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STUDIES CONCERNING THE TRACEABILITY OF BREATH ALCOHOL CONCENTRATIONS

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Metoda folosită de către specialiştii din cadrul Institutului National de Metrologie în scopul asigurării trasabilității măsurărilor de alcool etilic din aerul alveolar expirat în România este prezentată în acest articol . Etaloanele de alcool etilic preparate şi rezultatele obținute din măsurările efectuate acoperă întregul domeniu de concentrație de alcool din aerul alveolar expirat. Bugetele de incertitudine au fost calculate folosind abordarea ISO [1,2]. Măsurările de alcool din aerul expirat sunt prezentate în acest articol împreună cu incertitudinea extinsă, U, utilizând un factor de acoperire k=2, pentru un nivel de încredere de 95 %. Parametrii de calitate cheie sunt incertitudinile asociate valorillor certificate şi încrederea în incertitudinea estimată.

The method used by specialists from National Institute of Metrology in order to assure traceability of breath alcohol measurement in Romania is presented here. The prepared ethanol standards and results obtained from measurements cover the entire range of concentrations of breath alcohol analyzers. Uncertainty budgets have been calculated using the ISO approach [1,2]. Breath alcohol measurements are presented in this paper together with the expanded uncertainty, U, using a coverage factor k=2 which gives a level of confidence of approximately 95%.The key quality parameters are the uncertainties associated with the certified values and the reliability of the uncertainty estimate.

Keywords: traceability, reference materials, breath alcohol concentration, metrology.

1. Introduction

It's well known that the alcohol concentration from human body is measured using air from the lungs or venous blood. Breath testing has become over the years, a widely used method for qualitative and quantitative determination of the level of person suspected of driving while under the influence of alcohol. After recognition of the need for quantitative assessment of intoxications, blood alcohol concentration was considered the most important variable. However, concern about the invasiveness requirements of drawing a

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blood sample led to the development of the breath test as non-invasive means of assessing level of intoxication.

Scientists all over the world have started to look for new non-invasive principles to determine the alcohol concentration from human body. Depending on accuracy, specifity to alcohol, cross sensivity, long term stability etc. there are few measuring principles used for breath alcohol determination: chemical, bio-chemical (system based on oral fluids), physical (semiconductor cell - surface reaction), electrochemical (fuel cell), infrared spectroscopy, gas chromatography.

The breath-alcohol testing methods have changed over the years from chemical oxidation and calorimetric procedures to physico-chemical techniques such as gas-chromatography, electrochemical oxidation and multiple wave length infrared spectrophotometers.

The breath alcohol measurements are based on Henry's law: "When an aqueous mixture of a volatile substance reaches equilibrium with air, there will be a fixed ratio between the concentration of the substance in the air and its concentration in the solution".

It is well known that the liquid water and alcohol can be mixed in any ratio, resulting homogeneous mixtures. Both liquids have a tendency to evaporate from the liquid in the form of a gas. Alcohol has a greater tendency to do this. If an alcohol-water mixture of this type is kept in a partly filled and sealed system, the concentration of gaseous alcohol in the air above the liquid will increase until a certain concentration is reached. At this stage, there is a defined ratio between the alcohol concentration in the liquid and that in the air. Scientists all over the world accepted the value of this ratio in the range between 2000:1 to 2300:1.

The concentration of alcohol in vapor phase above liquid-water mixture depends on just two factors: the temperature of the mixture and the alcohol concentration in the liquid.

$$\rho_{\text{air}} = A \;\; x \; \rho_{\text{Eth}} \;\; x \; e^{B\,x\,t} \qquad (1)$$

where: t is solution temperature, ^{0}C;

The following experimental coefficients A and B were established on several studies on partition coefficient air/ethanol solution:

- A = 0.041 45 [mg/L / g/L];
- B = 0.065 83 [1 / ^{0}C];

In the case where t is 34.0 ^{0}C, the equation becomes:

$$\rho_{\text{air}} = 0{,}388\,66 \;\; x \;\; 10^{-3} \;\; \rho_{\text{Eth}} \qquad (2)$$

Henry's law applies to the exchange processes in the human body, especially in the lungs. The balance between the alcohol in the blood and in the breath is created in the lungs in the same way as described for alcohol in aqueous solution and air in semi closed system.

