oxygen. Any concentration of combustibles at or above this limit is flammable, and therefore extremely dangerous, and must be avoided.

"When a mixture of combustibles occurs, the LFL of the mixture is given in the following equation:

$$\frac{C_1}{L_1} + \frac{C_2}{L_2} + \text{---} + \frac{C_n}{L_n} = \sum \frac{C_i}{L_i} \simeq \frac{C_m}{L_m}$$

where

$C_i = C_1, C_2, \text{---}\ C_n$ = concentration of individual combustibles

$L_i = L_1, L_2, \text{---}\ L_n$ = LFL of individual combustibles

C_m = total concentration of all combustibles

L_m = LFL of mixture

If $\frac{C_m}{L_m} \geq 1$, the mixture exceeds or is equal to the LFL.

"This equation applies to gaseous mixtures and liquid solutions even at liquid oxygen temperature." (8)

If the solubility of a contaminant in liquid oxygen is below the lower flammability limit, the liquid phase will not support combustion. A flammable hazard does indeed exist, however, due to the resulting fuel-oxygen slurry that can occur when the contaminant precipitates. Table 5, for example, shows the solubility limit lower than the LFL for acetylene, which is known to be an explosion hazard.

TABLE 5. SOLUBILITY AND LOWER FLAMMABILITY LIMIT (METHANE EQUIVALENTS) OF HYDROCARBONS IN LOX[a]

Gas	Solubility at -297.3°F (-182.9°C) (ppm)	Lower flammability limit (ppm)
Methane	980,000	58,000
Ethane	430,000	60,000
Propane	150,000	63,600
Ethylene	55,000	55,000
Propylene	20,100	60,000
i-Butane	7,640	72,000
Butene-1	4,000	64,000
n-Butane	3,440	74,400
i-Butylene	530	72,000
Acetylene	10	50,000

[a] Taken from Bailey et al. (8)

The sudden addition of external energy to a local region can raise the local temperature and the reaction rate, resulting in a chain reaction when the heat released is greater than the heat adsorbed by the surroundings. Such a reaction may easily become explosive. A runaway reaction can be initiated in a variety of ways, most of which are unpredictable in effectiveness. Some of the more common ways for initiating reactions are mechanical (friction or impact), electrical (spark discharge), and addition of external heat.

All of the common combustible contaminants except carbon monoxide and hydrogen, are less volatile than oxygen (Table 4) and consequently will increase in concentration as the liquid oxygen is vaporized. Procurement levels of these combustibles must have a compensating safety factor.

Of these potentially combustible contaminants, those currently considered for analysis and control on a routine basis are methane, ethane, ethylene, other 2-carbon hydrocarbons, and acetylene--which, because of its low solubility, is considered in a class by itself.

Although other combustibles may appear as a result of unusual circumstances, the quantities are usually too small for routine detection. Hydrocarbon molecules with more than four carbon atoms are reduced in the air separation plant to insignificant concentrations.

Using the general principles discussed, common contaminants will be considered and an emergency limit proposed. In arriving at the proposed limit. consideration has been given to the frequency at which a given contaminant is a cause for rejection (20). If a given contaminant rarely causes failures in LOX production, relaxing its limits seems inappropriate.

Acetylene is limited in both type I and type II ABO by its explosion potential and combustibility. Physiologically, it is a simple asphyxiant (1). In type II ABO, acetylene should receive special attention among all of the combustibles for several reasons. First, it is quite insoluble in liquid oxygen (Table 5); second, it may show up in the airplant feed stream (Table 3) at concentrations above the ultimate solubility limit (Table 5); and third, it is readily triggered into ignition (21). Acetylene is thus a more serious hazard than methane, ethane, and ethylene.

Ethylene also is physiologically a simple asphyxiant and chemically a combustible. The potential fire hazard makes it necessary to limit ethylene concentration in liquid oxygen. From Table 5, the flammability limit of ethylene is 55,000 ppm (expressed in methane equivalents); and solubility in LOX is about the same. Use and procurement limit breaches, although rare, are usually in the 0.5- to 1-ppm range. At the LOX production plant any cause for levels above the MIL-O-27210D specification of 0.2 ppm should be eliminated. These causes could be similar to those giving increased acetylene concentrations.

In type I and II ABO, the limiting factor for methane is that high levels could mask other hydrocarbons that must be detectable at far lower levels. Also, high methane concentrations could indicate possible production of much more dangerous compounds. Sheinson (21) states that atmospheres from closed environments such as submarines can easily contain up to 500 ppm methane. The limit for methane in nuclear submarines is set at 13,000 ppm (13); i.e., one-fourth the flammability limit. However, it must be remembered that methane does concentrate upon LOX evaporation. Field studies show that there is a significant number of procurement and use limit breaches in the 50- to 100-ppm range (20).

