BREATH TESTING

Traceability of breath alcohol concentrations in Romania

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Abstract

The aim of this article is to provide results obtained by specialists from the Romanian National Institute of Metrology (INM) in their attempt to ensure traceability of breath alcohol measurement in Romania.

The Gas Concentration Group of the INM is prepared, from a technical and theoretical point of view, to provide support to National Authorities (Police Departments) with reference materials (RM) and traceable measurements of breath alcohol concentrations in Romania. The key quality parameters are the uncertainties associated with the certified values and the reliability of the uncertainty estimate. Depending on the different sources of uncertainty, an estimation of the uncertainties is presented regarding the generated alcohol concentration used for calibrating breath alcohol analyzers. The uncertainty budgets were calculated using the ISO approach [1,2]. Breath alcohol measurements are presented in this article together with the expanded uncertainty, U, using a coverage factor k=2 which gives a degree of confidence of approximately 95 %.

The tests and measurements were performed over two years in the Gas Concentration Laboratory of the INM using breath alcohol analyzers, breath alcohol simulators and pure ethanol. The results of the measurements, covering the entire range of concentration of breath alcohol analyzers, are summarized in tables.

Keywords: Traceability; reference materials; breath alcohol concentration; metrology

0 Introduction

The alcohol concentration is measured using air from the lungs or blood from the veins.

Over the years, breath testing has become a widely used method for the qualitative and quantitative determination of the alcohol level of persons suspected of driving while under the influence of alcohol. After recognizing the need for a quantitative assessment of intoxications, blood alcohol concentration was considered as the single most important variable. However, concern about the inconvenience of drawing a blood sample led to the development of the breath test as a non-invasive means of assessing the level of intoxication.

Scientists all over the world have started to look for new non-invasive methods to determine the alcohol concentration in the human body. Depending on the accuracy, specifically alcohol-related, cross sensitivity, long term stability, etc. a number of measuring principles are used for breath alcohol determination: chemical, bio-chemical (system based on oral fluids), physical (semiconductor cell - surface reaction), electrochemical (fuel cell), infrared spectroscopy, and gas chromatography.

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 wavelength infrared spectrophotometers.

1 Basics in breath alcohol concentration measurements

Breath alcohol measurements are based on Henry's law: "When an aqueous mixture of a volatile substance reaches equilibrium in 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 water and alcohol can be mixed in any ratio, resulting in a homogeneous mixture. Both liquids have a tendency to evaporate, but alcohol has a greater tendency to do so. 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 accept the value of this ratio as having a value of between 2000:1 to 2300:1.

The concentration of alcohol in the vapor phase above the liquid alcohol-water mixture depends on two factors: the temperature of the mixture, and the alcohol concentration of the liquid (Dubowsky formula):

$$C_{air} = 0.041445 \times 10^{-3}\, C_{H_2O} \times e^{0.06583\, t}$$

where t is the solution temperature in °C.

If t = 34.0 ± 0.1 °C, $C_{air} = 0.38866 \times 10^{-3}\ C_{H_2O}$

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 an aqueous solution and air in a semi-closed system.

In accordance with this law, the diffusion processes (which are also what cause oxygen to be taken up in the lungs) achieve a balance between the alcohol concentration in the blood and that 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 concentrations is still uncertain, evidential breath-alcohol instruments are used in many countries to determine the alcohol concentration level for prosecution purposes.

National authorities may require a specific conversion device that converts the measurement result obtained in terms of ethanol content and that can approve evidential breath analyzers for law enforcement purposes with a 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.

The INM Gas Concentration Laboratory is prepared to provide the following control procedures:

- type approval;
- initial and periodic verification of new evidential breath analyzers; and
- performance tests and calibrations.

It focuses on the development, implementation and use of such quality assurance programs for breath-alcohol testing.

An evidential breath analyzer is an instrument which accurately measures the concentration of alcohol in "end-expiratory" air to provide a result which can be used as evidence in drink-driving offences. End-expiratory air is a breath sample containing air from the end of a forced expiration from the lungs. An evidential breath analyzer, once type approved and having undergone independent official verification, ensures that the measurement results attain the extremely high level of reliability that European and national standards demand.

