REFERENCES

[1] Antonescu, N.N., ş.a., Fabricarea, exploatarea, mentenanţa şi asigurarea calităţii echipamentelor petroliere, Editura Universităţii din Ploieşti, Ploieşti, România, 2004.

[2] Buliga, Gh., Repere istorice ale industriei romanesti de petrol: 1857-2007, Editura SIPG, Bucureşti, România, 2007.

[3] Oroveanu, T., Stan, Al., V. Talle, V., Transportul Petrolului, Edit. Tehnică, 1985, Bucureşti, România.

[4] Raşeev, D., ş.a., Tehnologia fabricării şi reparării utilajului tehnologic, Edit. Didactică şi Tehnică, 1983, Bucureşti, România.

[5] Soare, Al., Transportul şi depozitarea fluidelor. Volumul 1 Editura Universităţii din Ploieşti, Ploieşti, România, 2002.

[6] Tudorache, V. P., Research on optimization of the National System of Pipeline Crude Oil Transportation in Romania, Thesis of Doctorate, UPG-Ploiesti, Ploieşti, România, 2014.

[7] Tudorache, V.P., ş.a., Maintenance of the Romanian National Transportation System of Crude Oil and Natural Gas, 2013, Procedia Engineering, DAAAM International Vienna, Austria, 2013.

[8] Tudorache, V. P., ş.a., Elements for the preventing and combating corrosion to cylindrical metal tank for destined storage of liquid hydrocarbons; EMERG 3, Edit. AGIR, Bucureşti, România, 2021.

[9] *** https://petrowiki.spe.org/Floating_roof_tanks

[10] *** https://robotics.koks.com

[11] *** www.google.com

RESPIRATORY GASES USED IN PROFESSIONAL DIVING

Mircea DEGERATU [1], Sergiu IONIȚĂ [2]

DOI 10.56082/annalsarscieng.2024.1.98

Rezumat. *Un rol important în conceperea, proiectarea, fabricarea și funcționarea aparatelor de respirație subacvatică îl joacă gazele de respirație utilizate în aceste aparate. Tipul de gaz de respirație utilizat este impus de tipul de aparat de scufundare utilizat și de tehnologia de scufundare adoptată. Pentru alegerea corectă a gazelor de respirație în diferitele aparate de respirație subacvatică și pentru stabilirea precisă a tehnologiei de scufundare, este necesar să se cunoască în detaliu caracteristicile fizice ale gazelor utilizate.*

Abstract. *An important role in the conception, design, manufacture and operation of underwater breathing apparatuses is played by the breathing gases used in these apparatuses. The type of breathing gas used is imposed by the type of diving device used and the diving technology adopted. For the correct choice of breathing gases in the various underwater breathing apparatuses and for the precise establishment of the diving technology, it is necessary to know in detail the physical characteristics of the gases used.*

Keywords: diving, gases, breathing apparatuses

1. General information on the gases used in diving

The first gas used in diving was air which is a natural breathing mixture. Used at great depths, air poses important problems with implications for the diver's return to atmospheric pressure, imposing severe precautions to avoid accidents due to either the appearance of abnormal conditions or improper decompression.

In order to avoid these problems, is being known that oxygen is the indispensable gas for life and considering it to be "harmless", diving was attempted only with pure oxygen. The use of pure oxygen, although it eliminated decompression accidents, led, in the case of diving to depths greater than 7...10 m, to other accidents specific to oxygen. These accidents were very serious and sometimes fatal, disproving the "harmlessness" of oxygen breathed at pressures higher than atmospheric pressure. Thus, the necessity of diluting oxygen and creating synthetic respiratory mixtures reappeared. The need to find new so-called "inert" gases also appeared to eliminate the shortcomings caused by nitrogen in the atmospheric air. Considered as inert, because they are neither metabolized nor produced by the body, they are

[1]Prof., PhD, Eng., Dept. of Hydraulics and Environmental Protection, Technical University of Civil Engineering Bucharest, Academy of Romanian Scientists (mircea.degeratu@yahoo.com)
[2]Professional diver, certified in the U.S.A. at Commercial Diving Institute of New York, was employeed by some prestigious submarine intervention companies specialized in underwater interventions at offshore oil installations in the Gulf of Mexico. (sergiu.ionita@rdslink.ro).

nevertheless generators of biochemical effects, all the more obvious as the partial pressure of the inert gas, from the respiratory gas mixture, increases with the increase of the diving depth.

