PROCESSES AND INSTALLATIONS FOR THE PREPARATION OF BREATHING GAS MIXTURES

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Rezumat. *Amestecurile de gaze respiratorii sunt amestecuri gazoase cu două sau trei componente, o componentă fiind oxigenul, iar celelalte componente fiind gazele inerte. Aceste amestecuri rezultă din amestecarea, în proporţie dorită, a două sau trei din gazele prezentate în paragrafele anterioare, unul dintre ele fiind întotdeauna oxigenul. După numărul componentelor principale din amestecurile respiratorii, acestea se împart în: amestecuri binare (cu două componente) şi amestecuri ternare (cu trei componente). Pentru scufundări cu amestecuri respiratorii se ţine seama nu numai de concentraţia oxigenului din amestec ci şi de natura gazului inert, din punct de vedere al efectelor lui narcotice.*

Abstract. *Breathing gas mixtures are gaseous mixtures with two or three components, one component being oxygen and the other components being inert gases. These mixtures result from the mixing, in the desired proportion, of two or three of the gases described in the previous paragraphs, one of which is always oxygen. According to the number of main components in breathing mixtures, they are divided into binary (two-component) and ternary (three-component) mixtures. For diving with breathing mixes, account is taken not only of the concentration of oxygen in the mixture but also of the nature of the inert gas in terms of its narcotic effects.*

Keywords: diving, gases, breathing apparatuses

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1. Special procedures for the preparation of NITROX binary breathing mixtures

Three processes are commonly used to prepare NITROX mixtures:

- mixture preparation considering partial pressures - NITROX mixture enriched with air;

- nitrogen separation using membranes - denitrogenated air;

- continuous homogenization of the gases forming the mixture - enriched NITROX mixture.

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1.1. NITROX mixture preparation process considering gas partial pressures mixture.

The process of preparing the mixture considering the partial pressures involves injecting pure oxygen into a diving cylinder where, then, "clean" compressed air, also called oxygen compatible air (Oxygen Compatible Air), is introduced, thus creating the desired mixture. It should be said that the term "clean" is a relative notion, the quality of breathing air being established in standards such as CGA Grade E, BS4275 or DIN 3188.

Regarding the notion of "compatibility" of compressed air used to prepare NITROX mixtures, this refers to a series of operational criteria related to mixing air with pure oxygen or an oxygen-rich environment. It should be noted that there is no single standard related to the quality of air used to create NITROX mixtures.

In 1992, dive training agencies and other government agencies in the United States, meeting in Orlando, Florida, agreed on a set of standards for oxygen-compatible air. These standards represent a unanimous approval based on the knowledge, experience, and technology available at the time. The air quality values are given in Table 1.

Table 1

The values of compatible air quality indicators with oxygen when preparing NITROX mixtures

Condensed hydrocarbons	0.1mg/m^3
Hydrocarbons in gaseous state	15 ppm
Water (dew point)	- 50°C
Carbon dioxide	500 ppm
Carbon monoxide	2 ppm

Figure 1 schematically shows an installation for preparing NITROX mixtures using the process based on partial gas pressures.

The advantages of this preparation process are:

- low initial costs;
- capable of producing mixtures of any percentage.

Disadvantages:

- the cylinder loading process requires a large amount of work and is slow, about 20 – 30 minutes per cylinder;
- the cylinders and the filling system must comply with oxygen purity standards;
- potentially dangerous if oil accidentally gets into the cylinder (diesel effect leading to explosion);

the entire amount of oxygen in the cylinder that stores this gas cannot be used; to overcome this shortcoming, a special pump (booster) is needed;
the correct and precise preparation of the mixture depends on the skill of the installation operator;
it is necessary to provide a stock of oxygen cylinders.

