

## **BREATHING AIR PURIFICATION FOR HYPERBARIC PURPOSES**

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### **ABSTRACT**

The determination of efficacy of the process of breathing air purification, for hyperbaric purposes, through the use of filtration systems is significant both from theoretical and practical points of view. The quality of the breathing air and the mixes obtained on its basis is of crucial importance for divers' safety. Paradoxically, alteration of regulations concerned with quality requirements for breathing mixes necessitated the undertaking of verification of technical and laboratory bases used in their production. The article discusses and presents issues related to this subject matter, starting from determining reasons and diagnosing the situation after the implementation of new regulations, to the choice of the direction of the necessary corrective measures. The results of these activities will be the subject of the following publication.

**Key words:** underwater works technology, sea engineering, breathing mixess.

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### **ARTICLE INFO**

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PolHypRes 2014 Vol. 48 Issue 3 pp. 49 – 58

**ISSN:** 1734-7009 **eISSN:** 2084-0535

**DOI:** [HTTP://DX.DOI.ORG/10.13006/PHR.48.4](http://dx.doi.org/10.13006/PHR.48.4)

Pages: 10, figures: 4, tables: 3.

**page www of the periodical:** [www.phr.net.pl](http://www.phr.net.pl)

**Original article:**

**Delivery date:** 29.06.2014 r

**Date of approval for printing:** 17.07.2014 r

**Publisher**

Polish Hyperbaric Medicine and Technology Society



## INTRODUCTION

The quality of breathing air is of key importance when it comes to diver's safety in the performance of underwater works. In the conditions of an increased ambient pressure  $p_h$ , with the assumption that the content of a given component ( $C_v$ ) in the breathing mix remains unchanged, the partial pressure of particular ingredients  $p_i$  of the breathing air will increase.

The above phenomenon applies to all air constituents, both natural (e.g. CO, CO<sub>2</sub>, H<sub>2</sub>O) as well as those supplied (e.g. aromatic hydrocarbons), and the generation systems of breathing air. Below we present relations (1.1–1.4) reflecting the behaviour of particular breathing air constituents in the conditions of an increased pressure.

$$p_h \uparrow = p_c \uparrow \quad (1.1)$$

$$C_v = \text{const} \rightarrow p_i = f(p_c) \quad (1.2)$$

$$X_i = \frac{C_v}{100\%} \quad (1.3)$$

$$p_i = p_c \cdot X_i \quad (1.4)$$

where:

$p_i$  - partial pressure of a given constituent of the breathing mix [Pa],

$p_h$  - hydrostatic pressure [Pa],

$p_c$  - total pressure of the breathing mix [Pa]

$X_i$  - mole fraction of a given mix constituent [mole/mole],

$C_v$  - percentage concentration of a given constituent of the gas mixture [%].

From a physiological perspective, management of the pollutants contained in the breathing air are crucial when we consider the diver's safety under water and during exposures in hyperbaric facilities [1,2].

As mentioned above, as the partial pressure increases with depth, the potential for an adverse impact on the divers' organism from any pollutant gases present in the breathing mix grows. As an example, at 10m the allowable content of a given constituent (e.g. CO<sub>2</sub>) in accordance with the relation (1.4) is half that which is allowed when compared with normobaric conditions (for atmospheric pressure). If we compare the same content (CO<sub>2</sub>) in the breathing mix we will find that at the depth of 90m it is already ten times smaller.

For the purpose of demonstrating the changes occurring in an increased pressure for a particular concentration of  $C_{CO_2}$  in the breathing mix, below (fig. 1) we present the effect of hydrostatic pressure changes on the partial pressure values

$p_{CO_2}$ .