Regardless of the inert gas used as an oxygen diluent, one of the great shortcomings of the inert gas is the narcotic effect it induces. Currently, it is accepted that the physiological effects of a respiratory gas mixture depend on its composition, the concentrations (volume fractions) of the gases that make up the mixture, as well as the pressure at which it is breathed. The last two factors, correlated with the physiological action of the respiratory mixture, determine the maximum allowed value of the partial pressure of the inert gas so that the narcotic effect does not occur. It is therefore important to know that all so-called "inert" gases have a narcotic power close to that of anesthetic gases (such as nitrous oxide), that this narcotic power is a function of their solubility in fats relative to their solubility in water (Mayer-Overton coefficient) and also a function of their specific mass (density), which is obvious for heavy gases. Thus, narcosis starts from a depth of 60 m with nitrogen, from 40 m with argon and even at atmospheric pressure with xenon, for mixtures with 80% inert gas. On the contrary, although it is the lightest of the gases used as a diluent for oxygen, hydrogen is more narcotic than helium, which is twice as heavy, which is why hydrogen is distinguished from other gases by its original properties. Helium may therefore be considered the most inert of gases, but its narcotic power, known to be very weak, is perfectly perceptible at very great depths. Table 1 shows some properties of the so-called "inert" gases, related to their narcotic power.

Table 1 Some properties of the so-called "inert" gases.

Gas	*Molar mass [kg/kmol]*	*Density []**	*Van der Waals number** a*	*Solubility []*		
				in water (at 37⁰ C)	*in fat (at 37⁰ C)*	*MO****
Helium	4	0.18	0.034	9.2	17	1.85
Neon	20	0.90	0.21	10.6	22	2.07
Hydrogen	2	0.09	0.24	18.0	57	3.17
Azote	28	1.25	1.39	14.5	76	5.24
Argon	40	1.78	1.34	33.0	150	4.54
Krypton	83.8	3.75	2.32	70.0	490	7.00
Xenon	131	5.90	4.19	130.0	1700	13.07

*Density values are at 0^0 C and normal atmospheric pressure;
** Van der Waals number a expresses the intermolecular attraction force;

$$\text{***Mayer-Overton coefficient} = \frac{\text{Fat solubility}}{\text{Solubility in water}}$$, in relation to narcotic power.

Another shortcoming, equally important, is that during decompression the inert gas can be released with the formation of bubbles, which can cause serious accidents if a special procedure for returning to atmospheric pressure is not followed. In addition, the prolonged absence of nitrogen from the respiratory mixtures can be the basis of important physiological changes, and during the change of the respiratory mixtures, an isobaric counterdiffusion of inert gases dissolved in the tissues occurs at the level of the membranes.

2. Presentation of gases used in diving

2.1. Oxygen

Oxygen is the most important of all gases used in diving because it is indispensable to life and is the most widespread chemical element in nature. Atmospheric air contains approximately 21% free oxygen, in molecular state. This odorless, colorless and tasteless gas is very active, easily combining with other elements. Table 2 shows the most important physical characteristics of oxygen.

In diving, pure oxygen was first used in World War II by Italian combat divers. They, equipped with closed circuit underwater breathing apparatus, carried out underwater interventions for military purposes. They didn't know anything about oxygen toxicity, which is why they had losses even during training.

Table 2 Physical properties of oxygen.