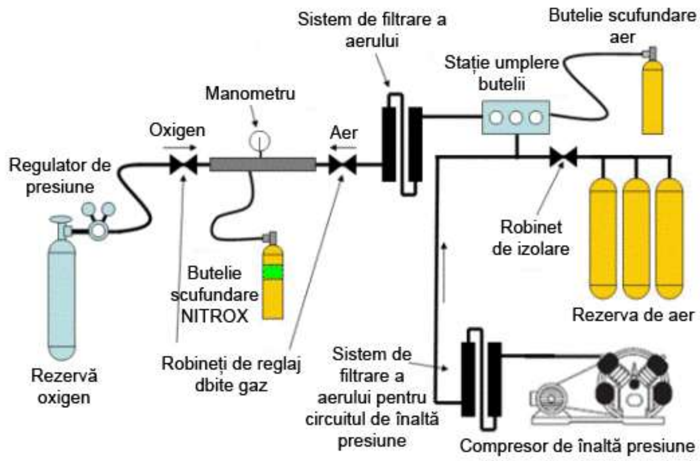

Fig. 1. Scheme of the NITROX mixture preparation plant using the process based on partial gas pressures

1.2. The process of preparing the NITROX mixture using membranes

The process of separating nitrogen using membranes was originally used in the welding industry for the production of nitrogen. It involves the use of a source of air supplied at a reduced pressure. The stream thus formed is directed through a special system of membranes. These are of two types, one intended for the passage of nitrogen, and the other for the permeate (oxygen-enriched mixture) which is distributed to the high-pressure compressor (figure 2).

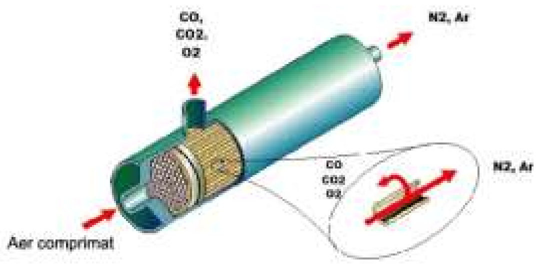

Fig. 2. Membrane separation device

The oxygen content is regulated either by changing the supply pressure to the membranes or by adjusting the opening for the passage of nitrogen. Optimal operation of the membrane system is achieved after about 30 minutes of commissioning.

The high-pressure compressor is connected either directly to the cylinders used for diving or to NITROX mixture storage containers (figure 3).

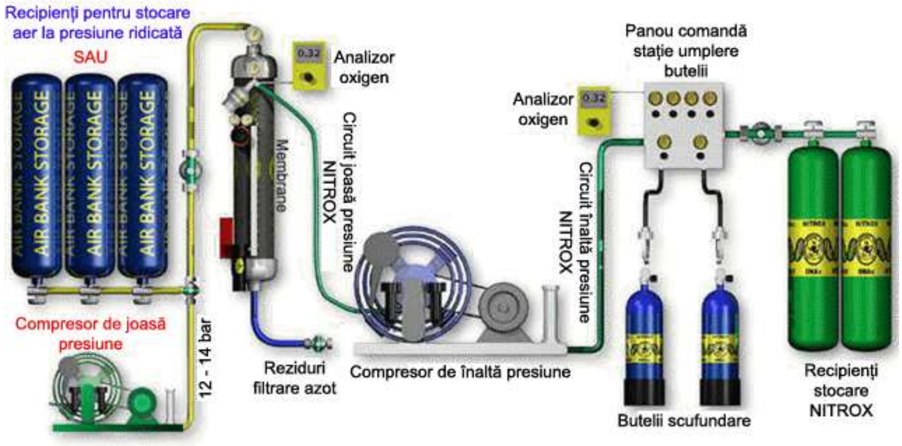

Fig. 3. Scheme of the installation for preparing NITROX mixtures through the membrane nitrogen separation process

Advantages of the procedure:

- does not require oxygen stored in cylinders (independence from oxygen producers);
- NITROX mixture can be prepared safely (up to 40% oxygen content);
- No prior cleaning of the cylinders and filling system is required.