In accordance with this law, diffusion processes, which are also what causes oxygen to be taken up in the lungs, achieve a balance between the alcohol concentration in the blood in the lungs and the alcohol concentration in the air in the lungs. Thus, the breath alcohol measurement involves directly determining this concentration.

Evidential breath analyzers are instruments that automatically measure the mass concentration of alcohol in exhaled breath that originates from the alveoli of the lungs.

Although the relationship between the breath and blood alcohol concentration is still uncertain, the evidential breath-alcohol instruments are used in different countries for determination of alcohol concentration level for forensic purposes.

National authorities may require specific conversion device that converts the measurement result obtained in terms of ethanol content and can approve evidential breath analyzers for law enforcement purposes with threshold limit of breath-alcohol concentration alongside the existing statutory blood-alcohol concentration limits.

Quality assurance has become an indispensable accompaniment to forensic breath-alcohol analysis. Gas Concentration Laboratory from National Institute of Metrology is prepared to provide the following control procedures: pattern approval, initial verification of new evidential breath analyzers, periodic verification, performance test and calibrations, and focuses on development, implementation and use of such Quality Assurance programs for breath-alcohol testing.

Evidential breath analyzer is an instrument which measures accurately the concentration of alcohol in "end-expiratory" air to provide a result which can be used as evidence in drinking and driving offences. End-expiratory air is a breath sample containing air from the end of a forced expiration from lungs. The evidential breath analyzer in conjunction with the type approval and the independent official verification, ensures that measurement results achieve the extremely high level of reliability that european and national standards demand.

The '*Guide to the Expression of Uncertainty in Measurement*' (GUM) provides general rules for evaluating and expressing uncertainty in measurement that are intended to be applicable to a wide range of measurements and for use within standardization, calibration, laboratory accreditation and measurement services.

Traceability of breath alcohol concentration is a new field of interest in Romania. About 1700 of breath alcohol analyzers were purchased by Ministry of Interior – Police Department few years ago following an European project of endowment of East European police departments. Since than, the traceability of measurement performed with such instruments was a priority in order to assure accuracy measurements and acceptance in court. Measurements made at different times or in different places are directly related to a common reference. Applying the concept of traceability to breath alcohol measurements is not easy, but it has to provide qualitative results and analytical techniques used in calibration laboratories.

Specialists from National Institute of Metrology start to prepare the basis necessary to transmit the specific measuring unit from high level standards (Reference Materials) to the working level measurements.

The measurements and tests were performed using the following equipment, in order to deliver test gases having ethanol concentrations analogous to those calculated theoretically and to those which evolve during a real exhalation.

- Evidential breath alcohol analyzers Alcotest 7110 MK III, manufactured by Dräger Safety AG & CO, KGaA, Germany, serial numbers: ARNC-0145, with Calibration Certificate no. 0347/2005 and ARND-0145, with Calibration Certificate no. 2040/2005, issued by EDN (Eichdirection Nord), Germany and traceability to PTB's standards (Physicalisch Technische Bundesanstalt) – Germany;
- Ethanol purity 99.8 %, manufactured by Merck, code K 22707783 608, batch 200-578-6;
- Wet bath simulator for testing and calibrating breath alcohol analyzers, type Mark II, serial no. DDSE P 0003 and DDSE P 0006, manufactured by Dräger Safety AG, Germany [8,9];
- Wet bath simulator for testing and calibrating breath alcohol analyzers, manufactured by ICIA – Cluj, Romania;
- Pippete, (10.0 ± 0.2) mL;
- Analytical balance, type XS 205 manufactured by Mettler Toledo;
- Distilled water;

The Evidential breath alcohol analyzers Alcotest 7110 MK III satisfies the requirements of DIN VDE 0405 and OIML R 126 and has been approved by Germany's national metrology institute, the PTB (Physikalisch Technische Bundesanstalt), and also by Romanian's National Metrology Institute, following a series of tests according to mentioned standards. This kind of measuring system can be used for breath alcohol concentration measurement either in Germany as in Romania [4-7].