Size	*Value*	*Size*	*Value*
Molar volume []	22.403		1.93
Molar mass []	31.999		
The critical temperature	154.4	Van der Waals constants: a – b –	1.36 0.0318
Boiling temperature at 1.013 bar (sc.abs.)	90.2	Critical pressure**	49.7
Thermal conductivity	58.5		0.58
The self-diffusion coefficient	0.189	The diameter of the molecule [Å]***	3.62
The density	1.429	Solubility in water []	0.0314
The dynamic coefficient of viscosity*	192.6	Solubility in ethyl alcohol []	0.1431
Mass specific heat at constant volume	0.157	Solubility in benzene []	0.163

*1 micropoise = 10-3 poise = 10-3 g/(cm s) = dyn s/cm^2 ;

** ata – atmosphere in absolute scale;

*** Å – angström (1 Å = 10-8 cm).

At present, when the toxicity phenomena of oxygen are known and controlled, oxygen is used in underwater breathing apparatuses, both pure and mixed with inert gases in the form of breathing mixtures. For the proper dosing of pure oxygen or breathing mixture to the diver, it is necessary to know the individual oxygen consumption depending on the underwater activity carried out by the diver (tab. 3).

Table 3 Individual oxygen consumption depending on the underwater activity.

No.	*The activity carried out by the diver*	*O_2 consumption []*	*Pulmonary ventilation []*
1.	Rest	0.4	8
2.	Light work, swimming with speed	0.8	18
3.	Moderate work, speed swimming	1.3	30
4.	Intense work, swimming at speed	1.7	40
5.	Very hard work, swimming with speed	2.5	60

* Nd – knot, unit of measurement of speed equal to 1 nautical mile per hour: 1 Nd = 1.852 km/h = 0.514 m/s.

In the case of hookah diving and autonomous diving from the surface, in the framework of underwater breathing apparatuses, superoxygenated binary gas mixtures are usually used. The use of breathing mixtures with high oxygen concentrations (with high volume shares of oxygen), is justified by the fact that the speed of returning to atmospheric pressure, therefore the speed of decompression, is dictated by the time required to eliminate the inert gas dissolved at a given moment in the body human. The amount of dissolved inert gas is a function of its partial pressure in the respiratory mixture, in other words, for a given depth, the greater the volume participation of oxygen in the respiratory mixture, the greater the amount of inert gas that will dissolve in the tissues will be lower and implicitly the speed of return to atmospheric pressure will be higher.

Thus, for a certain depth of immersion, which corresponds to a total pressure of the respiratory gas mixture, and for a nitrogen-oxygen gas mixture (NITROX) characterized by the volume shares of the components and, (1), the partial pressures of the two components of the mixture are respectively, (). It is obvious that, in order to reduce the decompression time, it is necessary to reduce the partial pressure of the inert gas (nitrogen) in the mixture, and therefore the corresponding increase in the partial pressure of the oxygen in the mixture. For one thing, the increase in the partial pressure leads to the need to use a nitrogen-oxygen gas mixture with a high volume share of oxygen in the mixture, so of an overoxygenated NITROX mixture (with a value of the volume share of oxygen, greater than 0.21, value corresponding to air). The same considerations are valid for helium-oxygen binary gas mixtures (HELIOX).

The increase in the volumetric participation of oxygen, in the respiratory mixture, for a certain depth of immersion and therefore for a certain value of the total pressure of the gas mixture, is limited by the increase above a certain value of the partial pressure of the oxygen in the mixture, beyond which hyperoxia phenomena may occur.

For example, for a one-hour dive at 90 m working depth (sc. abs.), if the HELIOX mixture breathed during work contains 2% oxygen (= 0.02 and therefore 0.02·10 = 0.2 bar (sc. abs.)), the decompression performed with a mixture of 24% O^2 (0.24) will last 15 hours and 30 minutes; if the HELIOX mixture breathed while working contains 20% O^2 (and therefore 0.2·10 =2 bar (sc. abs.)), the decompression performed with a mixture with 24% O^2 (0.24) will last only 10 hours and 40 minutes. Equally conclusive are tables 4 and 5, which compare decompression durations for dives performed with the use of breathing mixtures characterized by different oxygen concentrations.

Thus, from table 4.5 it can be seen that for a 100-minute dive with a nitrogen-oxygen mixture at a depth of 30 m (sc. abs.), the duration of decompression with air (0.21) is 88.4 minutes, with NITROX mixture with 30% O^2 (0.3) is 45.6 minutes, with NITROX mixture with 40% O^2 (0.4) is 20.8 minutes, and with NITROX mixture with 50% O^2 (0.5) is only 2.8 minutes.