Disadvantages:

- high acquisition costs;
- the system is cumbersome to start up and operate; the oxygen mixture is difficult to adjust; the heated air coming into contact with the membrane causes a chemical reaction in the oxygen sensor that leads to the oxygen analyzer being decalibrated;
- additional costs (electricity/maintenance) associated with operating the low-pressure compressor that provides air to the membrane system;
- if instead of the low-pressure compressor the membrane system is powered from pressurized containers for air storage, then as a result of the increased electricity consumption, operating costs increase and the wear of the high-pressure compressor, which in this situation produces the compressed air, is in this case greater;

- if the filters to improve air quality are not changed on time, then it is possible that the membranes become clogged with particles, which leads to the need to change them and implicitly to additional costs;
- membranes are fragile and can be easily damaged if the system is not operated correctly; if an air stream is supplied at a higher pressure or if it does not have an appropriate temperature, the internal structure can be damaged, which leads to the need to replace the membrane;
- for a system equipped with a low-pressure compressor, replacing the membrane costs about half the cost of the system;
- the system must be permanently monitored during operation;
- producing NITROX mixture using this system leads to the highest costs per diving cylinder.

1.3. The process of preparing the NITROX mixture with homogenization of the component gases

The continuous homogenization process of the component gases involves the use of containers for storing O_2 and a special, patented device (NITROX Stick), which ensures the homogenization of air and pure oxygen before being admitted to the high-pressure compressor (figure 4).

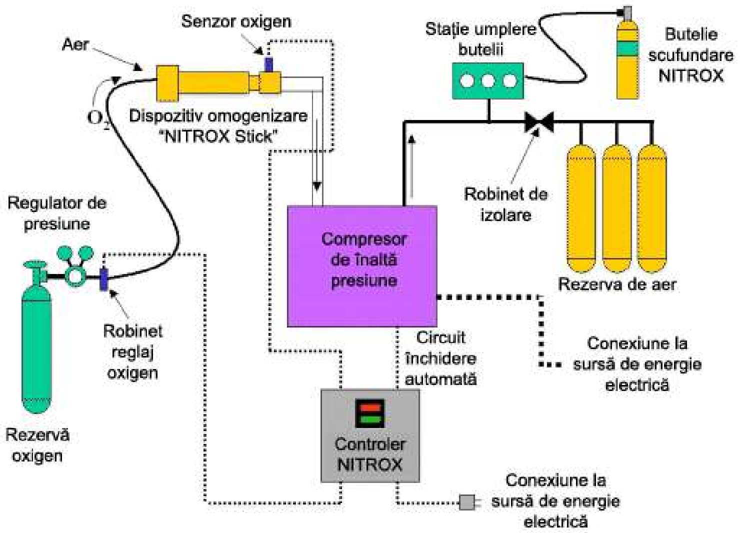

Fig. 4. Scheme of the NITROX mixture preparation plant using the continuous gas homogenization process

The construction diagram and image of such a homogenization device is presented in figure 5.

Starting the system involves first isolating the air storage containers, removing air from the system in the normal direction of flow (through the compressor discharge section), and then, while the compressor is running, connecting the oxygen cylinder and supplying an oxygen supply to achieve the desired concentration in the mixture. The purging process should be continued until the oxygen analyzer monitoring the compressor discharge indicates the desired oxygen concentration. From this point on, the air compressor, associated filters and air transport pipes are considered to be clean. The high-pressure compressor discharge can now supply either the diving cylinders or the NITROX mixture storage containers (figure 4). The entire operation, from putting the system into operation to starting to fill the cylinders or storage containers, takes about 5-10 minutes.

The advantages of using such a system are represented by:

- the moderate purchase cost of the equipment and the possibility of safely prepare a mixture of up to 40% oxygen;
- there are no loading restrictions regarding the presence of oxygen in the cylinders;
- the presence of the NITROX controller (figure 4) offers the operator the possibility to carry out other activities while the cylinder filling process is in progress;
- by applying this procedure, labor costs decrease;
- high precision in preparing the NITROX mixture;

increased operational safety;

- the lowest costs, compared to other systems, for filling a cylinder with NITROX mixture.