Traceability of breath alcohol concentration is a new field of interest in Romania. About 1700 breath alcohol analyzers were purchased by the Ministry of the Interior (Police Department) a few years ago following a European project to equip East-European Police Departments. Since then, the traceability of measurements performed by such instruments was a priority in order to ensure accurate measurements and especially acceptance in court. Measurements made at different times or in different places are thus directly related to a common reference. Applying the concept of traceability to breath alcohol measurements is not easy, but traceability has to provide qualitative results using analytical techniques used in calibration laboratories.

Specialists from the INM have started to prepare the basis necessary to transmit the specific measuring units 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 theoretically calculated and to those which evolve during a real exhalation.

- Evidential breath alcohol analyzer Alcotest 7110 MK III, manufactured by Dräger Safety AG & Co., KgaA, Germany, serial numbers: ARNC-0145, with Calibration Certificate no. 0347/14.10.2005 and ARND-0145, with Calibration Certificate no. 2040/14.10.2005, issued by EDN (Eichdirection Nord), Germany and traceable to the PTB's standards;
- 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;
- Wet bath simulator for testing and calibrating breath alcohol analyzers, manufactured by ICIA - Cluj, Romania;
- Syringe, (10.0 ± 0.2) mL;
- Analytical balance, type XS 205 manufactured by Mettler Toledo; and
- Distilled water.

The evidential breath alcohol analyzers Alcotest 7110 MK III satisfy the requirements of DIN VDE 0405 and OIML R 126 and were approved by the PTB and also by the Romanian INM following a series of tests according to the above Standard/Recommendation. This kind of measuring system can be used for breath alcohol concentration measurements either in Germany or in Romania [4-7].

2 Preparation of calibration standards

Traceability is defined as 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 international standards, through an unbroken chain of comparisons all having stated uncertainties.

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

The first step in this project was preparing 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 Alcohol concentrations obtained by mixing certain quantities of pure alcohol (ethanol) in distilled water

No.	$C_{C2H5\text{-}OH}$ mL	C_{H2O} g	C_{air} ‰	C_{air} mg/L
1	0.31	0.245	0.2	0.0952
2	0.62	0.490	0.4	0.1905
3	0.93	0.735	0.6	0.2857
4	1.24	0.980	0.8	0.3810
5	1.56	1.225	1.0	0.4762
6	2.33	1.838	1.5	0.7143
7	3.12	2.450	2.0	0.9524
8	3.90	3.063	2.5	1.1905
9	4.68	3.676	3.0	1.4286

3 Quantifying the uncertainty components

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

3.1 Uncertainty due to the syringe

One important source of uncertainty is related to the syringe, which has a nominal range of (0...10) mL. To establish this contribution to the final uncertainty budget, ten weighings were performed of 4.60 mL H_2O distilled water with a Mettler Toledo precision balance. The results are presented in Table 2.

Table 2 Result of 10 weighings (uncertainty related to the syringe)

Conventional value of distilled water g	Measured mass of distilled water g	Average value g	Standard experimental deviation, s g
4.60	4.59318; 4.57837; 4.61531; 4.59736; 4.59305; 4.59063; 4.61904; 4.63416; 4.61148; 4.57626	4.60088	0.01859

The associated uncertainty was estimated according to [1,2]. The combined standard uncertainty is:

$$u_{C\_seringa} = \sqrt{s^2 + u_{s1}{}^2 + u_{s2}{}^2} = \sqrt{0.00035^2 + 0.00816^2 + 0.00121^2} = 0.020336$$

where:

- s is the standard deviation for 10 measurements of the weight of 4.60 mL H_2O distilled water;
- $u_{s1} = \frac{0.02}{\sqrt{6}} = 0.00816$ is the standard uncertainty, calculated assuming a triangular distribution, as stated by the syringe manufacturer;
- $u_{s2} = 10\,(\text{mL}) \cdot \frac{2.1}{10^{-4}} \cdot \frac{1\,(°\text{C})}{\sqrt{3}} = 0.00121$ is the standard uncertainty, calculated assuming 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:

$U_{C\_seringa}$ = 0.002 × 2 = 0.004 mL;

Thus, the volume of the syringe is:

$V_{\_seringa}$ = (4.60 ± 0.04) mL

3.2 Uncertainty due to the recipient

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

$$u_{V1} = \frac{1}{\sqrt{3}} = 0.57735$$

The standard uncertainty, calculated assuming a rectangular distribution for the coefficient of the volume expansion, has the value:

$$u_{V2} = 1000\,(\text{mL}) \cdot \frac{2.1}{10^{-4}} \cdot \frac{1(°\text{C})}{\sqrt{3}} = 0.12124$$

