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Experimental verification of preparation accuracy of breathing gas mixtures by means of Nitrox Unit/Panel

SUMMARY

The paper presents results of an experimental verification of preparation accuracy of the typical NATO nitrogen-oxygen breathing gas mixtures by means of Dräger Nitrox Unit/Panel.

The sequence of gas mixture preparation was completely randomised and the results were verified by the Dixon's Q-test against gross error presence and randomness of the results by using the median test. The statistic test was performed to determine whether the dispersion of the experimental results were contained within the limits guaranteed by the manufacturer of the panel.

The results obtained from 30 experiments confirmed that it was possible to prepare nitrogen-oxygen mixtures of composition range 32.5÷60%O_2 by means of the tested panel with the relative error less than 2% at 95% confidence level.

INTRODUCTION

The Dräger Nitrox Unit/Panel has been tested in The Diving Gear and Underwater Work Technology Department, Polish Naval University of Gdynia. The manufacturer aimed at determination of the nitrox (standard NATO oxygen-nitrogen gas mixture [1]) preparation conformity with the declared accuracy of 2%.The panel in question and its basic technical data are shown in Tab.1 and Fig.1.

Dalton's Law is a principle of Dräger Nitrox Unit/Panel work (partial pressure method). Before preparation of nitrox of the assumed composition the operator should calculate the pressure that is to be reached by filling the gas cylinder.

Tab. 1. Basic technical data of the NITROX UNIT/PANEL

maximum working pressure	200 at
accuracy of gas mixture preparation	2% (relative)
maximal working temperature	40°C
main dimensions	600 x 450 x 300 mm
mass	24 kg

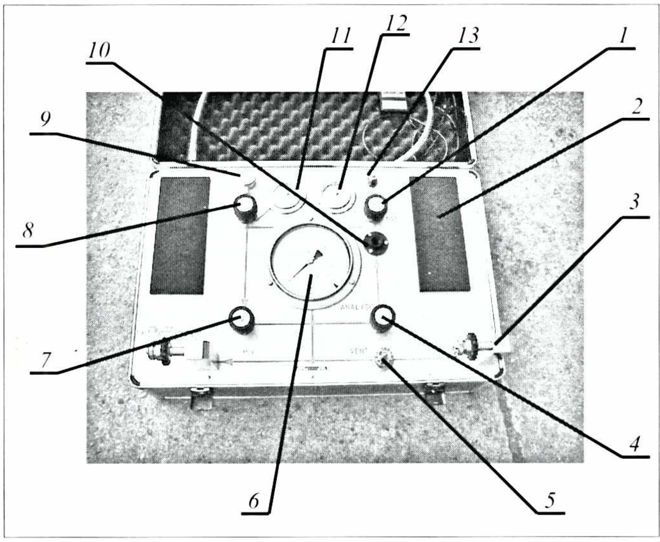

Fig. 1. Construction of Nitrox Unit/Panel

1. air cut-off valve
2. place for gas cylinder
3. gas cylinder connection
4. valve for the gas mixture analysis
5. vet valve
6. control pressure gauge
7. air cut-off valve
8. oxygen cut-off valve
9. oxygen connector
10. gas analyser connection
11. control pressure gauge (oxygen)
12. control pressure gauge (air)
13. air connector

INVESTIGATION METHOD

Test stand

Nitrox were prepared in a gas cylinder of 8 dm^3 in volume. The medical oxygen containing 99.9%$_{vol}O_2$ and compressed air containing 20.9%$_{vol}O_2$ - both complying with relevant Polish standards [7], [3] - were used for preparation of the nitrox mixture. Composition of the prepared gas mixture was investigated by means of gas chromatograph. Its operating conditions are presented in Tab.2.

Tab.2. *Gas chromatograph operating conditions*

Type of chromatograph: VA1400 gas chromatograph	
Gas chromatograph working parameters	
analysis time :	4 min
sampling :	metering valve with capillary (about 1 cm^3)
carrier gas :	helium 5N
carrier gas flow :	30 cm^3/min
chromatographic column dimensions :	l=120 mm ϕ=1 mm
chromatographic column package :	molecular sieves type 5A
sample injector temperature :	approximately 85°C
chromatographic column temperature :	approximately 60°C
detector temperature :	approximately 70°C
type of detector :	TCD
bridge current :	approximately150 mA
calibration method :	comparison with the standard sample
standard sample :	Poligaz S.A. 14.98$\%_{vol}O_2$ $\delta = \pm 1\%$ (relative)

Evaluation program

Such program of experiment was assumed as to determine completely randomized production sequence of three standard nitrox (oxygen-nitrogen gas mixtures). Every mixture should be prepared ten times.