Table 4 Comparison of decompression times when diving using helium-oxygen breathing mixtures (HELIOX) with different oxygen concentrations (decompressions calculated according to the COMEX method – France).

No.	*1 hour dive at 90 m depth*				
1.	Working breathing mixture	2/98*			20/80
2.	Breathing mixture at decompression	12/88	24/76	36/64	24/76
3.	Total duration of decompression [hours.minutes]	20.30	15.50	12.30	10.40

*The ratios in this table read: 2% O_2 and 98% He

Table 5 Comparison of decompression times when diving using nitrogen-oxygen breathing mixtures (NITROX) with different oxygen concentrations (decompressions calculated according to the method of the Hyperbaric Laboratory in Constanța).

100 minute dive at 30m depth				
Respiratory mixture	Air 21% O_2	NITROX		
		30% O_2	40% O_2	50% O_2
Total decompression time [minutes]	88.4	45.6	20.8	2.8

2.2 Diluent gases for oxygen

To counteract the effects of hyperoxia, oxygen must be diluted by mixing it with diluent gases, also called "inert" gases. Among these, the most commonly used diluent gases in the manufacture of respiratory mixtures are presented below.

2.2.1 Nitrogen

Like oxygen, nitrogen is a colorless, odorless and tasteless gas, found in all living organisms. It is the main component of atmospheric air, where it is found in a proportion of 78...79%. In diving, nitrogen is used as an oxygen diluent, either in the natural mixture, atmospheric air, or in synthetic mixtures. Table 6 shows the most important physical characteristics of nitrogen .

Table 6 Physical properties of nitrogen.

Size	*Value*	*Size*	*Value*
Molar volume []	22.403		1.95
Molar mass []	28.013		
The critical temperature	126.1	Van der Waals constants: a – at/(ℓ/mol)^2 b – ℓ/mol	1.39 0.0394
Boiling temperature at 1.013 bar (abs. sc.)	77.4	Critical pressure	33.5
Thermal conductivity	58.0		0.61
The self-diffusion coefficient	0.178	The diameter of the molecule [Å]	3.76
The density	1.251	Solubility in water [ℓ / ℓ]	0.0155
The dynamic coefficient of viscosity	167.4	Solubility in ethyl alcohol [ℓ / ℓ]	0.1304
Mass specific heat at constant volume	0.177	Solubility in benzene [ℓ / ℓ]	0.1038

From a chemical point of view, atmospheric air is composed of 78...79% nitrogen (0.78...0.79), 20...21% oxygen 0.03...0.04% carbon dioxide (0.0003...0.0004), 0.01% rare gases (0.0001) and 0.2...0.6% water vapor (0.002...0.006). Through its chemical composition, the air influences the exchange of gases between the body and the environment. In this sense, man inhales 14...15 m^3 of air daily, volume expressed in normal conditions, which represents a much larger amount compared to water (2.5 dm^3) or food (1.5 kg). In addition, the contact between the air and the body, measured at the level of the respiratory system, takes place on a surface of over 90 m^2 .

During breathing, the air composition changes according to the data presented in table 7.

For diving needs, in order to perform various calculations, including the calculation of decompression tables, the following approximation of the composition of the atmospheric air can be made: nitrogen 79% (0.79); oxygen 21% (0.21).

Table 7 Changing the composition of the air during breathing.

Component	*Proportion of components in air [%]*	
	inhaled	*exhaled*
Azote	78...79	78...79
Oxygen	20..21	16...17
Carbon dioxide	0.03...0.04	3...4

In synthetic breathing mixtures, nitrogen is used for saturation diving up to 50...70 m deep. Also in synthetic mixtures, nitrogen is also used for autonomous diving with the so-called overoxygenated mixtures, in which the oxygen concentration can be 30 (32 or 32.5), 40, 50, 60%, which corresponds to volume participations of 0.30 (0.32 or 0.325); 0.40; 0.50; 0.60. The depth of diving with such mixtures is limited by the toxic effect due to the increased partial pressure of oxygen.