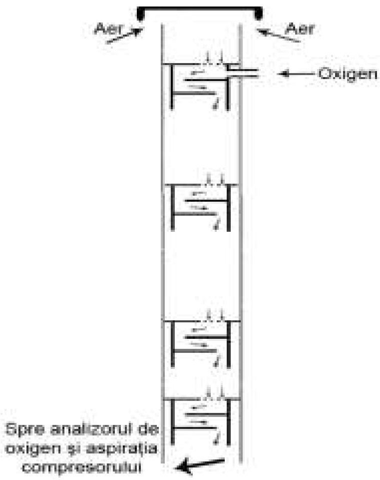

Fig. 5. Construction diagram and image of a "NITROX Stick" device

The disadvantages are the need for constant supervision of the system if it is not equipped with a NITROX controller and the need for a permanent oxygen reserve. It should be noted that the operation of such a system is justified especially when it is equipped with a NITROX controller.

Although the device for producing the respiratory mixture was previously presented and included in a scheme for producing the NITROX mixture, there are more complex constructive variants that also ensure the preparation of TRIMIX mixtures (figure 6).

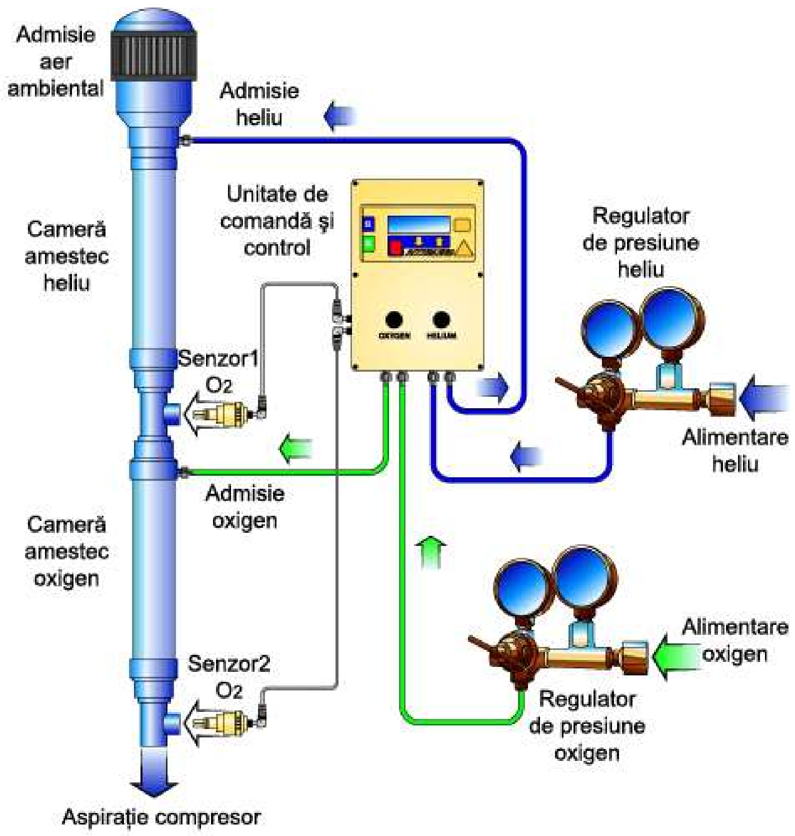

Fig. 6. Device for making the mixture for producing NITROX/TRIMIX

The device is connected to the oxygen and helium source by means of two high-performance regulators that ensure the regulation, with very high precision, of the gas quantity. Each regulator communicates with a control unit on whose screen the percentage of the two gases can be read. The control unit also ensures the interruption of the oxygen or helium supply if:

- the automatic calibration command is active while the compressor is running;
- a voltage drop occurs;
- the oxygen sensor registers a value of 39.9% oxygen;
- the sensor cables are disconnected;
- the power supply switch is off;

- compressor operation is interrupted.

