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EVALUATION OF THE IMPACT OF BREATHING AIR CONTAMINATION ON SAFE PERFORMANCE OF HYPERBARIC EXPOSURE

ABSTRACT

The evaluation of the impact of contamination in breathing air intended for hyperbaric purposes is essential both for practical and theoretical reasons. The quality of breathing air and the breathing mixes obtained on its basis is of crucial importance with regard to divers' safety in the course of underwater works. The existing contaminants, as well as substandard quality gases have an adverse impact on divers' health and life, both in terms of the physiological impact on the body, and fire hazards in hyperbaric complexes. In the process of breathing air production we deal with a few sources of potential contaminants stemming from technical measures. The human body is also responsible for the release of contaminants in hyperbaric conditions. The article presents the above issues and provides insight into existing threats.

Key words:
underwater work technology, diving gases, breathing air.

INTRODUCTION

The analysis of the impact of contaminants has been prepared on the basis of the previously published research results which, in spite of a considerable passage of time, have remained up-to-date [5]. They have been, however, complemented by the results of subsequent research results [7].

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It is well known that the contamination of diving gas with components that have a toxic impact on men is highly undesirable. Breathing air contaminants can be separated into three groups:

– contaminants originating in the air that is a substrate;
– contaminants from technical measures that come into contact with the diving gas[1];
– contaminants that originate from the human body [6].

Each of the abovementioned types of contamination deeply affects the quality of the product, which in the present case is the breathing air produced for the purposes of hyperbaric oxygen conditions[2].

TOXICOLOGICAL HAZARD

Generally, it may be assumed that the reaction of the body to an isolated toxic component in the form of vapour or gas, is dependent on its partial pressure:

$$p_i = p \cdot x_i, \tag{1}$$

where:

p_i — partial pressure of the i-th component;

p — total pressure of gas mixture;

x_i — mole fraction of the i-th component [$mol \cdot mol^{-1}$].

In the conditions of increased ambient pressure p, with the assumption that the content of a given component $x_i = idem$ in the diving gas remains unchanged, the partial pressure p_i of particular ingredients of breathing air will increase: $\forall_{C_v=idem \to p_i=f(p)} \ p \nearrow \Rightarrow p_i \nearrow$. If for the atmospheric pressure p_0 the permissible content X_i of a given component i is equal to $x_i^{max}(p_0) \leftarrow X_i$, then withe the pressure of $p \cong 2 \cdot p_0$ equivalent to depth $H = 10 \ mH_2O$ the permissible content of this component $x_i^{max}(p)$ is half as much: $x_i^{max}(p = 2 \cdot p_0) = 0{,}5 \cdot x_i^{max}(p_0)$. The maximum content in the diving gas $x_i^{max}(p = 2 \cdot p_0)$ at the depth of $90 \ mH_2O$ is ten times smaller $x_i^{max}(p = 2 \cdot p_0) = 0{,}1 \cdot x_i^{max}(p_0)$. When there is more than one

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[1] E.g. volatile paint components, volatile components of thermal insulation, maintenance products, etc.

[2] Oxygen conditions are such conditions where the system or its element is operated in a direct contact with pure oxygen; this operation is due to the fact of using air as a substrate for the production of breathing mixes which are frequently enriched by oxygen in relation to atmospheric air, and therefore increasing fire hazard.

type of contamination in the diving gas[3], then the law of cumulative contaminants is applicable[4] [1]: $\sum_i \frac{x_i}{x_i^{max}} \leq 1{,}5$. Maximum permissible concentrations x_i^{max} of toxic substances are most frequently determined in reference to atmospheric pressure p_0. Drawing on the definition of the percentage concentration $C_i \overset{\text{def}}{=} x_i \cdot 100\%$ and the (1) relationship, one may calculate the maximum partial pressures p_i^{max} for toxic substances in normobaric circumstances p_0:

$$\sum_i \frac{C_i}{C_i^{max}} = \sum_i \frac{x_i}{x_i^{max}} = \sum_i \frac{p_i}{p_i^{max}} \leq 1{,}5, \qquad (2)$$

where:

C_i — the concentration of the i-th contaminant [$\%_{obj.}$];

C_i^{max} — maximum permissible concentration of the i-th contaminant [$\%_{obj.}$];

x_i — mole fraction of the i-th contaminant [$mol \cdot mol^{-1}$];

x_i^{max} — maximum permissible mole fraction of the i-th contaminant [$mol \cdot mol^{-1}$];

p_i — partial pressure of the i-th contaminant [Pa];

p_i^{max} — maximum permissible partial pressure of the i-th contaminant [Pa].

