THE DETERMINATION OF THE CONCENTRATION OF POLLUTANTS IN THE COMPRESSED AIR WHEN DIVING AND ELIMINATING THESE POLLUTANTS

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ABSTRACT
The diving center owns patented personel, specialized in underwater interventions, authorized for diving at the depth of 50 m water col. The breatheable used by the divers is kept in cylinders under pressures of up to 200 bar, with the help of the compressors. The verification of the quality of the repressed air is necessary for the following reasons: the harmfulness of some components from the air (CO2, CO, dust) rises with the pressure; the water vapors from the air stocked in the cylinders are condensed in some conditions of pressure and temperature; the occurrence of oil traces because of the prolonged use of a compressor. The oil vapors being present because of the direct contact under pressure between water and the lubrication oil of the compressor. Also, there is a risk of filling the cylinders with impure air in zones with high air pollution. To recap, the main toxicities that may appear are: CO2, CO, water vapors, traces of oil and dust.

KEYWORDS: carbon dioxide, carbon oxide, point of dew, oil

1. Introduction
Respiration is the function through which the contribution of oxygen from the atmospheric air all the way to the cellular level is assured in an adequate and continuous manner, as well as the circulation, in reverse, of the carbon dioxide, produced by the cellular metabolism.
It includes the following steps:
- External respiration – ventilation
- The transportation of gases through blood
- Internal respiration – by tissues

The breathable air has in its composition the active gases (oxygen and carbon dioxide), which participate at the breathing process and are transported by nitrogen, which is the diluents gas. Their circulation during the breathing process is presented in Figure no. 1 (Boron, 2012).

2. Presentation of the Main Nuisance (toxicities)

The purity of the air in the cylinders, used in diving, is covered by the SREN 12021/2003 standard. The maximum limits accepted for the nuisances contained by this air are:
- Oil: 0.5 [mg/m³];
- CO₂: 500 [ml/m³];
- CO: 5 [ml/m³];
- Water vapors:
  - 50 [mg/m³] for a pressure of 40-200 [bar]
  - 35 [mg/m³] for a pressure > 200 [bar];
- The lack of taste and smell

The air or the synthetic breathing mixture must satisfy the following:
- At the depth of usage, the partial pressure of the CO₂ must be smaller than 0.01 [bar], and the partial pressure of the CO smaller than 0.5 [mbar];
- It must be treated for water vapors, dust, oxides or metal particles, oil vapors or hydrocarbons.

The air given by the compressors, destined for the breathing machines, must be analyzed at least once per year, after every major restoration of the compressors, as well as when anomalies are signaled by the divers. During the filling of the cylinders, the aspiration of the compressor must be placed in such a way that there are no risks of pollution, especially from the exhaust gases, the oil vapors or hydrocarbons, the CO₂ or CO (SMMM, 1996).

2.1. Carbon Dioxide

Carbon dioxide is colorless, odorless, oxide of tetravalent carbon. It is found in the atmospheric air in a proportion of about 0.02-0.033 % or at partial pressures of 2.0-3.3 [KPa].
Table no. 1

<table>
<thead>
<tr>
<th>PCO2 [mbar]</th>
<th>Exposure time [hours]</th>
<th>Observations regarding the exposure of the diver</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.5</td>
<td>May be tolerated in case of necessity</td>
</tr>
<tr>
<td>40</td>
<td>2.0</td>
<td>Tolerable at exceptional exposures</td>
</tr>
<tr>
<td>30</td>
<td>2 ... 8</td>
<td>Tolerable at exceptional exposures</td>
</tr>
<tr>
<td>20</td>
<td>8 ... 24</td>
<td>Maximum authorized in diving operations</td>
</tr>
<tr>
<td>10</td>
<td>unlimited</td>
<td>Maximal exposure normal in hyperbaric enclosures</td>
</tr>
<tr>
<td>6</td>
<td>unlimited</td>
<td>Maximal exposure, optimal, for hyperbaric</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ambiances for saturated dives</td>
</tr>
</tbody>
</table>

It enters the organism through respiration, it dissolves in blood and it is carried to the tissues. Carbon dioxide is a soluble gas in water: its solubility at a temperature of 0 Celsius degrees and a pressure of 1.01 [bar] is: 100 volumes of CO₂ in 100 volumes of water.

The exposure of the organism to this gas depends on its partial pressure (Degeratu, 2008).