In this paper where used the following terminology according to International Vocabulary of Basic and General Terms in Metrology [0] was used:

- Uncertainty of measurement is a parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand.
- Experimental standard deviation for a series of n measurements of the same measurand, is the quantity that characterizes the dispersion of the results and is given by the formula:

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})}{n-1}}$$

where x_i being the result of the "i"th measurement and $\bar{x}$ being the arithmetic mean of the "n" results considered.

In the same time, the breath alcohol measurements use specific measuring units. To determine the blood alcohol concentration (BAC) the following measurement units are used:

- Per mille, ‰ (thousandth; one gram alcohol in 1 L of blood);
- Per cent, % (hundredth);

The measurement units used to determine the alcohol concentration in breathing air (BrAC) are:

- Milligram per liter, mg / L (one milligram alcohol in one liter of breathing air);
- Microgram per liter, µg / 100 mL;

The following relations express the conversion between blood alcohol concentration (BAC) and breath alcohol concentration (BrAC):

$$‰ = \frac{1}{2100}\frac{\text{g}}{\text{L}};\ 1‰ = 0.1\,\% = 0.476\,\frac{\text{mg}}{\text{L}} = 476\,\frac{\mu\text{g}}{\text{L}} = 476\,\frac{\text{mg}}{\text{m}^3} \quad (3)$$

2. Preparation of Calibration Standards

Traceability is the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or internatioanl standards, through an unbroken chain of comparisons all having stated uncertainties [3].

It is known that traceability requires an 'unbroken chain of comparisons' between a measurement and the 'stated references'.

First step in this project was to prepare standard mixtures. Table 1 presents alcohol concentrations, expressed in ‰ (promile) and mg/L (milligram alcohol in a liter of air) obtained by mixing certain quantities of pure alcohol (ethanol) in distilled water.

Table 1

Breath alcohol concentration

No.	Volume of ethanol in standard mixture, $V_{C2H5\text{-}OH}$, mL	Quantity of ethanol in distilled water, m_{H2O}, g	Breath alcohol concentration ρ_{air}, ‰	Breath alcohol concentration ρ_{air}, mg/L
1	0.31	0.245	0.2	0.095 2
2	0.62	0.490	0.4	0.190 5
3	0.93	0.735	0.6	0.285 7
4	1.24	0.980	0.8	0.381 0
5	1.56	1.225	1.0	0.476 2
6	2.33	1.838	1.5	0.714 3
7	3.12	2.450	2.0	0.952 4
8	3.90	3.063	2.5	1.190 5
9	4.68	3.676	3.0	1.428 6

3. Quantifying the Uncertainty Components

In order to estimate the associated uncertainty for each prepared concentration all source of uncertainties were taken into consideration. The influence quantities that can affect the measurement result are generated by the following devices used: pipette, recipient, purity of ethanol, temperature established by the simulator's thermostat.

3.1 Uncertainty due to pippete

One important source of uncertainty is related to the pippete, which has the nominal range between (0...10) mL. In order to establish this contribution to the final budget of uncertainty 10 weightings of 4.60 g H_2O with a Mettler Toledo precision balance were performed; results are presented in Table 2, and the associated uncertainty was estimated according to ISO Guide [1,2] and the associated uncertainty was estimated according to ISO Guide [1,2].