Ethane is physiologically inactive but chemically combustible. Table 5 shows that ethane has a flammability limit of 60,000 ppm in LOX and a solubility in LOX of 430,000 ppm (methane equivalent); thus it should be similar to methane in terms of hazard. Furthermore a significant number of use and procurement failures occur in the 5-10-ppm range.

Carbon dioxide is an odorless, nonflammable gas with a TLV of 5000 ppm (15). By ASCC standards, it should have a limit of 500 ppm (1/10 TLV). Carbon dioxide is normally present in the air feed to oxygen plants at concentrations of about 200-500 ppm (Table 3). Although most of the CO_2 in the air feed is removed in the separating process, the use requirements and economics of LOX manufacture do not require the complete removal of CO_2. If LOX contains CO_2 dissolved at the saturation point, slight changes in temperature or pressure may cause the CO_2 to precipitate. Thus, solid CO_2, which can clog type II ABO supply lines, might appear with a sharp decrease in pressure at a valve or orifice, or with a cooling through flash evaporation of the LOX at a local hot spot. It is difficult to redissolve the precipitate even though the LOX may no longer be saturated with CO_2. The large difference between the rate of precipitation and the rate of resolution can easily result in the buildup of solid CO_2 in quiescent regions. Even if carbon dioxide is not present initially, it will be introduced by every transfer operation exposing cold internal parts to the atmosphere. The quantity of CO_2 introduced with each transfer operation depends on the operator and on the procedures followed. To further aggravate the problem, continuous vaporization due to heat leak to stored liquid oxygen increases the concentration of CO_2. For these reasons, the standards for CO_2 should not be relaxed even in emergency conditions.

Nitrous oxide in the levels considered here is physiologically inert (only at very high levels is it an anesthetic) and odorless, and it is not flammable. In type II ABO, it does have a limited solubility (70 ppm). As discussed by Sheinson (21), 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 70% nitrous oxide will sink and can detonate. 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.) It is important to note that field studies show nitrous oxide is frequently a cause for rejection in the range from 3 to 6 ppm.

Carbon monoxide, as such, is unspecified in both MIL-0-27210D (procurement) and TO 42B6-1-1 (use), but is limited to 0.1 ppm by the "other - as discernible by infrared" category in both specifications. Carbon monoxide in moderate concentrations can degrade aviator abilities, including judgment, coordination, and visual acuity. The ACGIH threshold limit value is 50 ppm (15) and the submarine exposure limit is 25 ppm (13) for a 90-day continuous exposure. Hence, the implied limit of 0.1 ppm for ABO appears overly restrictive, particularly when coupled with an enriched oxygen-air breathing mixture. Although CO is almost never observed in ABO, an emergency use limit of 5 ppm (1/10 TLV) appears entirely acceptable on the basis of known toxic hazard.

Another toxin group is the solvents, which are of varying toxicity. Some solvents have a TLV as low as 10 ppm, such as carbon tetrachloride (15), so limits should not be relaxed even in emergency conditions.

ABO specifications also include the fluorinated hydrocarbons used in LOX production plants for interstage cooling. These refrigerants carry trade names such as Freon, Genetron, Isotron, or Ucon. Refrigerant leaks upon initial plant startup, and leaks developing with time, have appeared as liquid oxygen contaminants. A practical reason to maintain low emergency limits is that presence of fluorocarbon may indicate refrigerant leaks.

Table 6 summarizes suggested emergency use limits for ABO type II, based on the discussion above. Note that no relaxation of use limits is suggested for acetylene, CO_2, solvents, and refrigerants. Emergency use limits of 100 ppm for methane, 2 ppm for ethylene, 10 ppm for ethane, and 6 ppm for nitrous oxide are set to commonly occurring contaminant levels found in field studies, and all are below the 1/10 TLV; flammability limit, or solubility. Carbon monoxide, at 5 ppm, was set exclusively by the TLV.

TABLE 6. EMERGENCY USE LIMITS FOR LOX (ABO TYPE II)

Contaminants (ppm)	Current suggestion	Sheinson's suggestion, Navy (21)
Methane	100	500
Nitrous oxide	6	2
Carbon dioxide	10	10
Carbon monoxide	5	5
Ethylene	2	20
Ethane	10	20
Solvents	0.2	0.1
Acetylene	0.1	0.1

Note: Ethane equivalents are not included because they represent a group of compounds which contain organics such as acetaldehyde (CH_3CHO), acetone (CH_3COCH_3), and formaldehyde (HCHO), as well as hydrocarbons (IR determination of CH bond stretch).