The control unit, through its software, offers the operator the possibility to establish various NITROX and TRIMIX mixtures and, at the same time, can specify the equivalent depth at which narcosis can occur and also, through it, existing NITROX and TRIMIX mixtures can be modified without emptying the containers.

2. Methods and processes for preparing respiratory mixtures according to the US Navy

The choice of breathing mixture preparation method and equipment used depends largely on the environmental conditions. Thus, some of the methods described below are preferred for use on board vessels, while others are preferred for preparing mixtures in cylinder filling centers or hyperbaric laboratories on land.

2.1. Method of preparing respiratory mixtures considering the partial pressures of the component gases

This method involves creating the gas mixture by injecting the component elements into the storage containers in various proportions, monitoring the partial pressure of each of the gases in the mixture thus formed.

The fundamental principle of the method is Dalton's law of partial pressures. To calculate the partial pressure of gases in the mixture, one of two working procedures can be applied, namely:

-calculation procedure under the ideal gas hypothesis;
-the calculation procedure considering real gas.

a. Calculation procedure under the ideal gas hypothesis

This procedure assumes that the pressure is directly proportional to the temperature and density of the gas. Since the differences in compressibility of the gases are not taken into account, the preparation of respiratory mixtures using this calculation procedure is done in stages. For example, oxygen being more compressible than helium, initially a smaller amount of oxygen will be introduced than was estimated, the mixture is analyzed and completed accordingly. For the accurate calculation of the partial pressures of the gases in the mixture, correction methods (tables) are used.

The equipment required for preparing the breathing mixture by this process is: cylinders or containers for storing the inert gas and oxygen and for storing the prepared mixture (Figure 7). There are also compact transfer devices, equipped with all the necessary monitoring devices and control devices, to which the three categories of cylinders are directly coupled (Figure 8).

The preparation of respiratory mixtures using the ideal gas method involves the following steps:

-is measured the pressure at which the inert gas/gases are stored in the cylinders P_i;

-is estimated by calculation the pressure in the mixture storage container(s) at the end of the preparation process.

The US Navy Diving Manual recommends the following calculation relationship to estimate this value:

$$p_F = \frac{p_I + p_{at}}{r_i} - p_{at} \tag{1}$$

where: p_F is the final pressure in the cylinder for storing the mixture [Pa] (expressed in manometric scale); cannot exceed the value of the working pressure corresponding to the cylinder for storing the inert gas; p_I - the pressure in the inert gas storage cylinders [Pa] (expressed in manometric scale); r_i - the volume share of the inert gas in the prepared mixture.

Then:

- is measured the pressure în oxygen storage cylinder/cylinders p_0;
- check whether the preparation of the mixture can be assured with the pressure value measured at the previous point (p_0);

According to the same source cited above, in order to complete the preparation of the respiratory mixture, it is necessary that the following inequality be respected throughout the preparation process:

$$p_0 \geq \left(2p_F - p_I\right) + 3{,}45 \cdot 10^5 \tag{2}$$

where: p_0 is the pressure in the oxygen storage cylinder/cylinders in [Pa] (expressed in manometric scale); $3{,}45 \cdot 10^5$ - the minimum required overpressure [Pa] expressed in manometric scale (50 *psi* according to the cited material); p_I - the pressure in the inert gas storage cylinders, expressed in manometric scale [Pa].

The work steps are as follows:

a. Connect the oxygen and inert gas cylinders/cylinder banks in a configuration similar to that in Figure 7 or Figure 8.
b. Open the valves corresponding to the containers for storing the breathing mixture.
c. Open the valve associated with the oxygen cylinder(s) and fill the storage cylinder(s) of the mixture until the final p_F pressure value is reached .
d. Close the valves associated with the oxygen and breathing mixture storage cylinders.
e. Leave the cylinders for at least six hours to ensure homogenization of the mixture, or if homogenization equipment is available, the process will take about an hour.
f. Check the amount of oxygen in the mixture, which is usually lower than the estimated value.
g. Add oxygen until a mixture with the desired characteristics is obtained.