Table 2

Means value and standard deviation for 10 weightings

Conventional true value of distilled water, m_0, g	**Average value of 10 weightings, m_m, g**	Standard experimental deviation, s, g
4.60	4.600 88	0.018 59

The combined standard uncertainty is:

$$u_{\text{C\_pippete}} = \sqrt{s^2 + u_{\text{s1}}^2 + u_{\text{s2}}^2} = \sqrt{0.000\,35^2 + 0.008\,16^2 + 0.001\,21^2} = 0.020\,336\ \text{mL}$$

where:

s - standard deviation for 10 measurements of weight of 4.60 mL H_2O distilled water;

$$u_{\text{s1}} = \frac{0.02\ \text{mL}}{\sqrt{6}} = 0.008\,16\ \text{mL}$$

is the standard uncertainty calculated assuming a triangular distribution, as stated by the pippete's manufacturer;

$$u_{\text{s2}} = 10\ \text{mL} \cdot \frac{2.1}{10^{-4}} \cdot \frac{1\ {}^{0}\text{C}}{\sqrt{3}} = 0.001\,21\ \text{mL}$$

is the standard uncertainty calculated assuming of a rectangular distribution for a temperature variation and the coefficient of the volume expansion.

The expanded uncertainty is obtained by multiplying the combined standard uncertainty with a coverage factor of 2, giving

$U_{\text{C\_pippete}}$ = 0.002 mL x 2 = 0.004 mL;

Thus, the volume of pipete is:

$V_{\text{\_pippete}}$ = (4.60 ± 0.04) mL

3.2 Uncertainty due to recipient

Standard uncertainty specified by manufacturer in recipient's Calibration Certificate, calculated assuming a rectangular distribution is:

$$u_{\text{V1}} = \frac{1}{\sqrt{3}} = 0{,}577\ 35\ \text{mL}$$

Standard uncertainty calculated assuming of a rectangular distribution for the coefficient of the volume expansion has the value:

$$u_{\text{V2}} = 1\ 000\ \text{mL} \cdot \frac{2.1}{10^{-4}} \cdot \frac{1\ {}^{0}\text{C}}{\sqrt{3}} = 0.121\ 24\ \text{mL}$$

The combined standard uncertainty is:

$$u_{\text{C\_Volum}} = \sqrt{u_{V1}^2 + u_{V2}^2} = \sqrt{0.577\ 35^2 + 0.121\ 24^2} = 0.589\,944\ \text{mL}$$

leading to the following value for the volume of recipient used for preparing the standard mixture:

$V_{\text{\_Volum}}$ = (1 000.00 ± 0.59) mL

3.3 Uncertainty due to purity of ethanol

The ethanol used for preparation of different standards was 99.8 % by volume. Standard uncertainty has the value:

$$u_{\text{etalon}} = \sqrt{\left(\frac{1-0.998}{\sqrt{3}}\right)^2} = 0.001\ 155$$

3.4 Uncertainty due to temperature established by the simulator's thermostat

The simulator's thermostat was set to la (34.0 ± 0.1) ^{0}C during the experiments. Standard uncertainty calculated assuming of a rectangular distribution for the variation of thermostat's temperature has the value:

$$u_{\text{termostat}} = \sqrt{\left(\frac{0.1}{\sqrt{3}}\right)^2} = 0.005\ 577\ {}^0\text{C}$$

4. Example of total uncertainty budget calculation for a concentration of 1.0 ‰ corresponding to a concentration of 0.476 mg/L (mg alcohol in a liter of air)

The result of measurement and uncertainty buget calculation are presented in Table 3.

Table 3

Spreadsheet calculation of uncertainty:

$\rho_{ethanol}$	1.222 95	$u_{ethanol,\ g}$	0.016 045
Purity	0.998	u_p	0.001 155
Volume	1	u_V	0.000 59
$\rho_{0(ethanol/L)}$	1.220 504	$u_{(ethanol/L)}$	0.016 013
	1.238 995	1.222 950	1.222 950
	0.998	0.999	0.998
	1	1	1.000 590
$\rho_{i(ethanol/L)}$	1.236 517	1.221 916	1.219 784
ρ_0-ρ_i	0.016 013	0.001 412	-0.000 720
$(\rho_0$-$\rho_i)^2$	0.000 256	0.000 002	0.000 001
$\sum(\rho_0$-$\rho_i)^2$			0.000 256

$$u_{\text{(ethanol/L)}} = \sqrt{(\rho_0 - \rho_{\text{i}})^2} = \sqrt{0.000\ 256\ \text{mL}} = 0.016\ 013\ \text{g/L}$$

Uncertainty of alcohol concentration in air due to another quantity input: temperature of solution, u_t=0.005 577 ^{0}C, calculated according to Dubowsky formula (1); spreadsheet calculation of uncertainty is presented in Table 4.