The combined standard uncertainty is:

$$u_{C\ \ Volum} = \sqrt{{u_{V1}}^2 + {u_{V2}}^2} = \sqrt{0.57735^2 + 0.12124^2} = 0.589944$$

which gives the following value for the volume of the recipient used for preparing the standard mixture:

$V_{\_volum}$ = (1.000.00 ± 0.59) mL

3.3 Uncertainty due to the purity of the ethanol

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

$$u_{etalon} = \sqrt{(\frac{1-0.998}{\sqrt{3}})^2} = 0.001155$$

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

The simulator's thermostat was set to (34.0 ± 0.2) °C during the experiments. The standard uncertainty, calculated assuming a rectangular distribution for the variation of the thermostat's temperature, has the value:

$$u_{thermostat} = \sqrt{(\frac{0.2}{\sqrt{3}})^2} = 0.011547$$

4 Example of a total uncertainty budget calculation for a concentration of 0.8 ‰ corresponding to a concentration of 0.381 mg/L (alcohol in a liter of air)

For the uncertainty of the alcohol concentration in air generated by the temperature:

Table 3 Spreadsheet showing the uncertainty calculation

$C_{ethanol}$	0.98625	$u_{ethanol,\ g}$	0.016045		1.00230	0.98625	0.98625
Purity	0.998	u_p	0.001155		0.998	0.991955	0.998
Volume	1	u_V	0.00059		1	1	1.00059
$C_{0(ethanol/L)}$	0.984278	$u_{(ethanol/L)}$	0.016013	$C_{i(ethanol/L)}$	1.000291	0.978315	0.983697
				C_0-C_i	0.016013	-0.00596	-0.00058
				$(C_0$-$C_i)^2$	0.000256	3.55E-05	3.37E-07
				$\Sigma(C_0$-$C_i)^2$			0.000256

$$u_{(e\tan ol/L)} = \sqrt{(C_0 - C_i)^2} = \sqrt{0.000256} = 0.016013$$

Table 4 Uncertainty calculation for a temperature value t = 34 °C

$C_{0(ethanol/L)}$	0.984278	$u_{solution}$	0.016013		1.000291	0.984278
t, °C	34	$u_{temperature}$	0.011547		34	34.01155
$C_{0(ethanol/L\ air)}$	0.38255	$u_{ethanol/L\ air}$	0.006230	$C_{i(ethanol/L\ air)}$	0.388774	0.382841
‰	0.80	Index, %	1.63	C_0-C_i	0.006224	0.000291
				$(C_0$-$C_i)^2$	3.87E-05	8.46E-08
				$(C_0$-$C_i)^2$		3.88E-05
				Index, %	99.78	0.22

$$u_{(ethanol/Lair)} = \sqrt{(C_0 - C_i)^2} = \sqrt{3.88 \cdot e^{-5}} = 0.006230$$

The simulator's temperature was set to (34.0 ± 0.2) °C

$$u_{termostat} = \sqrt{(\frac{0,2}{\sqrt{3}})^2} = 0.011547$$

according to the Dubowsky formula:

$C_{air} = 0.041445 \times 10^{-3}\, C_{H_2O} \times e^{0.06583\, t}$

where t represents the solution temperature, expressed in °C.

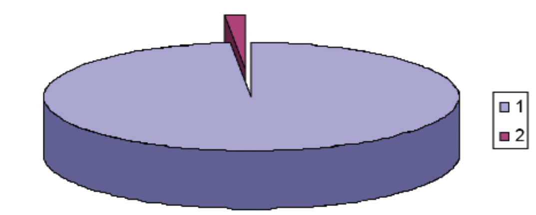
The corresponding spreadsheet uncertainty calculation for a temperature value t = 34 °C is shown in Table 4.