Tab. 1. The composition of dry air in volume and mass percentage [5]

Gas	N_2	O_2	Ar	CO_2	H_2	Ne	He	Kr	Xe
C [$\%_{obj.}$]	78.03	20.99	0.93	0.030	0.01	0.018	0.0005	0.001	0.00001
C [$\%_{mas.}$]	75.47	23.20	1.28	0.046	0.001	0.0012	0.0001	0.0003	0.0004

Drawing on the fact that the partial pressure of a toxic substance i equals $p_i = p_0 \cdot \frac{C_i}{100\%}$, the (1) relationship for hyperbaric circumstances may be expressed as: $\frac{p}{p_0} \sum_i \frac{C_i}{C_i^{max}} \leq 1{,}5$, where p — absolute pressure at the diving depth [Pa]. Typical contaminants of breathing air include: carbon dioxide CO_2, nitric oxides NO_x, aromatic hydrocarbons C_xH_y, carbon monoxide CO, water vapour H_2O, etc. Some of the contamination comes from the air that is subjected to the process of compression, and some from compression systems (compressors, filling units) [5]. The composition of dry atmospheric air has been demonstrated in table 1. Classification societies provide standard types of contamination that originates from technical measures together with their maximum permissible concentrations. The overview of the selected

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[3] In many situations interactions occur not only between contaminants, but also between a contaminant and oxygen, or seemingly inert gases such as nitrogen or helium.

[4] Some authors postulate that instead of the value 1.5 value needs to be assumed 1.0.

contaminants from technical measures is demonstrated in table 1 [7]. The data concerning safe concentration levels of contamination can be found in some instructions regarding survival under specific conditions tables 2–4 [7]. Therefore, measurements are conducted and the obtained results of contaminant concentration may serve to determine the maximum safe depth at which the diving gas may be used on account of the surface equivalent value of toxic substances — SEV[5]. Surface equivalent value may be calculated according to the formula:

$$x_{SEV} = x \frac{p}{p_0},$$ (3)

where:

x_{SEV} — surface equivalent value of the contaminant i [ppm_v^{SEV}];

x_i — contaminant value i in the sample [ppm];

p — absolute pressure in the complex at the time of collecting the sample [Pa];

p_0 — normal pressure [Pa].

Tables 2–4 demonstrate example permissible surface equivalent values x_{SEV} for the selected contaminants i with different exposure times [6]. As previously mentioned, from the practical point of view, the obtained results of contaminant values may serve to determine the maximum safe depth for breathing with contaminated diving gas.

Tab. 2. Maximum permissible concentrations of some toxic substances in submersible objects for normal conditions [7]

Chemical compound		The source of contamination	Maximum permissible concentration for exposure time		
			1 hour	24 hours	90 days
acetylene	C_2H_2	fried dishes	6000 ppm	6000 ppm	6000 ppm
acrolein	CH_2CHCHO	fried dishes	—	0.1 ppm	—
ammonia	NH_3	metabolism	400 ppm	50 ppm	25 ppm
stibine	SbH_3	battery gassing	—	0.05 ppm	0.01 ppm
arsine	AsH_3	battery gassing	—	0.1 ppm	0.1 ppm
benzene	C_6H_6	solvent	—	100 ppm	1.0 ppm
methyl chloride	CH_3Cl	solvent	—	—	25 ppm
chloroform	$CHCl_3$	solvent	—	—	1 ppm
hydrogen chloride	HCl	freon disintegration	10 ppm	4.0 ppm	1.0 ppm
nitrogen dioxide	NO_2	compressors	10 ppm	1.0 ppm	0.5 ppm

[5] Surface Equivalent Value.