Table 4

Spreadsheet calculation of uncertainty, for a temperature value t = 34 ^{0}C

$\rho_{0\text{(ethanol/L)}}$	1.220 504	u_{solution}	0.016 013
temperature, ^{0}C	34	u_t	0.005 577
$\rho_{air\ 0\ \text{(ethanol/L air)}}$	0.474 363	$u_{\text{ethanol/L air}}$	0.006 226
‰	1.00	Index, %	1.31
		U (k=2)	0.012 452
		1.236 517	1.220 504
		34	34.01
$\rho_{\text{i(ethanol/L air)}}$		0.480 586	0.474 543
ρ_0-ρ_i		0.006 224	0.000 180
$(\rho_0$-$\rho_i)^2$		0.000 039	0.000 000
$\sum(\rho_0$-$\rho_i)^2$			0.000 039
Index, %		99.92	0.08

$$u_{\text{(ethanol/L air)}} = \sqrt{(\rho_0 - \rho_{\text{i}})^2} = \sqrt{0.000\ 039\ \text{mg/L}} = 0.006\ 226\ \text{mg/L}$$

The alcohol concentration expressed as milligram in a liter of air is then:

ρ_{air} = (0.474 363 ± 0.006 226) mg/L

taking in account the number of digits available on the breath alcohol analyzers:

ρ_{air} = (0.474 ± 0.006) mg/L, presented graphically in Fig. 1.

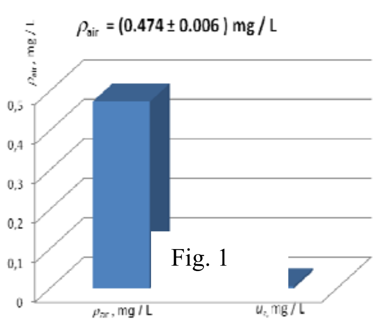

Fig. 1

Alcohol concentration prepared accordingly to Dubowsky formula and the associated uncertainties calculated according to the latest guide to the expression of uncertainty in measurement [1,2] are presented in Table 5 and Fig. 2.

Table 5

Associated uncertainty of breath alcohol concentration

Breath alcohol concentration, ρ_{air}, ‰	Breath alcohol concentration, $\rho_{air\ calc}$, mg/L	Associated uncertainty, u_c, mg/L	Index, %
3.0	1.438 390	0.006 319	0.43
2.5	1.193 557	0.006 289	0.52
2.0	0.948 725	0.006 265	0.66
1.5	0.719 195	0.006 248	0.87
1.0	0.474 363	0.006 226	1.31
0.8	0.382 550	0.006 230	1.63
0.6	0.275 436	0.006 227	2.26
0.4	0.183 624	0.006 225	3.39
0.2	0.091 812	0.006 224	6.78

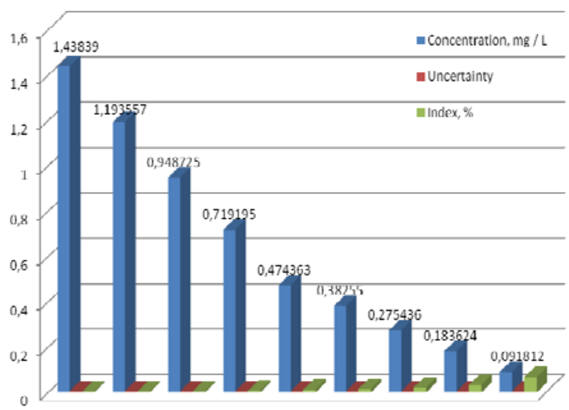

Fig. 2.