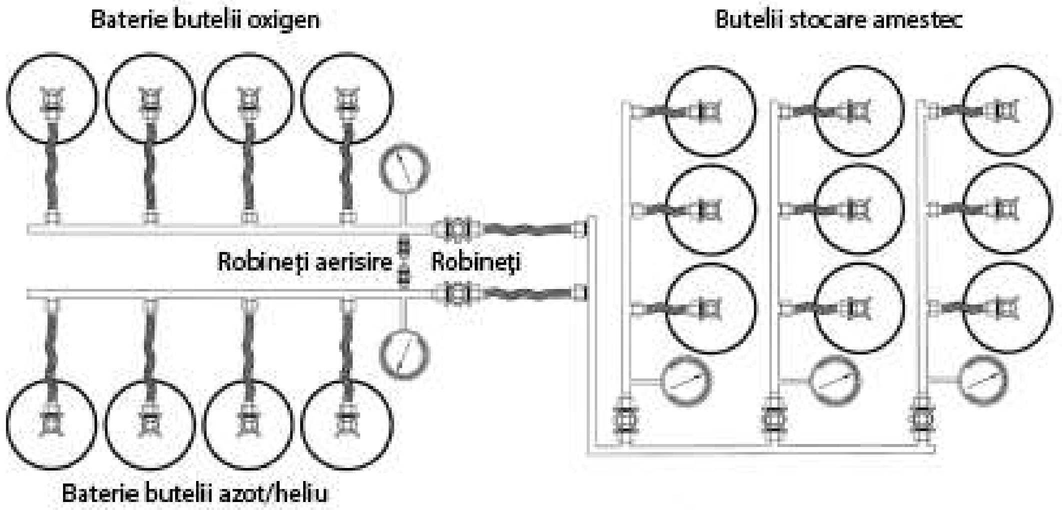

Fig. 7. Scheme of the installation for the staged preparation of respiratory gas mixtures

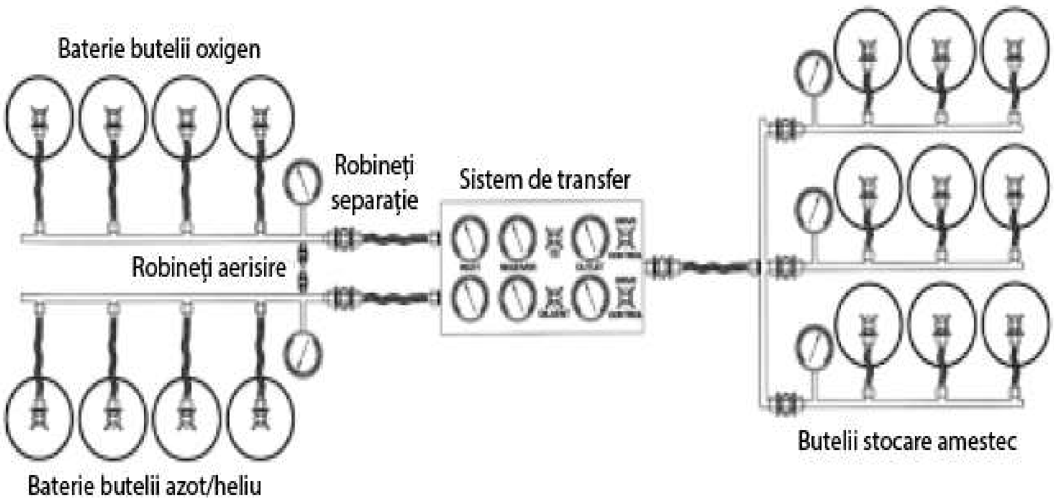

Fig. 8. Scheme of the installation with transfer device for the stepwise preparation of respiratory gas mixtures

It should be noted that, since in reality the mixed gases are compressible, the feeding process will generate an increase in temperature of the mixture cylinders, a phenomenon that vitiates the pressure value read on the pressure gauge corresponding to these containers. Therefore, in reality, in the manufacturing process of the respiratory mixture there will be temperature differences between the component gases and the temperature of the manufactured mixture. However, in the calculations, pressure values of p_F respectively p_I are used for gases having the same temperature. This explains why it is necessary to supplement the amount of oxygen, the real value being lower than the expected one.

b. Calculation procedure under the real gas hypothesis

The calculation procedure considering the real gas also takes into account the compressibility as a specific property of each gas, between the components of a mixture there being differences regarding this property. Thus, considering two different gases, at the same pressure value, different quantities of these gases will be able to be stored in the unit volume.