Chemical compound		The source of contamination	Maximum permissible concentration for exposure time		
			1 hour	24 hours	90 days
sulphur dioxide	SO_2	lavatories	10 ppm	5.0 ppm	1.0 ppm
carbon dioxide	CO_2	metabolism	2.5%	1.0%	0.5%
ethanol	C_2H_5OH	solvent	—	—	100 ppm
hydrogen fluoride	HF	freon disintegration	8 ppm	1.0 ppm	0.1 ppm
formaldehyde	$HCHO$	boiled dishes	5 ppm	5 ppm	5 ppm
phosgene	$COCl_2$	freon disintegration	1.0 ppm	0.1 ppm	0.05 ppm
freon 113	$CClF_2CCl_2F$	cooling devices	—	—	100 ppm
freon 11	CCl_3F	cooling devices	—	—	100 ppm
freon 12	CCl_2F_2	cooling devices	—	—	100 ppm
freon 114	$CClF_2CClF_2$	cooling devices	—	—	100 ppm
methyl ethyl ketone	$CH_3COC_2H_5$	solvent	—	—	20 ppm
methyl butyl ketone	$CH_3COC_3H_7$	solvent	—	—	20 ppm
xylene	$C_6H_4(CH_3)_2$	paint solvents	—	—	50 ppm
methane	CH_4	lavatories	1.3%	1.3%	1.3%
methanol	CH_3OH	solvent	—	—	10 ppm
nitric oxide	NO	compressors	10 ppm	1.0 ppm	0.5 ppm
toluene	$C_6H_5CH_3$	solvent	—	—	20 ppm
aromatic hydrocarbons except for benzene		paint solvents	—	—	$10\ mg \cdot m^{-3}$
aliphatic hydrocarbons except for methane		paint solvents	—	—	$10\ mg \cdot m^{-3}$
hydrogen	H_2	battery gassing	1000 ppm	1000 ppm	1000 ppm

Tab. 3. Maximum permissible concentrations of toxic vapours and gases [7]

Duration	Carbon monoxide	Nitric oxides	Benzene	Toluene	Xylene	Formaldehyde	Acetaldehyde
[min]	$[mg \cdot m^{-3}]$						
5	700	60	—	—	—	—	—
10	600	45	90	—	—	—	—
15	400	35	70	270	—	—	—
20	360	30	60	—	—	—	—
30	300	25	50	170	130	8	100
40	240	20	45	—	—	—	—
60	200	15	37	165	123	—	—
120	150	—	25	115	110	—	—
240	100	—	15	80	90	—	—
480	60	10	—	—	79	—	—
1440	40	—	—	—	60	—	—

Tab. 4. Maximum permissible concentrations of some toxic substances
in submersible objects [7]

Chemical compound		Maximum permissible concentration for exposure time [$mg \cdot m^{-3}$]			
		4 hours	8 hours	24 hours	[2000; 3000]hours
stibine	SbH_3	0.5	0.3	0.15	—
arsine	AsH_3	—	0.1	—	0.003
benzene	C_6H_6	—	5	—	2
phosgene	$COCl_2$	—	0.5	—	—
freon 12	CCl_2F_2	6000	3000	—	150
freon 114	$CClF_2CClF_2$	—	1000	—	100
xylene	$C_6H_4(CH_3)_2$	—	50	—	12
mercury	Hg	—	0.01	—	0.003
nitric oxide	NO	5	5	—	0.5
nitric oxide	CO	30	20	18	5
toluene	$C_6H_5CH_3$	—	50	—	8
hydrocarbons	C_xH_y	—	300	—	35

Table 5 demonstrates normative requirements for breathing air applicable in Polish Armed Forces [8]. The demonstrated quality requirements have been referred to two air classes. Class one is intended for diving and underwater work performance, and for use as components for making breathing mixtures intended for deep diving and saturation diving, where the purity of diving gas is of utmost importance. Class two only meets the requirements in terms of using the air for diving and underwater works[6] mostly at small and medium depths.

Tab. 5. Air purity in accordance with NO-07-A005:2010 [8]

Primary constituents and harmful admixtures	Required or allowable content		Permitted relative error in marking allowable content
	Cl. II	Cl. I	%
Oxygen [$\%_v$]	20–22	20–22	0.5
Nitrogen [$\%_v$]	78–80	78–80	0.5
Noble gases [$\%_v$]	<0.9	<0.9	—
Carbon dioxide [$\%_v$]	0–0.05	0–0.01	<5
Carbon monoxide [$\%_v$]	<10	<3	<20
Nitric oxides, in ppm, not more than	<1.0	<0.5	<20

[6] Underwater works — operations conducted by qualified persons below the surface of water, in diving gear, or in the conditions of artificially induced increased atmospheric pressure, as well as operations conducted above the surface by persons who organise the works and operate the devices of the underwater works base.