It enters the organism through respiration, it dissolves in blood and it is carried to the tissues. In small doses the gas is an incentive of the breathing center, but in larger quantities it is depressive and toxic for myocardium. Locally, it expands the blood vessels and it is easy irritating. The lethal concentration is 12 % gas volume (Loghin, 1994).

The symptoms depend on the concentration of the gas:
- 0.5-2 % easy dyspnea and irritation of the airways
- 4-6 % dyspnea, headache, irritability and high blood pressure
- 8-10 % convulsions or sleepiness, syncope state
- > 12 % death.

2.2. Carbon Oxide

Carbon oxide is a gas that cannot be naturally produced, being a result of an incomplete combustion of carbon; it can be found in small quantities in volcanic gases. It can appear in compressed air when atmospheric air from polluted zones with exhaust is used.

Carbon oxide is a colorless, odorless and flavorless gas. It is highly toxic, very chemically active, combining very easily with hemoglobin. It is very hard liquefiable, not very soluble in water, soluble in ethanol, having a small reducing character. The gas manifests its toxicity at a cellular and blood level. Its ability to combine with hemoglobin is 210 higher than oxygen (US Navy, 1999). The principal toxic effect is the formation of carboxihemoglobin, HbCO, through reversible reaction:

\[ H_bO_2 + CO \leftrightarrow H_bCO + O_2 \]  

The allowed limit is: \( P_{pco} = 0.05 \) [mbar] – maximum in dives.

2.3. Water Vapors

The atmospheric air components can be found in the 3 stages of aggregation: solid, liquid, gas. That is why water vapors can be found in the breathing mixture, the normal limit being of max. 80° H.

Humidity depends on temperature and pressure, parameters which determine the change in aggregation stage. The change in phase is accompanied by a change in energy with the environment, respectively latent heat \( L \) [J]. The 3 stages: solid, liquid, gas coexist in the triple point \( \tau \). The processes of change of the aggregation stages are highlighted in Figure no. 2 (Constantin, 2002).
Over the critical point \( K \), only the gas state is present. Between the point \( \tau \) and \( K \) (critical point) the liquid stage coexists with the gas state. The isobaric cooling of the unsaturated humid air leads to a saturation with water of the mixture. The temperature at which the partial pressure of the vapors becomes equal with the pressure of saturation is called the temperature of the point of dew.

The temperature of the point of dew \( \tau \) is the saturation temperature of the humid air which is cooled and which keeps its absolute humidity \( x \) constant (Leonâchéscu, 1981). Cooling beyond this point of dew leads to the transformation of water vapors into liquid state.

For each respiratory air mixed is important to determine the point of dew, for avoid the vapors condensing. It is not admited the excessive humidity into the respiratory air for diving. The great humidity become heavier the respiration, can produce the freezing of breathing way, the cooling of the body, the irritation of the sinus.

![Figure no. 2 Transformers of phases of first order](image)

**Figure no. 2 Transformers of phases of first order**

- Processes accompanied by the receipt of latent heat from the outside environment
- Processes accompanied by the release of latent heat from the outside environment

### 2.4. Oil Traces

These appear in the breathing mixture because of the usage in time of the compressor. The aerosols of oil in larger concentrations than the accepted limit cause irritations of the airways and eyes, dizziness and headache. The maximum limit accepted is: aerosols of oil 5 \([\text{mg/m}^3]\).

### 2.5. Other Impurities

The most frequently met impurities are particles of dust and acrolein.

Dust particles may appear in the breathing mixture by using an inadequate filter for the compressor. These particles are irritating for the airways and may lead to some pulmonary diseases. Dust particles are not accepted in the breathing mixture.

By decomposing oils under pressure from the breathing air, acrolein is formed. This is a colorless or slightly yellow liquid with a very strong smell, an irritating burned fat smell. The limit of smell perception is 4 \([\text{mg/m}^3]\).

Acrolein is soluble in three parts water and miscible in any proportion of alcohol and ether. It is flammable. The maximum concentration accepted is 0.5 \([\text{mg/m}^3]\) of air and the average concentration is 0.3 \([\text{mg/m}^3]\). Exceeding this limit may cause pulmonary edemas.

Acrolein is irritating for the airways and eyes. It enters the organism threw respiration and only partially leaves the same way.