The difference between the desired and the prepared concentration are very small; this means that the from theoretical and practical point of view the laboratory is prepared to assure traceability existing measuring analyzers of breath alcohol concentration.

Using the equipment existent in Gas Concentration Laboratory from Romanian National Institute of Metrology several ethanol concentrations were prepared, covering a usual range of a breath alcohol analyzer. The results are presented in Table 6.

Table 6

Breath alcohol concentration related to conventional true value

Alcohol concentration, ‰	Conventional true value of alcohol concentration, $\rho_{air\ 0}$, mg/L	Prepared alcohol concentration, $\rho_{air\ i}$, mg/L
3.0	1.428 6	1.438 4
2.5	1.190 5	1.193 6
2.0	0.952 4	0.948 7
1.5	0.714 3	0.719 2
1.0	0.476 2	0.474 4
0.8	0.381 0	0.382 5
0.6	0.285 7	0.275 4
0.4	0.190 5	0.183 6
0.2	0.095 2	0.091 8

The Fig. 3 presents the final alcohol concentration prepared in laboratory (ρ_i, mg/L) against theoretical concentrations (ρ_0, mg/L) calculated according to the Dubowsky formula.

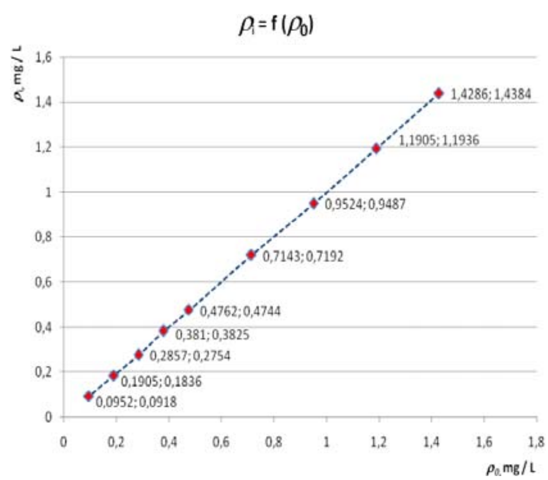

Fig. 3

The differences between the desired and the prepared concentrations are very small; this means that from theoretical and practical point of view the laboratory is prepared to assure traceability of existing measuring analyzers of breath alcohol concentration.

5. Preparation of Ethanol in Air Concentrations by Variation of Temperature

According to Dubowski's equation (1), the alcohol concentration in vapor phase above liquid-water mixture depends on two factors: the temperature of the mixture and the alcohol concentration in the liquid. So, ethanol in air standards can be prepared by varying mixture's temperature while alcohol concentration in liquid is maintained constant, at 0.977 g/L.

Using this method the following standards were prepared in laboratory and each of them has been measured 40 times, in order to calculate the metrological characteristics. For each 10^{th} series of measurement the calculated mean values, corresponding standard deviations and relative standard deviations are presented in Table 7.

Table 7

Relative standard deviation for a no. of measurement

Number of measurement, n						
	Temperature of the solution (mixture of alcohol in the liquid) t, °C	32	33	34	35	36
	Theoretical alcohol concentration according Dubowski's equation, $\rho_{air\ 0}$, mg/L	0.333	0.355	0.382	0.405	0.433
20	Average value of the solution, $\rho_{air\ m}$, mg/L	0.332 3	0.355 1	0.381 8	0.405 1	0.434 2
	Standard deviation, σ, mg/L	0.000 6	0.000 6	0.000 9	0.001 5	0.003 2
	Relative standard deviation σ_{rel} , %	0.17	0.18	0.22	0.38	0.73
30	ρ_m, mg/L	0.331 8	0.354 5	0.380 6	0.4034	0.431 0
	σ, mg/L	0.000 9	0.001 0	0.001 9	0.002 8	0.005 7
	σ_{rel}, %	0.26	0.28	0.51	0.69	1.31
40	ρ_m, mg/L	0.331 3	0.353 8	0.379 2	0.401 6	0.427 7
	σ, mg/L	0.001 3	0.001 7	0.002 9	0.004 1	0.007 6
	σ_{rel}, %	0.38	0.47	0.76	1.02	1.78