Regardless of the procedure chosen for calculating the partial pressures of the gases that make up the mixture, it will not be delivered to the user without first analyzing the oxygen content.

2.2. Method for preparing respiratory mixtures based on the volumes of component gases

The principle of the method consists in delivering the component gases, the volumes of which are initially known, to an isobaric container, with an internal pressure value close to atmospheric pressure, which acts as a mixing chamber. This container is made in the form of a deformable bag large enough to store the influent gas volume under the specified pressure conditions. Subsequently, the resulting mixture is compressed and stored in high-pressure containers.

For the successful application of the method, in addition to knowing the exact volume of each gas, another important factor in the preparation process is temperature, as the gases to be mixed must have the same temperature. Otherwise, the measuring devices must provide thermal compensation.

Creating the breathing mixture using this method requires high-precision equipment to accurately measure the volume of each component gas. The calculation of these volumes depends on the percentage that must be found in the final mixture.

If the condition is met that the temperature of the component gases have equal values, this method can prepare, with very high accuracy, respiratory mixtures. At the same time, in the preparation process, it must be taken into account that initially the mixing chamber should be completely empty or filled with a known mixture that does not pose risks to the user of the prepared mixture.

2.3. Method of preparing respiratory mixtures by weighing their components

This method is mainly used for preparing small volumes of breathing mixture, such as when filling scuba diving cylinders.

The dosage of gases to form the final mixture is done according to the weight they add to the initial weight of the cylinder. Thus, the first element that must be known is the weight of the empty container and, if applicable, the weights of all gases in the cylinder before starting the preparation process.

Unlike other methods of preparing breathing mixtures, in this case the variation in gas temperature does not affect the accuracy of the mixture. The essential factor for the accuracy of the preparation is the accuracy with which the weight of each component gas is measured. Analyzing the composition of the resulting mixture is a safety measure before it is used.

The choice of the most suitable method for preparing a respiratory mixture from its component elements depends on a number of technical and economic factors.

Thus, the method of preparation based on the partial pressures of the gases in the mixture and the continuous flow preparation method are methods used in particular for the preparation of respiratory mixtures on board ships. In contrast, the methods of preparation based on the volumes and weights of the component gases involve the use of precision equipment (high-precision balances) sensitive to external actions, such as the oscillatory movement of ships. For these reasons, they are preferred as a preparation method in mixture preparation centers or in hyperbaric laboratories located on land.

3. Method for preparing binary and ternary respiratory mixtures in continuous flow

Continuous flow preparation of breathing mixtures involves controlling the flow rate of each gas as it is delivered to form the mixture.

To apply this method, a special, pre-calibrated installation is needed, which distributes, individually and in the required quantity, the component gases to a mixing chamber. The component gases are brought from the pressure and temperature at which they are stored in the cylinders to the same values before being dosed by means of high-precision control elements. These elements of the installation are pre-calibrated. Based on the calibration curves, made available by the system manufacturer, the adjustment of these elements is correlated with the percentage of gas in the mixture that is desired to be achieved. During the formation process, the mixture is constantly analyzed in order to finally establish the entire history of the percentage of oxygen.

Many of the current installations in this category have automatic control and correction systems that modify the percentage of oxygen in the mixture by operating the control elements when the recorded values and those initially set do not match.

The breathing mixture thus formed can be delivered directly to the diver, to a pressure chamber, or can be stored in cylinders for later use.

Continuous flow preparation systems, due to their operating principle, are installations that prepare mixtures with great accuracy.

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