Diving with superoxygenated nitrogen-oxygen (NITROX) mixtures is advantageous at depths between 18 and 54 m due to the safety it provides compared to diving with air. These superoxygenated NITROX mixtures are commonly used in open, closed, semi-closed and mixed circuit self-contained underwater breathing apparatus. Nitrogen is also used injected in mixtures based on helium-oxygen for deep diving, in a proportion of 5...10% (0.05...0.1), in order to improve the nervous syndrome of high pressures (SNIP). These helium-nitrogen-oxygen ternary mixtures are also called TRIMIX. In our country, through the research and experimentation carried out at the Hyperbaric Laboratory near the Diving Center in Constanţa, belonging to the Romanian Naval Forces, technologies for underwater penetration with air and nitrogen-oxygen mixtures were developed, drawing up tables of decompression for diving with air, decompression tables for diving with superoxygenated NITROX mixtures and decompression tables for diving with NITROX mixtures under saturation conditions. These technologies have found their application in the operations with divers carried out at offshore oil installations from the Black Sea, for the placement and periodic control of marine drilling platforms and submarine pipelines.

2.2.2. Helium

Helium is a monoatomic, colorless, odorless and tasteless gas. It is totally inert, so inert that it does not even combine with itself. It is a gas insoluble in water. Helium is a rare element, found in atmospheric air only in a ratio of 1:200000. Table 8 shows the most important physical characteristics of helium.

Table 8 Physical properties of helium.

Size	*Value*
Molar volume []	22.43
Molar mass []	4,002
The critical temperature	5.26
Boiling temperature at 1.013 bar (sc. abs.)	4.26
Thermal conductivity	352.0
The self-diffusion coefficient	-
The density [g/ ℓ]	0.1785
The dynamic coefficient of viscosity	188.7
Mass specific heat at constant volume	0.745

Size	*Value*
	2.50
	-
Van der Waals constants: a – at/(ℓ /mol)2 b – ℓ /mol	0.034 0.0236
Critical pressure	2.26
	0.81
The diameter of the molecule [Å]	2.17
Solubility in water [ℓ / ℓ]	0.0088
Solubility in ethyl alcohol [ℓ / ℓ]	0.0281
Solubility in benzene [ℓ / ℓ]	0.0180

Helium was discovered in 1868, through spectrographic analysis of the Sun, hence the name Helios, the Greek name for the Sun. Helium is 70 times lighter than air and was used at the beginning of the 20th century to fill balloons and airships. Helium is found in slightly larger quantities in natural gas in some areas of the USA, Canada and the Russian Federation.

In diving, helium is used as an oxygen diluent. Helium has the disadvantage of distorting the sound spectrum causing the phenomenon known as the effect Donald Duck and a very high thermal conductivity, which causes rapid cooling of the body through breathing.

The idea of using helium as a replacement for nitrogen in breathing mixtures, to eliminate the narcotic effect of the latter, belongs to Edgar End, an internist at the hospital in Milwaukee County, Wisconsin, USA and dates back to 1937. He, together with a diver, Max Gene Nohl, they breathed a binary helium-oxygen mixture in a hospital barochamber at a depth of 30 m. This experiment was followed by a series of dives in Lake Michigan to ever greater depths. Finally, using Nohl's self-contained apparatus, Frank Crilley set a new world record in December 1937 by diving to a depth of 128 m. After these experiments and due to the fact that operational needs required working underwater at ever greater depths, the use of helium became widespread, reaching the record depth of 686 m within the ATLANTIS program, through a dive carried out by the Americans at Duke University. The Europeans, for their part, have expanded underwater penetration technologies with helium-oxygen mixtures. Thus, more and more countries interested in exploiting the seas and oceans announce performances around the depth of 500 m, including France, England, Norway, Germany, Romania, etc.

2.2.3. Hydrogen

Hydrogen is a diatomic, colorless, odorless and tasteless gas. It is so active that it is rarely found in a free state. Table 9 presents the main physical characteristics of hydrogen.

Table 9 Physical properties of hydrogen.