Groups of tested results :

- in search of gross errors on the value range limits
- for checking randomness of the obtained group of results
- for checking if the obtained dissipation of measurement results is contained within the limits guaranteed by the manufacturer.

Investigation of normal distribution of the obtained results was not performed.

Randomization

Sequence of mixture preparation was determined by means of the standard tables of random numbers [5]. The method consists in searching in the random numbers tables the digits ranged from 1 to 3 respectively attributed to the mixtures :

$$1 - 32{,}5\%O_2 \qquad 2 - 40\%O_2 \qquad 3 - 60\%O_2$$

The first digit which has been found from this range informed about kind of gas mixture to be prepared. If such digit has not been found the next digit from the random number was taken into account. In the case when none of three digits was involved in random number it was moved to the next random number. After limits of 10 mixtures of the same kind have been depleted, only the other kinds of mixtures were chosen. The results obtained by means of gas chromatography are presented in Tab.3.

Tab.3. *The composition analyses of the chosen nitrox*

Kind of mixture		
1 32.5%O_2	2 40.0% O_2	3 60.0% O_2
Percentage contents of oxygen ± 0.2$\%_{vol}$		
33.9	38.9	59.1
33.6	38.8	59.0
33.4	38.6	57.2
33.0	38.2	58.0
30.4	38.0	57.6
31.0	38.0	58.4
30.6	38.1	59.0
30.8	38.6	58.2
31.0	38.6	58.0
31.0	38.7	58.1

Searching of gross errors on the range value limits

The obtained results (Tab.3) were statistically tested by the Q--Dixon's test [4] at the end of the range (Tab.4). It was established that at 95% confidence level there is no basis for concluding that data at the range limits were gross-error burdened.

Tab.4. *The Q-Dixon's test result*

	Kind of mixture								
	1			2			3		
	X	Q	Decision	X	Q	Decision	X	Q	Decision
	30.4	0.06	H_0	38.0	0.00	H_0	57.2	0.21	H_0
	30.6			38.0			57.6		
	30.8			38.1			58.0		
	31.0			38.2			58.0		
	31.0			38.6			58.1		
	31.0			38.6			58.2		
	33.0			38.6			58.4		
	33.4			38.7			59.0		
	33.6	0.09	H_0	38.8	0.11	H_0	59.0	0.05	H_0
	33.9			38.9			59.1		
n	10			10			10		
Q_{cr} (α = 0.05)	0.41			0.41			0.41		

x - measurement result *Q - Dixon's test result*
n - sample size *Q_{cr} - Dixon's critical value*
H_0 - measurement not burdened with gross error

Randomness trial test

Randomness trial test was performed with the use of the median test [2]. Statistical hypothesis was defined as follows :

⇨ null hypothesis H_0 : random selection of the measurement results for the trial

⇨ alternative hypothesis H_1: not random selection of the measurement results for the trial.

The median test is one of the series' tests. Each of identical sequence elements in the set ordered according to the assumed criterion is defined as series. A value of statistics from the trial was determined as follows :

- The measurement results from Tab.3 were arranged in ascending order and the median Me was determined.
- The values in the result sequences different from median were denoted as A or B as follows :

  if x < Me denote it A
  if x > Me denote it B
  if x = Me neglect it.

- By observing setting of A and B symbols, the formed number of series, k, was counted. The number of series is the statistic value for comparison.

The critical range of the test is two-sided because random character of the trial is contradicted both by too low and too high number of series. Therefore critical values of the test fulfil the relationship :

$$P(k \le k_1) = \frac{\alpha}{2} \qquad \text{where:} \qquad k_1\left(\frac{\alpha}{2}; n_A; n_B\right)$$

$$P(k \ge k_2) = \frac{\alpha}{2} \qquad \text{where:} \qquad k_2\left(1-\frac{\alpha}{2}; n_A; n_B\right)$$

where :

n_A - number of A elements
n_B - number of B elements
α - probability of I-type error
k_1,k_2 - critical values from the distribution tables [2]
k - number of series
P - probability value.