Primary constituents and harmful admixtures	Required or allowable content		Permitted relative error in marking allowable content
	Cl. II	Cl. I	%
Hydrocarbon vapours calculated into CH_4 $[10^{-3} g \cdot m^{-3}]$	5.0	1.0	<10
Particle-size dust<5 μm	No	No	—
Scent	No	No	—
Water vapour $[10^{-3} g \cdot m^{-3}]$			
$<20\ MPa$	50	35	<10
$[20\ MPa; 30]MPa$	30	20	<10
All values refer to normal conditions, i.e. the atmospheric pressure of 101.3 kPa and ambient temperature $20°C$			

Negative impact of contaminants in diving gases on human body has been widely studied and described [1], therefore the pathogenesis and the effects of diving illness have not been presented in the article.

FIRE HAZARD

From the point of view of technical security, the impact of breathing air contamination plays an essential role in the operation of technical systems in hyperbaric facilities. Adverse impact of contaminants from petroleum products, aromatic hydrocarbons may cause the ignition of high-pressure distribution systems of breathing gases. So far many similar events have been reported. Figures 1 and 2 demonstrates real effects of the ignition in the RLKZH power system[7] in hyperbaric conditions. The effects of similar incidents may be a significant threat to divers staying in the diving complex in hyperbaric conditions.

For the outbreak of fire one needs the oxidizer, combustible material and exceeding the flash point. Breathing air contains oxygen which creates a fire hazard. Oxygen is not a flammable gas but a strong oxidizer which may enter into exothermic chemical reactions, which may be slow, quick or even explosive. A slow oxidation of metal and other materials is called corrosion. This adverse phenomenon is also witnessed in rubber and other materials used in hyperbaric technologies. For example, the damaging of seals often results from the slow process of oxidation. A quick oxidation is called combustion. An explosion can follow a very quick process of oxidation. Problems related to fire safety while obtaining gas mixtures, including those based on breathing air, are commonly referred to as t e c h n i c a l   o x y g e n   s a f e t y.

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[7] RLKZH — The Containerized Hyperbaric Treatment Chamber.

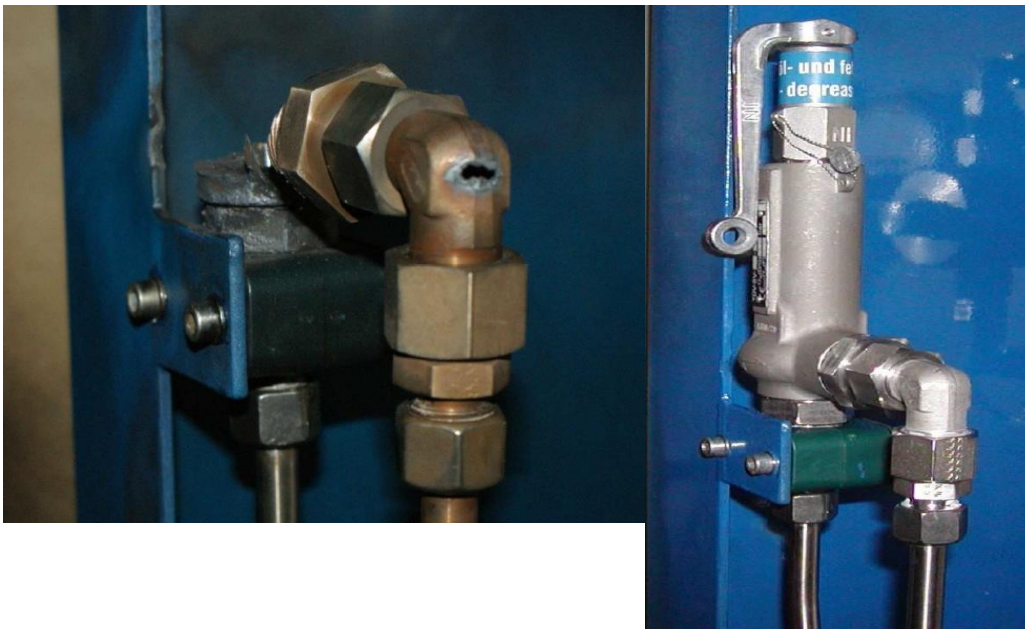Fig. 1. Safety valve system of oxygen supply after oxygen ignition [PHU 'AQUATICUS', 2011][8]

Fig. 2. Power fittings and safety valve system of oxygen supply before and after oxygen ignition
[PHU 'AQUATICUS', 2011]

[8] Information for the owner on the spontaneous combustion of the oxygen in the energy and breathing gases installations of the RLKZH in unit 511 Technical information on safety of PHU 'AQUATICUS', 2011 oxygenation systems.