Size	Value	Size	Value
Molar volume []	22.428		2.03
Molar mass []	2.016		
The critical temperature	33.3	Van der Waals constants: a – at/(X/mol)^2 b – ℓ/mol	0.245 0.0267
Boiling temperature at 1.013 bar (sc. abs.)	20.4	Critical pressure	12.8
Thermal conductivity	416.0		0.61
The self-diffusion coefficient	1.285	The diameter of the molecule [Å]	2.72
The density [g/X]	0.0899	Solubility in water [ℓ / ℓ]	0.0182
The dynamic coefficient of viscosity	85.0	Solubility in ethyl alcohol [ℓ / ℓ]	0.0769
Mass specific heat at constant volume	2.411	Solubility in benzene [ℓ / ℓ]	0.06590

The first attempts to use hydrogen in diving, as a substitute for nitrogen and helium, were carried out by the Swedish Navy. In 1945, Swedish engineer Arne Zetterström investigated for the first time the possibilities of using the hydrogen-oxygen mixture (HIDROX) in diving. He dived to a depth of 156 m in the Baltic

Sea. Unfortunately, Zetterström dies in an accident, during the return to atmospheric pressure, due to a failure of the lifting winch, an accident that had nothing in common with the use of the hydrogen-oxygen breathing mixture.

After this tragic event, the issue of using hydrogen in diving remained in limbo for many years. Only in 1968, the French from COMEX took up the idea by initiating the HYDRA program, which culminated in 1992 with the HYDRA X human experiment at a depth of 701 m. The breathing mixture used was a ternary hydrogen-helium-oxygen mixture (HYDRELIOX).

Next, the main reasons why it was necessary to use hydrogen in the creation of breathing mixtures intended for diving technologies are presented.

First of all, hydrogen is a light gas, it is found in abundance in nature and, in addition, it has the ability to dilute oxygen to make it breathable in convenient doses.

After numerous experiments on animals, carried out by Brauer in the USA, Orhagen in Sweden and the team led by H.G. Delauze in France, it was demonstrated that hydrogen is not toxic. The use of hydrogen as an oxygen diluent in respiratory mixtures has a double perspective:

- improvement of the professional compartment of underwater interventions, between 300 and 500 m deep;
- the possibility of reaching the threshold of 700 m depth, under conditions of security, comfort and efficiency, which no other gas allows.

The other inert gases were less used in diving. However, *neon* stands out among these, which, due to its properties of not distorting the sound spectrum and being a superior thermal insulator, has become a subject of research in the field of breathing mixtures used for human penetration under water.

R E F E R E N C E S

[1] J.E. Cayford, *Underwater Work* (Lorella Maritime Press Centreville, Maryland, 1982).

[2] A. Constantin, *Transportul gazelor prin sistemul respirator uman şi mijloacele de protecţia respiraţiei, în procese hiperbare* (PhD Thesis, "Ovidius" University Constanţa, 1998).

[3] M. Degeratu, A. Petru, V. Beiu, *Computer – aided Simulation of Theoretical Processes in Binary and Ternary Mixtures of Hyperbaric Systems Used in Deep Diving* (Biochem. Methods, Columbus, Ohio, U.S.A., 1986) Vol. 107, p. 346.

[4] M. Degeratu, A. Petru, Şt. Georgescu, S. Ioniţă, *Tehnologii hiperbare pentru scufundări*

unitare şi în saturaţie (Matrix ROM, Bucureşti, 2003).

[5] B. Gardette, *HYDRA IV and HYDRA V, human deep hydrogen dives 1983-1985. In hydrogen as a diving gas* (33-rd Under sea and Hyperbare Medical Society Workshop. BRAUER R. W., 1987).

[6] C.J. Lambertsen, *Effects of Excesive Pressure of Oxygen, Nitrogen, Helium, Carbon Dioxide and Carbon Monoxide.* (V.B. Mountcastle, Missouri, 1980) Vol. 2.

[7] G. Poulet, R. Barincou, *La plongée* (Denöel, Paris, 1988).

[8] * * *, *U.S. Navy Diving Manual* (U. S. Government Printing Office, Washington, 1975).

[9] * * *, *Linde Gasekatalog* (Linde AG, Werksgruppe Technische Gase, München).