By comparing the numbers of series, k, observed in the trial with the test critical values, it is possible to draw conclusion concerning rejection of H_0 and acceptation of H_1 in the case when $k \geq k_2$ or $k \leq k_1$. The test results are presented in Tab.5. It follows from Tab.5 that the chosen trials are of the random character (not burdened with systematic errors).

***Tab.5.** The test of randomness for the results of the measurement series presented in Tab.3*

	Kind of mixture		
	1	*2*	*3*
	33.9	38.9	59.1
	33.6	38.8	59.0
	33.4	38.6	57.2
	33.0	38.2	58.0
	30.4	38.0	57.6
	31.0	38.0	58.4
	30.6	38.1	59.0
	30.8	38.6	58.2
	31.0	38.6	58.0
	31.0	38.7	58.1
Me	31.00	38.60	58.15
n	10	10	10

	Kind of mixture		
	1	*2*	*3*
	A	A	A
	A	A	A
	A		B
	A	B	B
	B	B	B
		B	A
	B	B	A
	B		A
			B
		A	B
n_A (x<Me)	4	3	5
n_B (x>Me)	3	4	5
m	7	7	10
k	3	3	4
k_1 (α/2:n_A:n_B)	1	1	2
k_2 (1-α/2:n_A:n_B)	7	7	9
Conclusion	H_0	H_0	H_0
α	0.05		

Me - median, n - sample size
α - probability of I-type error, k - the number of series in sample
m - the number of measurements different from Me

Dissipation of the results

Dispersion is one of the more important properties of distribution of the investigated feature in population. Comparison between the obtained dispersion of the measurement results and the limits guaranteed by the manufacturer (Tab.1) was performed with the use of the test of variance.

First it was necessary to calculate the expected variance for the case of preparation of each of the selected mixtures, 10-times. The manufacturer ensures preparation of all mixtures with the accuracy of 2% (relative) of the oxygen percentage in nitrox. It conforms the following values of absolute errors for the selected mixtures :

$$\Delta(60\%O_2) = 1{,}2\%_{vol}$$
$$\Delta(40\%O_2) = 0{,}8\%_{vol}$$
$$\Delta(32.5\%O_2) = 0{,}65\%_{vol}$$

Confidence interval at the assumed confidence level p is determined by means of the relationship given by Grosset (Student) [6] :

$$\langle x \rangle - s\frac{t(p, f = n-1)}{\sqrt{n}} \leq x_{tr} \leq \langle x \rangle + s\frac{t(p, f = n-1)}{\sqrt{n}}$$

where :

x_{tr} - true value of measured quantity
$\langle x \rangle$ - mean of measured quantity
$t(p,f)$ - Student's coefficient
p - confidence level
f - degree of freedom ($f = n-1$)
n - total number of measurements.

The above given equation can be transformed to the form :

$$x_{tr} = \langle x \rangle \pm \Delta\langle x \rangle$$

$$\Delta\langle x \rangle = \pm\left[s\frac{t(p, f = n-1)}{\sqrt{n}} \right]$$

where: $\Delta\langle x \rangle$ - confidence interval (absolute error of the mean at an assumed confidence level).

Hence the expected variance of oxygen concentration in the obtained gas mixtures is as follows :

$$\sigma^2 = s^2 = \frac{n}{t(p, f)}\Delta\langle x \rangle$$

$$\sigma^2(60\%O_2) = 2.345$$
$$\sigma^2(40\%O_2) = 1.564$$
$$\sigma^2(32.5\%O_2) = 1.270$$

In the test of significance for hypothesis of the variance normal variable distribution is assumed. The assumption cannot be verified in the case in question because of the small sample size . However the results of such measurements have mostly normal distribution if they are not burdened due to gross or systematic errors . In such case in the zero hypothesis it is assumed that variance in population is equal to an expected variance (hypothetical). Whereas the alternative hypothesis can be of a different form :

$$H_0 : \sigma^2 = \sigma_0^2$$
$$H_1 : \sigma^2 \neq \sigma_0^2 \qquad \sigma^2 > \sigma_0^2 \qquad \sigma^2 < \sigma_0^2$$

The statistics described by the following equation is the test for sample of size n < 30 [2] :

$$\chi^2 = \frac{n \cdot s^2}{\sigma_0^2}$$

where:

$$s^2 = \frac{1}{n}\sum_{i}^{n}\left(x_i - \langle x \rangle\right)^2$$

The statistics is of chi-square distribution of f = n – 1 degrees of freedom. The critical range in this statistics distribution is determined as a function of the assumed alternative hypothesis.