Gaseous aviator's breathing oxygen is generally derived from liquid oxygen by vaporization. The expected contaminants will therefore be the same as in liquid oxygen, so the specifications for type I and type II ABO differ not in kind but in concentration of contaminants. For both ABO types, therefore, the source of contaminants is the air used to make the oxygen and the contaminants contributed by the factory.

There are some differences between types I and II however. In gaseous oxygen, contaminants do not concentrate in storage and are not added in transfer operations, as occurs in liquid oxygen.

The rationale used in setting contaminant concentration limits for gaseous oxygen (Table 1) was the same as discussed for LOX (Table 2) and involved consideration of odor, explosion potential, TLV, detection, and production methodologies. Of these, the last is usually the limiting factor in the sense that limits are for the most part based on what a well-run LOX production plant can reasonably produce. The contaminant levels listed for type II ABO under emergency conditions should be easily met by a well-run production plant, and should in our opinion be used as emergency use limits for type I ABO as well. The reasons are not that higher concentrations would be dangerous for subjects to breathe, but that higher concentrations would indicate serious problems in production which would need correction.

REFERENCES

1. AFP 161-26. Threshold limit values of airborne contaminants. Washington, D.C., 14 June 1972.

2. AF Technical Manual TO 42B6-1-1. Section I: General, paras. 1-7, 1966.

3. AF Technical Manual TO 42B6-1-1. Section III: Quality control of aviator's liquid breathing oxygen, paras. 3-10, 1966.

4. AF Technical Manual TO 42B6-1-1. Section V: Quality control of aviator's gaseous breathing oxygen, paras. 5-6, 1967.

5. Arrick, C.D. Contaminants in liquid oxygen as related to safety in liquid oxygen production and distribution equipment. In Advances in cryogenic engineering, vol. 3, p. 218. New York: Plenum Press, 1960.

6. Aviators breathing oxygen purity standard. Aeronautical Standard No. 1065. Society of Automotive Engineers, Warrendale, Pa., Dec 1969.

7. Aviators breathing oxygen purity standard. Aeronautical Standard No. 8010 (proposed). Society of Automotive Engineers, Warrendale, Pa., 10 Oct 1974.

8. Bailey, B. M., C. J. Stenner, and V. J. Vignate. Study of liquid oxygen contamination. API Research Project No. 03-9-28. Edwards AFB, Calif., 1960.

9. Breathing liquid oxygen characteristics. STANAG 3545 (CENTO). Central Treaty Organization Combined Military Planning Staff, Ankara, 7 June 1971.

10. Breathing oxygen characteristics, supply pressures, and hoses. Air Standardization Coordinating Committee report of the 13th meeting of Working Party 14 of the English-speaking allied countries, Appendix 14, Air Standard 14/9. Wellington, New Zealand, 8 May 1962.

11. Breathing oxygen characteristics, supply pressures, and hoses. STANAG 3053 (NATO). Military Agency for Standardization, Brussels, 16 July 1970.

12. Dept of the Army TB Med 265. Threshold limit values of airborne contaminants. Washington, D.C., 14 June 1972.

13. Dept of the Navy NAVSEA 0938-011-4010. Ch. 3: Submarine atmosphere, pp. 3-11. Naval Sea Systems Command, Washington, D.C., 1974.

14. Dept of the Navy OPNAVINST 4790.2A. Vol II, Ch. 7: Amplifying information on selected maintenance programs, pp. 7-29. Office of the Chief of Naval Operations, Washington, D.C., 14 Nov 1974.

15. Documentation of threshold limit values for substances in workroom air, 3d ed., p. 39. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1971.

16. Military Specifications MIL-0-27210D (ASG). Oxygen, aviator's breathing, liquid and gas, paras. 3.3.2.-3.3.4. Aeronautical Standards Group, Silver Springs, Md., 16 May 1969.

17. Occupational Safety and Health Administration. Federal Register, vol 39, #125, part II, p. 23671. Dept of Labor, 1974.

18. Safety in air and ammonia plants. Chem Eng Prog 54(8):52 (1958).

19. Safety in air and ammonia plants. Chem Eng Prog 55(6):54 (1959).

20. San Antonio Air Logistics Center (AFLC), Kelly AFB, Tex. Personal communication, 18 Oct 1974.

21. Sheinson, R. S. and F. W. Williams. Aviator's breathing oxygen purity. Naval Research Laboratory, Memorandum Report 3314, Washington, D.C., June 1976.