There are several ways of approaching this issue. First of them is the concept of similarity to the use of gaseous oxygen under pressure. The second is the concept of absolute flammability of all materials [5]. As regards the hazard of fire incidence in diving gas systems, the contaminants that pose a threat include hydrocarbon contaminants. The source of hydrocarbons in diving gas systems is the greasing oil for lubricating compressors and filling units, which may accumulate in gaseous systems. The dangerous content of condensed hydrocarbons at high air pressure in terms of fire hazards has been experimentally determined to be at the level of about $C \cong 200 \, mg \cdot m^{-2}$ [4]. In the case of low pressure systems the value amounts to $C \cong 500 \, mg \cdot m^{-2}$ [4]. With regard to rigorous requirements in high-pressure oxygen installations operated in military conditions, the preferred level of hydrocarbon contamination content was determined at about $C \cong 55 \, mg \cdot m^{-2}$ [2], [9]. The content of the contaminants is strictly proportional to the amount of compressed air and depends on the quality of the filters used. Other flammable contaminants may come from grease used for lubricating valves, reducers, seals, etc. In order to minimise the risk of ignition one must withdraw from using mineral or silicone grease, which are commonly used for valves and seals, and use grease for oxygen conditions instead [4, 5]. The purified surfaces operating in oxygen conditions must be periodically reviewed, e.g. in visible light[9] and ultraviolet light[10] with the wavelength of $\lambda \in [0,32; \, 0,37] \, \mu m$ [9], by wiping with a white, lint-free cloth[11], water[12] or extraction[13] inspection. A preferred level of permissible contaminants in oxygen conditions for pressure higher than $p > 0,3 MPa$ was determined at $C \cong 55 \, mg \cdot m^{-2}$ [2], for safety reasons it must not be higher than $C < 200 \, mg \cdot m^2$ [2]. Where the permissible number of individual contaminant particles must not exceedć $N = 215 \, m^{-2}$, and their size may not be larger than an eyelet with the following dimensions[14] $l = [500 \times 1000] \, \mu m$ [3]. Safety conditions and the employed technological methods of cleansing the elements that operate in oxygen conditions have been presented in detail [9].

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[9] Ability to detect contaminants larger than $l > 50 \, \mu m$.

[10] This enables the detection of fluorescent substance in ultraviolet, e.g. oil contaminants.

[11] Preferably cotton.

[12] Spraying the surface with water from a pulveriser and observing the shape of the forming drops for about $5 \, s$ — if water collects in drops, then the surface is greasy.

[13] Cleansing the impurities with an organic solvent, which must be then analysed by, e.g. spectroscopic and chromatographic methods.

[14] For elongated particles of up to 2000 μm.

QUALITY

The evaluation of the quality of diving gases is most frequently effected by the methods of quantitative instrumental analysis which provides an opportunity to determine the vapours and gases contained in breathing air, which include carbon dioxide CO_2, carbon monoxide CO, ammonia NH_3, methane CH_4, nitric oxides NO_x, argon Ar, acetone vapours $(CH_3)_2O$, water vapour H_2O and hydrocarbon vapours C_xH_y. Most methods require the instruments to be calibrated by standards. With accurate[15] determinations such calibration is required before every measurement taken. Reviewing and the capacity of measuring methods have been described before and will not be presented here [5, 7, 12].

EFFICIENCY

High quality breathing air must continuously ensure safety of operation and meet the requirements of the users as regards the security of:
– ventilation of the submarine;
– supplying decompression chambers and hyperbaric complexes;
– as a substrate for preparing breathing gases;
– replenishing pressure vessels of diving equipment;
– supplying stationary and ship power supply systems of submersibles[16];
– as an operating medium of pneumatic pumping equipment and supplying pneumatic filling units in the system of breathing gas formation.

The process of securing air should be resistant to interferences. Periodic deactivation of power supplies caused by the inability to ensure quality requirements of the product may considerably impede or even prevent underwater operations.