1. For $H_1 : \sigma^2 > \sigma_0^2$ – right-hand critical range determines the probability of $P\left(\chi^2 \geq \chi_\alpha^2\right) = \alpha$. The critical value is read as that for the significance level α and (n – 1) degrees of freedom. If $\chi^2 \geq \chi_\alpha^2$ the zero hypothesis is rejected.

2. For $H_1 : \sigma^2 \neq \sigma_0^2$ – double-sided critical range is defined as $P\left(\chi^2 \leq \chi_{\alpha 1}^2\right) = P\left(\chi^2 \geq \chi_{\alpha 2}^2\right) = \alpha/2$. The critical value $\chi_{\alpha 1}^2$ is read as that for the significance level (1-α/2) and (n – 1) degrees of freedom, whereas $\chi_{\alpha 2}^2$ for the significance level α/2 and (n – 1) degrees of freedom. In the case when $\chi^2 \leq \chi_{\alpha 1}^2$ or $\chi^2 \geq \chi_{\alpha 2}^2$ the zero hypothesis is rejected.

3. For $H_1 : \sigma^2 < \sigma_0^2$ – left-hand critical range determines the probability of $P\left(\chi^2 \leq \chi_\alpha^2\right) = \alpha$. The critical value is read as that for the significance level α and (n – 1) degrees of freedom. If $\chi^2 \leq \chi_\alpha^2$, the zero hypothesis is rejected.

The variance test results for the data presented in Tab.3 are given in Tab.6.

Tab.6. *The variance test results for the data presented in Tab.3*

	Kind of mixture		
	1	2	3
σ^2	1.99	0.12	0.39
n	10	10	10
f	9	9	9
χ^2	7.64	0.67	2.79

α =		0.05		
σ_o^2 =		2.345	1.564	1.270
H_o: $\sigma^2 = \sigma_o^2$		*1*	2	3
H_1: $\sigma^2 \neq \sigma_o^2$	$\chi_{\alpha 1}^2$	19.02	19.02	19.02
	$\chi_{\alpha 2}^2$	2.70	2.70	2.70
	decision	**H_0**	**H_0**	**H_0**
H_1: $\sigma^2 \geq \sigma_o^2$	χ_α^2	16.92	16.92	16.92
	decision	**H_o**	**H_o**	**H_o**
H_1: $\sigma^2 \leq \sigma_o^2$	χ_α^2	3.33	3.33	3.33
	decision	**H_0**	**H_1**	**H_1**

σ^2 - calculated variance, σ_o^2 - comparative variance
n - total number of measurements, f - the number of freedom degrees
χ^2 - test value (chi-square-test)

As it follows from Tab.6, at 95% significance level there is no reason to reject the zero hypothesis for composition measurements of the nitrox containing 32.5%O_2. However for composition measurements performed for mixtures of the oxygen percentage 40%O_2 and 60%O_2 at the same significance level the zero hypothesis should be rejected and the alternative hypothesis accepted. The alternative hypothesis indicates that mixtures were prepared with a higher accuracy than it was assumed. Series of 30 measurements performed for the nitrox within the composition range of 32.5÷60%O_2 showed that the panel used for nitrox mixture preparation provides preparation accuracy of 2% (relative) within this concentration range.

CONCLUSIONS

On the basis of the analysis of 30 measurements performed for nitrogen-oxygen mixtures within the composition range of 32.5÷60% O_2 it can be concluded that :

- ❖ The Dräger NITROX UNIT/PANEL makes it posible to prepare nitrox mixtures with the relative error smaller than 2% at 95% significance level.
- ❖ The panel can be used for preparation of the standard nitrox mixtures used by NATO [1].

Appraised by Jerzy Świtek, D.Sc.

NOMENCLATURE

H_o	-	zero hypothesis
H_1	-	alternative hypothesis
k	-	number of series
Me	-	median
n	-	sample size (total number of measurement results)
n_A , n_B	-	number of A and B elements, respectively
p	-	confidence level
P	-	probability
s	-	standard deviation
x	-	measurement result
< x >	-	mean value
α	-	probability of I-type error
σ^2	-	variance
σ_o^2	-	comparative variance
χ^2	-	chi-square-test value

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Note : *The experiments were performed within the framework of the project KBN 7 T07C 034 19 on „Technology of nitrox combat dives".*