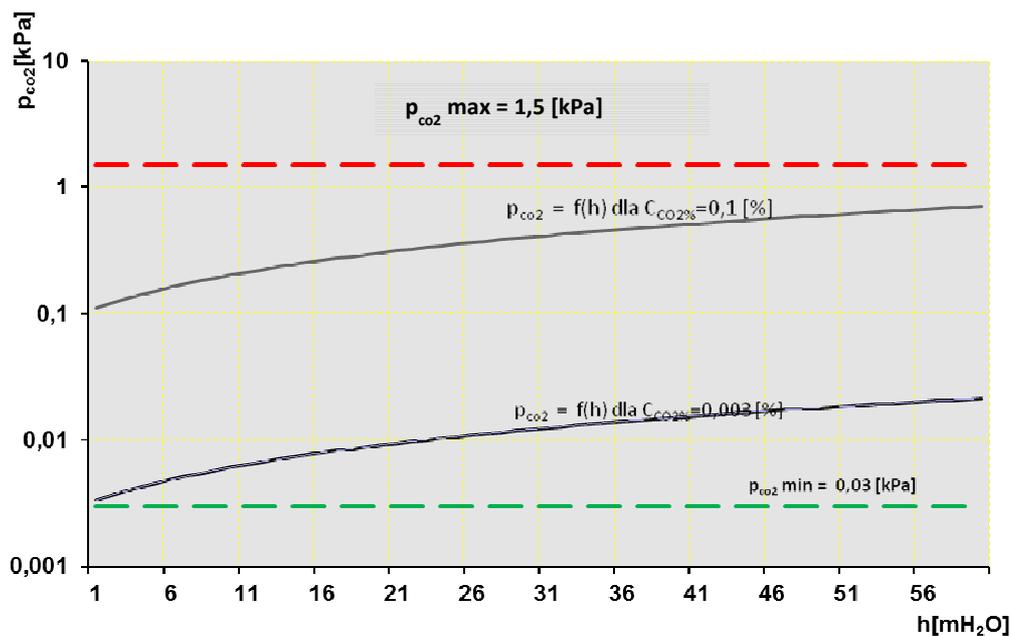


Fig. 1. The effect of hydrostatic pressure variation on CO<sub>2</sub> partial pressure.

The chart presents the case where the initial concentration of CO<sub>2</sub> in the breathing air intended for divers is first equal to C<sub>CO2</sub>=0.003[%], i.e. it is within the permissible range [3], whereas in the second case it amounts to C<sub>CO2</sub>=0.1[%], i.e. by far exceeds the threshold criteria as determined by normative requirements.

The permissible threshold partial pressure value for CO<sub>2</sub> in hyperbaric conditions pursuant to the applicable regulations [4] is the value p<sub>CO2</sub>=1.0[kPa].

The difference between initial concentrations reaches only 0.07[%], yet despite this fact, in the second case the partial pressure of CO<sub>2</sub> with the diving depth of ca. 60m H<sub>2</sub>O comes dangerously close to the allowable limit defined for CO<sub>2</sub>.

In the first case it reaches the value of P<sub>CO2</sub>=0.709[kPa], while in the second P<sub>CO2</sub>=0.021[kPa], i.e. almost 33 times less.

In diving conditions, after the breathing mix is decompressed at a breathing apparatus's second stage, it is supplied under the ambient pressure of a given diving depth. In the event of exceeding the allowable content of harmful admixture (e.g. CO<sub>2</sub>) in such a breathing mix, a situation may be produced with a diver being supplied with a toxic mix, thus resulting in a diving accident.

Such cases have been documented in the history of diving with detailed descriptions of the pathogenesis of poisoning with pollutants, for instance in publications by Prof. Olszański [1].

Thus, the quality of the breathing mix has a significant impact on the safety of diving and constitutes an important element in preventing diving incident. The above phenomenon is extremely important with regard to diver's safety, therefore it is necessary to use only the appropriate quality mixes.

### BASIC REQUIREMENTS REGARDING THE QUALITY OF BREATHING MIXES

The content of harmful admixtures in the breathing mix should be compliant with specified quality requirements defined by normative regulations [3].

The said regulations set out the specific quality requirements in relation to pure gases and breathing mixes used in underwater works and dives. Generally speaking, the air for divers' use should not:

- contain harmful substances;
- have a flavour;
- contain any particulate pollutants;
- contain harmful admixtures in higher doses than those specified in Table 1.