The alcohol concentration, expressed as mg in a litre of air, is then:

C_{air} = (0.382550 ± 0.006230) mg/L

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

C_{air} = (0.382 ± 0.006) mg/L



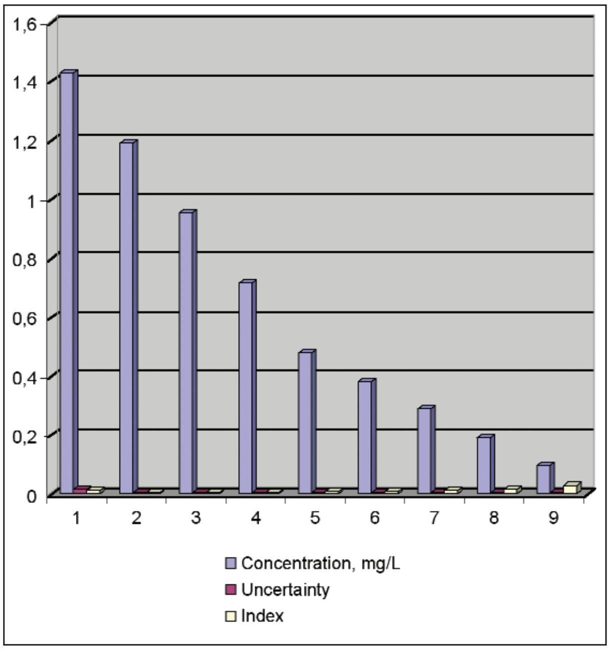
1 Alcohol concentration in air

2 Associated uncertainty

Table 5 and its associated graph present the alcohol concentration prepared according to the Dubowsky formula and the associated uncertainties calculated according to the most recent edition of the Guide to the expression of Uncertainty in Measurement (GUM) [1,2].

Table 5 Alcohol concentration prepared according to the Dubowsky formula and the associated uncertainties

Alcohol concentration ‰	Calculated alcohol concentration mg/L	Calculated uncertainty mg/L	Index %
3.0	1.425861	0.012274	0.86
2.5	1.188088	0.002685	0.23
2.0	0.950315	0.002630	0.28
1.5	0.712930	0.002586	0.36
1.0	0.475158	0.002554	0.54
0.8	0.380126	0.002545	0.67
0.6	0.285095	0.002538	0.89
0.4	0.190063	0.002533	1.33
0.2	0.095032	0.002529	2.66



Using the equipment in the INM Gas Concentration Laboratory the ethanol concentrations presented in Table 6 were prepared.

Table 6 Ethanol concentrations

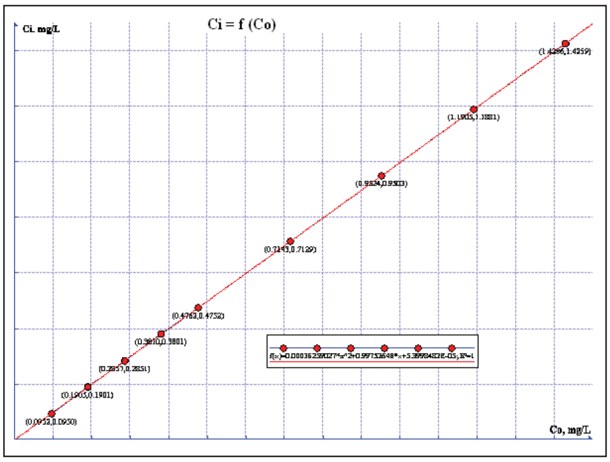
Alcohol concentration ‰	C_0 mg/L	C_i mg/L
3.0	1.4286	1.4259
2.5	1.1905	1.1881
2.0	0.9524	0.9503
1.5	0.7143	0.7129
1.0	0.4762	0.4752
0.8	0.3810	0.3801
0.6	0.2857	0.2851
0.4	0.1905	0.1901
0.2	0.0952	0.0950

C_0 Conventional true value of alcohol concentration, mg/L

C_i Prepared alcohol concentration, mg/L

The graph presents the final alcohol concentrations prepared in the laboratory (C_i, mg/L) against the theoretical concentrations (C_0, mg/L) calculated according to the Dubowsky formula.

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



Conclusion

Breath alcohol analyzers are widely accepted as legal measuring instruments used for determining the mass concentration of alcohol in exhaled breath. Nowadays, the Road and Traffic Department of the Romanian Ministry of the Interior uses some one thousand several hundred electronic devices for testing breath alcohol concentration.

The INM Gas Concentration Laboratory has started a project to prepare standards for ethanol in air in order to provide the following control procedures:

- initial verification of new evidential breath analyzers;
- periodic verification; and
- performance tests and calibrations.

During two years of sustained research activity different alcohol concentrations were prepared; their associated uncertainties were evaluated according to the most recent standards [1,2].

The results obtained show that the INM standards, prepared according to the European and International Standards and with the knowledge and equipment in existence in the INM laboratory, are of the required accuracy and can be used to transmit the measuring unit, mg/L, to breath alcohol analyzers.

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