The average values of 20 measurements performed with alcohol concentrations obtained by variation of temperature (at 32 ^{0}C, 33 ^{0}C, 34 ^{0}C, 35

^{0}C, 36 ^{0}C**)** against theoretical alcohol concentrations calculated according to Dubowski's equation are presented graphicallyin Fig. 4:

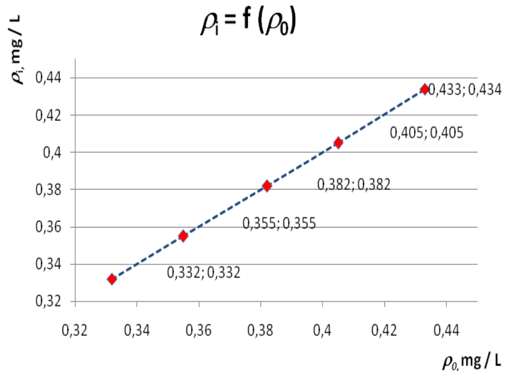

Fig. 4

6. Stability of Prepared Solutions During Repeated Measurements

In order to evaluate long term stability of solutions prepared in laboratory two different concentrations were used, 0.39 ‰ and 0.80 ‰ exhaled air alcohol concentration. All data obtained from reproductibility experiment under reproductibility conditions (different time, various instruments, same sample) were calculated according to standard ISO 8258:1991, *Shewhart control chart* [11]. The following parameters were calculated for each series of 30 measurements performed with alcohol concentrations:

$$R = \frac{\rho_{\text{air m}}}{\rho_{\text{air 0}}}; \qquad \rho_{\text{air corr}} = \frac{\rho_{\text{air m}}}{R}; \qquad E_{\text{n}} = \frac{\rho_{\text{air m}} - \rho_{\text{air 0}}}{\sqrt{s^2_{(\rho_{\text{air}})} + u^2_{\rho_{\text{air 0}}}}};$$

$$u_{\text{c}} = \sqrt{s^2(\rho_{\text{air}}) + s_R^2(\rho_{\text{air}})} \qquad (3)$$

where:

$\rho_{\text{air i}}$ measured concentration value, mg/L;
R prepared solution recovery, %;
$\rho_{\text{air 0}}$ conventional true value of reference material, mg/L;
$\rho_{\text{air corr}}$ corrected value, mg/L;
$\rho_{\text{air m}}$ mean value of measured alcohol concentrations, mg/L;
ε_{i} intrinsic error, mg/L;
ε_{t} maximum permissible error, mg/L;
E_{n} accuracy score;
$u_{\rho\text{air 0}}$ uncertainty of reference material, mg/L;

$s(\rho_{air})$ experimental standard deviation, mg/L;
$s(\rho_{air})rel$ relative standard deviation, mg/L;
s_R standard deviation of recovery, mg/L;
RSU relative standard deviation, %

The stability for 0.39 ‰ (0.184 mg/L) and 0.80% (0.382 mg/L) alcohol concentration and solution recovery at 34 ^{0}C, are presented in Table 8.

Table 8

Stability for 0.39 ‰ (0.184 mg/L) and 0.80 ‰ (0.382 mg/L)alcohol concentration and solution recovery at 34 ^{0}C

Theoretical alcohol concentration according Dubowski's equation, $\rho_{air\ 0}$, (mg/L)	0.184	0.382
Number of measurements, n	30	30
Range of values of concentration measured, (mg/L)	0.181 …0.185	0.376 …0.383
Average values, (mg/L)	0.184	0.381
Range of recovery of the solution, *R*	0.992 …1.014	0.994 …1.012
Average recovery of solution, R_m	1.000	1.000
Range of intrinsic error, ε_i, (mg/L)	- 0.003…0.001	- 0.006…0.001
Maximum permissible error, ε_t, (mg/L)	± 0.009	± 0.019

The final result of breath alcohol concentration with corresponding combined standard uncertainty [1,2] is:

$$\rho_{air} = (0.184 \pm 0.006)\ \text{mg/L and } \rho_{air} = (0.382 \pm 0.006)\ \text{mg/L}$$

The standard deviation, spreadsheet with uncertainty calculation and corrected concentration with it's associated uncertainty are presented in Tables 9,10 and 11.