Table 1 below presents requirements in relation to the breathing air as laid down in standard NO-07-A005:2010.[S1]

The content of particular harmful inclusions refers to the maximum allowable content of a given pollutant which does not have a negative physiological impact on a diver, on condition of using the air within the permissible depth range (p<sub>CO2</sub><160kPa).

The reduction of unwanted pollutants to an acceptable level through the process of filtration in the course of production of the breathing air results in the elimination of the breathing mix as a potential cause of a diving incident.

The quality requirements shown in Table 1 relate to two air classes. The first class is intended for diving purposes and as a component in the preparation of two- and three-component breathing mixtures, whereas the second air class is compliant only with the requirements applicable to its use in diving and performance of underwater works.

The presented requirements constitute the currently applicable provisions.

Tab. 1

Air purity requirements [3].

No.	Primary constituents and harmful admixtures	Required or allowable content		Permitted relative error in marking allowable content
		Cl. II	Cl. I	%
1.	Oxygen, in % <sup>1</sup>	20 - 22	20 - 22	0,5
2.	Nitrogen, in %	78 - 80	78 - 80	0,5
3.	Noble gases, in %, not more than	0,9	0,9	not measured
4.	Carbon dioxide, in %, not more than	0 - 0,05	0 - 0,01	5
5.	Carbon monoxide, in ppm <sup>2</sup> , not more than	10	3	20
6.	Nitric oxides, in ppm, not more than	1,0	0,5	20
7.	Hydrocarbon vapours calculated into CH <sub>4</sub> , in mg/m <sup>3</sup> , not more than	5,0	1,0	10
8.	Water vapour, depending on compression pressure:			
	up to 20 MPa, in mg/m <sup>3</sup> not more than	50	35	10
	from 20 MPa up to 30 MPa, in mg/m <sup>3</sup> not more than	30	20	10
9.	Dust with particle sizes up to 5 µm	no	no	measured
10.	Scent	flavourless	flavourless	-

NOTE 1: All values refer to normal conditions, i.e. the atmospheric pressure of 101.3 kPa and ambient temperatures equal to 20°C.

## PROBLEM SITUATION

The incorporation of the Polish Armed Forces into NATO in 1999 exerted the necessity to ensure mutual collaboration. A significant condition in relation to the breathing mixes intended for divers consisted in the necessity to meet the requirements regarding their compatibility.

Due to the need to implement the standardisation requirements of STANAG 1458<sup>1</sup> concerning breathing mixes, measures were taken to adapt the effective domestic requirements to those standards.

Table 2 below provides the comparison between the newly introduced domestic provisions (NO), NATO requirements (STANAG) and the regulations effective before joining NATO (PN-W).

Tab. 2.

Quality requirements with regard to the breathing air for divers.

No.	Normative requirement	Primary constituents and harmful admixtures						
		O <sub>2</sub> [%]	CO <sub>2</sub> [%]	CO [ppm]	H <sub>2</sub> O [mg/m <sup>3</sup> ]	NO, NO <sub>2</sub> [ppm]	Hydrocarbon vapours calculated into CH <sub>4</sub> [mg/m <sup>3</sup> ]	Noble gases [%]
1.	NO-07-A010:1999 kl.II	20÷21	0,03÷0,05	30	50 <sup>1</sup> 30 <sup>2</sup>	1,0	5,0	0,9
2.	NO-07-A010:1999 kl.I	20÷21	0÷0,01	20	35 <sup>1</sup> 20 <sup>2</sup>	0,5	1,0	0,9
3.	NO-07-A010:2010 kl.II	20÷22	0÷0,05	10	50 <sup>1</sup> 30 <sup>2</sup>	1,0	5,0	0,9
4.	NO-07-A010:2010 kl.I	20÷22	0÷0,01	3	35 <sup>1</sup> 20 <sup>2</sup>	0,5	1,0	0,9
5.	PN-W - 88503 kl.I	<21	0÷0,6	30	50 <sup>1</sup> 30 <sup>2</sup>	1,0	1,0	0,9
6.	PN-W - 88503 kl.II	<21	0÷0,01	20	35 <sup>1</sup> 25 <sup>2</sup>	0,5	0,5	0,9
7.	STANAG 1458 kl.A	20÷22	0,05	5	35	-	12,47	1,0
8.	STANAG 1458 kl.B	20÷22	0,1	50	500	-	14,97	1,0