### 3. Determination of the Main Toxicities

The air compressors must have their filters changed, according with the exploitation instructions. When filling the cylinders, the compressors suction must be in an unpolluted zone. Compressors, suppressors and transfer pumps must be lubricated with specific products, such that the compressed gases which pass through them will satisfy the conditions imposed for air quality. Annually, the compressors are checked for the quality
of the repressed air. These checks are made also after restorations and also when there are signals questioning the quality of the air (SMMM, 1996).

The analysis of the composition of air is made through chemical and physical methods.

Chemical methods:
• The volumetric method, for CO₂, CO and acrolein
• The titrimetric method for CO₂ and CO.

These methods of evaluation are not exact and therefore cannot be used in determining small concentrations of CO₂ and CO specifically for the diving activity.

Physical methods:
• Chromatography
• Mass spectrometry
• Infrared spectrophotometry.

3.1. Chromatography
Chromatography is a physical method based on the absorption with different speeds of the components of a gas mixture when passing over an absorbent environment. The content of carbon oxides (CO₂ and CO) from the breathing air used by divers can be determined very well with a chromatography analyzer.

3.2. Mass spectrometry
Mass spectrometry is a physical method of research and evaluation of the energy link between the atoms of a covalent molecule, based on the observation that under a beam of accelerated electrons, the molecules of a substance in the gas phase will break, with the forming of a free radical and a positive gas ion:

\[ R - R + e \rightarrow R^+ + 2 e \]  

(2)

By using the spectrometer, one can determine: CO₂, CO, water and oil vapors (Albu, 1974).

3.3. Infrared Spectrophotometry
Infrared spectrophotometry is based on the principle of absorption in infrared of gases, assuring a continuous measure of its content in a complex binary mixture.

The Diving Center has a Schlumberger analyzer, which works on this principle (ANIR type). With its help the CO₂ levels and the existence of CO is determined.

It’s a drawer type, for assembling it in the analysis rack.

The minimum measure scale is:
• CO₂ from 0 to 50 ppm;
• CO from 0 to 100 ppm.

The response time depends on the length of the measuring camera and the debit of the gas mixture. The alimentation is pneumatic. For avoiding the intrusion of foreign particles in the device, it is equipped with a filter. Some more technical data about the device:
• Alimentation pressure 0.5-1.5 [bar]
• Recommended debit 60 [l/h]
• Functioning temperature 15-35 [°C]
• Alimentation 100 [VA].

3.4. Filtering and Weighing Oil Traces
The method consists of passing of a constant debit of gas through an installation which contains a filtering device (a filtering crucible and a filter paper with small porosity), a debitmeter and a cylinder with a gas probe which must be analyzed. The crucible and the paper are weighed before and after the passing of the gas and the difference calculated represent the quantity of oil contained in the gas probe. The pneumatic scheme of measurement is represented in Figure no. 3.
3.5. Indicating Colorimetric Set of Tubes

Very practical and present are the indicating colorimetric set of tubes, used for determining the impurities in the breathing air compressed at a pressure of maximum 300 bar, from cylinders and compressors. The compressed air is redirected in every indicator tube (see Figure no. 4) (Dräger Company, 2004). The testing formation contains a tube for every nuisance which has to be determined (humidity, oil, carbon dioxide, carbon oxide) and the tubes are placed in a box which can be transported by hand.

The colorimetric tubes are used by divers with Dräger Aerotest for the Navy. The purity of atmospheric air, compressed air, medicinal gases (oxygen) and even carbon dioxide can be tested within a few minutes using the Aerotest systems.

Dräger Aerotest for the Navy measures Oil, CO2 and CO and other typical impurities in the air stream which are supplied by high pressure compressors or compressed air at a max. pressure of 300 [bar]. The pressure is set by a pressure reducer valve whilst a flow meter measures the air being tested. Compressed air is fed by a special pipe which permits a quantitative evaluation.
4. Conclusions

For avoiding crossing the acceptable limits of nuisances (toxicities) from the breathing air used by divers, the following norms are imposed:

- The correct use of the compressors, respecting the rules with carefully watching the functioning hours and replacing the filters according instructions.
- Annual and on demand verification of the air quality, whenever it is necessary.

This is done by collecting some air samples from the compressor and checking its composition for determining the nuisances, according to the procedure described above.

- Checking the breathing air repressed by the compressor after every inspection. (SMMM, 1996).

This responsibility falls on the Hyperbaric Laboratory of the Diving Center and on the supervisor, every time is necessary.

REFERENCES