Each phase of breathing mix production entails a potential risk of its pollution. A significant element eliminating the said risk in the production process is the filtration system, which is an element that assures quality. The absorbing ability of the filter cartridge is dependent on its temperature. In most cases, after a certain scope of temperature is exceeded its ability to clean the air decreases together with increasing temperature. What plays an important role in increasing the longevity of the cartridge is the remaining oil and water content at the compressor outlet. Taking into account

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[15] Responsible.
[16] E.g. diving bell.

a high ambient temperature in the engine room and an increased temperature at the compressor outlet, the absorbing ability of filter cartridges and the duration of protection needs to be assumed at the minimum level provided by the producer. For the reasons above, the employed filtering set must be adapted to the actual requirements. The use of purification filters should remove undesirable contaminants, most importantly: particles and vapours of oil, particles of water and water vapour, any mechanical impurities, chemical impurities, carbon monoxide and dioxide, nitric oxide, etc. from the delivered compressed air. Owing to this, the purified air may be stored in diving systems up to three months [8]. The system of purifying breathing air used in the hyperbaric system should ensure a long duration of protection, which should correspond to at least 2000 Nm^3 of filtered air. On account of the various types of compression systems, the optimal solution is to use a series of filter cartridges ensuring a wide range of use, depending on the technical parameters of the compression systems[17]. Filter cartridges should be easily replaceable and designed in a manner that prevents the occurrence of possible errors on the part of the crew.

CONCLUSIONS

It follows from the presented evaluation that for safe operations of hyperbaric systems used in the Polish Armed Forces, as well as for ensuring life and health of the divers, it is of utmost importance to provide them with the highest quality diving gases. It is only possible on condition that the Polish Armed Forces are supplied with appropriate systems for generating, storing and distributing breathing air. The achievement of this aim will not be possible by merely replacing compression, filtration and distribution systems with newer counterparts. The expected requirements are determined by the need to modernise the laboratory facilities and to build a workroom for purifying the elements of technical systems used for generating, storing and distributing breathing air as for oxygen conditions. Modernising distribution systems required a partial or complete replacement of such elements as valves, reducers, particulate filters, moisture traps, manometers, high-pressure automatic elements, etc. The selection of the appropriate products and their preparation for oxygen conditions and defining the principles of assembly and operation was made possible through separate projects, based on the laboratory facilities and the laboratory for adapting materials to oxygen conditions. The air used as a component of breathing mixtures must meet much higher purity standards to avoid fire hazards

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[17] Maximum pressure, efficiency.

while generating the mixtures, as well as toxicological standards when used for supplying diving equipment, especially with a semi-closed or closed circuit of diving gases. With respect to the discussed issue, it is also significant to establish a proper system of educating based on qualification and codified training courses within the competence of the Ministry of Defence for future operators of diving chambers, diving equipment, systems of breathing mixture generation, rescue divers and submarine crews. The participation in the system should enable the acquisition of adequate qualifications in the Polish Armed Forces which enable the operation of hyperbaric systems [10, 11] in compliance with the applicable norms and procedures that minimise the occurrence of potential threats to the users.

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OCENA WPŁYWU ZANIECZYSZCZEŃ POWIETRZA ODDECHOWEGO NA BEZPIECZEŃSTWO WYKONYWANIA EKSPOZYCJI HIPERBARYCZNYCH

STRESZCZENIE

Ocena wpływu zanieczyszczeń powietrza oddechowego przeznaczonego do stosowania w celach hiperbarycznych jest bardzo ważna. Jakość powietrza oddechowego oraz otrzymywanych na jego bazie mieszanin oddechowych ma kluczowe znaczenie ze względu na bezpieczeństwo nurków wykonujących prace podwodne. Występujące zanieczyszczenia i dopuszczenie do stosowania czynników o niewłaściwej jakości ma negatywny wpływ na zdrowie i życie nurka zarówno w ujęciu oddziaływania fizjologicznego na organizm, jak również zagrożenia pożarowego w kompleksach hiperbarycznych. W procesie wytwarzania powietrza oddechowego mamy do czynienia z kilkoma źródłami potencjalnych zanieczyszczeń pochodzącymi między innymi ze środków technicznych. Organizm człowieka jest także źródłem emisji zanieczyszczeń w warunkach hiperbarycznych. W artykule przedstawiono te zagadnienia, przybliżając istotę występujących zagrożeń.

Słowa kluczowe:
technologia prac podwodnych, nurkowe czynniki oddechowe, powietrze oddechowe.