NOTE:

- 1- up to 20MPa;

- 2- up to 30MPa.

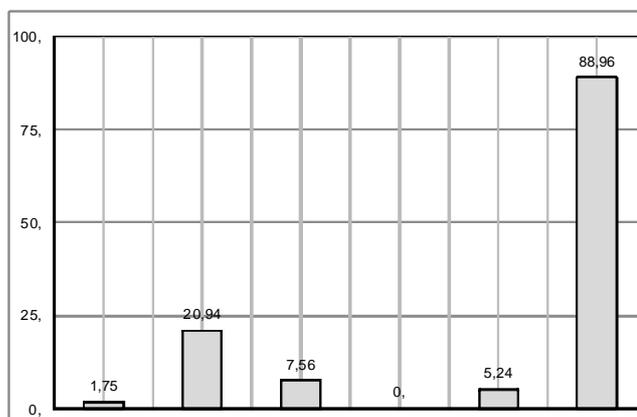
- flavourless breathing air

Due to the above reasons, in the years 2002–2004 an analysis of the level of adjustment of the domestic air supply sources to the requirements resulting from normative provisions set out in the agreement STANAG 2458 was carried out.

## INITIAL ANALYSIS OF THE BREATHING MIX SUPPLY SYSTEMS

In the first phase of works the results of laboratory tests were considered. Such results were obtained in a physical-chemical laboratory of the Central Institute for Rescue Equipment of the Polish Navy, realising chemical qualitative<sup>2</sup> and quantitative<sup>3</sup> analyses of the breathing air in concord with the criteria specified in NO-07-A005.

The figure below presents graphical results of the said analysis.



\*Primary constituents and harmful admixtures.

Fig. 2 The percentage share of the breathing air test results failing to meet quality requirements in the years 2002 – 2003.

Based on the results shown in fig. 2, we may observe that nearly 89[%] of the entirety of executed measurements related to H<sub>2</sub>O content in the breathing air exceeded the permissible norms, and almost 21[%] failed to meet the requirements regarding allowable CO<sub>2</sub> content.

## CONCLUSIONS

With regard to the scale of the discussed phenomenon it seemed proper to investigate the reasons for this situation as well as the fact of so many samples of the breathing air failing to meet the requirements.

What was particularly important was providing an answer to the question of if, and subsequently what, mistakes are made in the process of obtaining the breathing mix and/or in the course of evaluation of its quality. Consequently, in order to achieve quality improvement it was necessary to identify and gradually eliminate potential errors.

First, for the purpose of elimination of possible measurement irregularities it was decided to conduct an overhaul and modernisation (retrofitting) of the measuring equipment used in the physical-chemical analysis of breathing mixes. Such a procedure allowed obtainment of a reliable device for monitoring quality of the breathing air.

The key element identified during an analysis of breathing air production technologies, with various supply sources, was the one ensuring quality related to the applied treatment.

The prevailing technology used in the production of the breathing air for divers was at that period based on the use of breathing air compressors, as documented on Photographs 1 & 2, produced by Russia (EK2-150, EK-7.5) and the former GDR (A3HW1).

The above devices were incapable of meeting the new requirements, as they were equipped with simple filtration systems prepared for other (older) quality standards of breathing mixes. In comparison with modern supply sources, for instance the compressors made by SAUER & SOHN, WP5000 type, were characterised by a high oil content at the outlet and a low quality of the obtained breathing air.