Tabel 9

Standard deviation

$\rho_{air\ m}$	$s(\rho_{air})$	$s(\rho_{air})^2/n$	R_m	$s_R(\rho_{air})$
0.1835	0.0010	0.0002	1.0000	0.0055
0.3806	0.0019	0.0004	1.000	0.0051

Table 10

Spreadsheet showing the uncertainty calculation:

$\rho_{\text{air m}}$	0.1835	0.1837	0.1835	0.3806	0.3810	0.3806
$\rho_{\text{air }0}$	0.1840	0.1840	0.1900	0.3820	0.3820	0.3880
function	0.9975	0.9985	0.9660	0.9963	0.9973	0.9809
dif		-0.0010	0.0325		-0.0009	0.0163
dif^2		0.000001	0.0011		0.000001	0.0003
sum(dif^2)			0.0011			0.0003
index		0.001%	0.999%		0.003 %	0.997 %
R_{m}			1.0000			1.0000
$s_{\text{R}}(\rho_{\text{air}})$			0.0325			0.0164
RSU			3.25 %			1.64 %

Table 11

Corrected concentration and it's associated uncertainty

$\rho_{\text{air }0}$	0.1840	0.3820
$\rho_{\text{air m}}$	0.1835	0.3806
R_{m}	1.0000	1.0000
$\rho_{\text{air corr}}$	0.1835	0.3806
$u_{\rho\text{air }0}$	0.0060	0.0060
$s(\rho_{\text{air}})$	0.0061	0.0063
$s_{\text{R}}(\rho_{\text{air}})$	0.0325	0.0164
$u_{\rho\text{ air corr}}$	0.0085	0.0089
RSU$\rho_{\text{air corr}}$	4.64 %	2,33 %

where: $u_c = \sqrt{s^2(\rho_{\text{air}}) + s_R^2(\rho_{\text{air}})}$

So, the corresponding trueness for the concentration ρ_{air} = (0.184 ± 0.006) mg/L and ρ_{air} = (0.382 ± 0.006) mg/L measured for 30 times under the same condition of measurement is:

$$E_{\text{n}} = 0.05 \quad \text{and} \quad E_{\text{n}} = 0.13$$

The results of the recovery study, using two different breath alcohol concentrations: 0.184 mg/L and 0.382 mg/L are presented in Table 12:

Tabel 12

Trueness - Score E_n

No.	ρ_{air}, mg/L	$u_{c\ \rho\text{air}}$, mg/L	E_{n}
1	0.184	0.006	0.05
2	0.382	0.006	0.13

The accuracy is confirmed [9] due to values for E_n less then 1, for both reference materials.

7. Summary and Conclusions

Breath alcohol analyzers are widely accepted as legal measurement instruments used for determination of the mass concentration of alcohol in exhaled breath. Nowadays, Traffic Road Department from Romanian Ministry of Interior is using about one thousand and few hundred of electronic devices for testing breath alcohol concentration.

Gas Concentration Laboratory from National Institute of Metrology has started a project to prepare ethanol in air standards in order to provide the following control procedures: initial verification of new evidential breath analyzers, periodic verification, performance test and calibrations. During two years of sustained research activity different alcohol concentrations were prepared and the associated uncertainties according to the latest standards were evaluated [1,2].

The results obtained show that National Institute of Metrology standards, prepared according to the European and international standards and with the knowledge and equipment existent in Romanian laboratory, have the necessary accuracy and can be used to transmit the measuring unit, mg/L**,** to breath alcohol analyzers.

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