To illustrate this, the residual oil content at the outlet of WP5000 compressor prior to filtration, under normal conditions, i.e. the temperature of 20°C and pressure of 1013[mbar] oscillated around 3–5 [ppm] +/- 5%. As high as these readings are, it is alarming to note that this value is many times lower than that recorded for the EK 2-150 compressor also in use.

Therefore, the first aim was to eliminate causes having the largest impact on the process, these being identified as contamination coming from the supply sources and measured by the residual oil content at the outlet.



Fig. 3. Diving air compressor EK 7.5-3 manufactured by the USSR.



Fig. 4. The supply system for underwater works security base "ORTOLAN" with diving air compressors EK 2-150 manufactured by the USSR.

An insufficient air treatment system configuration and the use of air-purifying filters filled, for instance with a single absorbent<sup>4</sup> or adsorbent<sup>5</sup> (such as active carbon or soda lime) was not able to ensure the expected quality.

Considering the fact that the obtained breathing air from compressors greased with petrochemical oil was subject to contamination in the compression process by becoming saturated with oil vapours, polluted with rust and shavings and absorbing carbon dioxide (in compressors powered by internal-combustion engines), the significant element in dealing with this issue consisted in the proper selection of active methods for the removal of particular pollutants [9].

The disposal of unwanted substances is conducted by their successive elimination with the use of various sorption materials both through chemisorption (chemical adsorption) and physical adsorption [10,11,12].

The most commonly applied (widespread) methods encompass the use of filter cartridges on the basis of substances presented in table 3 below.

Types of substances used in air-purifying filter cartridges for hyperbaric purposes.

No.	Substance type	Type of removed contamination
1	Molecular sieves (titanium silicate)	Water and water vapour depending on size, also aromatic hydrocarbons
2	Active carbon	Oil and flavour absorption
3	Hopcalite (mix of MnO <sub>2</sub> , CuO, CO <sub>2</sub> O <sub>3</sub> , Ag <sub>2</sub> O)	Enables oxidation of CO to CO <sub>2</sub>
4	Soda lime (mix of NaOH, Ca (OH) <sub>2</sub> , H <sub>2</sub> O and silicates)	Absorbs CO <sub>2</sub>
5	Silica gel	Water and water vapour
6	Sofnocat (mix of ZnO, Pt, Pd)	Hydrogen and CO, volatile organic compounds

Active carbon and soda lime have been so far the most widely used absorbents; however, their role was limited due to their incapability to absorb all types of contamination present in the breathing air.

Moreover, it should be observed that the filtration system used thus far functioned in cooperation with the manual water-oil separators of the compressors', allowing mechanical removal of an aggregating water-oil condensate. In the case of an unsystematic dehydration of the separator the condensate produced in the course of the working process was not properly disposed of, thus saturating the filter bed and significantly reducing its protective function.

The above information indicates that the applied technical solution was unreliable and incapable of ensuring adequate quality of the breathing mix in accordance with the new standards.

For this reason it was necessary to consider application of other types of technical devices allowing the complex solution of the problems connected with improper quality of the breathing air produced for diving purposes. The above activities shall constitute the subject of another article devoted to the discussed subject matter.

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<sup>1</sup>STANAG 1458 - Diving Gas Quality - standardisation agreement issued by NATO, an equivalent of the Defence Standard (DS) effective in the AFRP,

<sup>2</sup> Chemical quantitative analysis - a set of techniques allowing to determine the numerical values (expressed with the use of suitable units of measurement, for instance in grams or other (sub)quantities,

<sup>3</sup> Chemical quantitative analysis - a set of techniques allowing to determine the numerical values (expressed with the use of suitable units of measurement, for instance in grams or other (sub)quantities,

<sup>4</sup> Absorption - gas absorption by a liquid - or rarer - gas or liquid absorption by a solid is a process occurring in the entire absorbent mass,

<sup>5</sup> Adsorption - gas absorption by a liquid - or rarer - gas or liquid absorption by a solid, is a process occurring on the surface of an absorbent,

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