ROAD SAFETY

Breath analyzers: Implementation of traceability in Portugal

Daniela Vaz & Isabel Castanheira
Instituto Portugues da Qualidade, Portugal
Helena Fino
UNINOVA, Portugal
Adriaan M.H. van der Veen
Nederlands Meetinstituut, The Netherlands

Summary

Alcohol breath analysis is used in most countries to enforce driving under the influence of alcohol (DUI) legislation. The accuracy of the "breath test" is critical to ensure the successful prosecution of DUI cases in court - this accuracy in turn directly depends on that of the calibration source used to verify the breath analyzers, and ethanol in nitrogen gas mixtures are prepared and certified for this purpose. These reference materials should be traceable to SI units in order to establish test reliability: this ensures that the results obtained during calibration/verification as well as those from breath analysis are accepted as evidence.

The objective of this paper is to outline the impact of the certification of ethanol in nitrogen gas mixtures on the verification and calibration of breath analyzers. The composition of the reference gas mixtures thus prepared can be verified by analytical reference methods such as non-dispersive infrared spectroscopy using a proper calibration method. The analysis is carried out by comparing the mixture to be certified with a set of primary reference materials (PRMs) of known composition and uncertainty.

Introduction

The abuse of alcohol is receiving more and more attention. Within the European Union it is estimated that 20 % of all fatal road traffic accidents are alcohol-related. Breath analysis was introduced in Portugal over fifteen years ago, but the authorities have only recently been granted permission to replace blood tests by breath tests. A law enforcement officer has the right to subject a driver to a breath test in the case of careless driving, an accident, or suspicion of DUI. Before the case is heard in a court of law, the suspect can request a blood test. In the case of DUI evidence, the driver has to pay all the costs involved, which has served to significantly reduce the number of blood tests requested.

Compared to blood analysis, breath tests have several advantages: they are efficient, the results are available rapidly, and the costs are low. The accuracy and reliability of breath-alcohol testing devices can be subject to debate and speculation, especially in those cases where the suspected driver's employment is at stake. Based on the experience of other EU countries, a regulation was put into force that stipulates the operational procedures as well as the requirements of the National Legal System. At first, a screening device is used as an on-the-spot analyzer by the police; if the result is positive, the driver is obliged to undergo a test with an evidential breath analyzer (EBA); thus, two types of analyzers are in use.

A portable device containing an electrochemical cell that responds to ethanol can provide initial evidence of recent drinking and blood alcohol. For these screening devices a quality assurance and quality control plan shall be designed and implemented in a such a manner that it will verify that test results differ by not more than 10 %; such screening devices should be certified by the Road Traffic Department.

The EBA adopted must be submitted to metrological control. Measuring instruments used for evidential purposes must pass pattern approval and each instrument must be submitted to initial and subsequent annual verification. Currently, the metrological requirements for analyzer performance are based on OIML specifications [1].

All evidential models approved by IPQ use the principles of IR absorption and Lambert-Beer law for quantitative analysis. The instruments measure the absorption of IR radiation at 9.4–9.5 μm, which is associated with O–H bond stretch and bending vibrations, in order to avoid interference from acetone and hydrocarbons, which can occur in poorly treated insulin dependent diabetes or during ketoacidosis. Based on the scientific work of Jones [2], the EBA must be operated at 34 °C, and the instrument uses thermostats to measure the breath temperature and to harmonize inter- and intra-individual variations. The measurements could be affected by the volume of breath discarded before sampling; to avoid this, the instruments incorporate a flow meter to monitor the breathing.

In order to carry out reliable and reproducible calibrations and metrological operations, standard operations procedures have to be approved by legal authorities. For this purpose, two types of calibration devices have

been accepted: wet simulators and compressed gaseous ethanol standards in nitrogen or air. The calibrations must be traceable to the appropriate SI units.

The approved wet simulator is based on the principle reported by Dubowski [3], which employs a mixture of liquid ethanol and water maintained at a constant and outlet temperature of 34 °C. The gas phase concentration is predicted from the aqueous concentration based on Henry's Law, when ambient air is bubbled at constant flow. Critical points in the use of the wet simulator are the outlet gas concentration caused by depletion, liquid temperature maintenance, absence of monitoring concentration and lack of traceability evidence on outlet gas.

Compressed gas standards are mixtures of ethanol vapor in nitrogen or air in a pressurized cylinder. Working standards can be certified and made directly traceable to primary gravimetrically prepared standards. The stability and the homogeneity of the mixtures should be tested prior to use.

Dry standards do not have a long history and some controversy is described in the literature. The criticism is that dry gas could not resemble human breath due to the lack of moisture content. Recent work by Dubowski [3] and results from Silverman [4] with different commercial breath analyzers concluded that there is a satisfactory degree of equivalence between both types of calibration devices for those instruments. This has led to the result that the system based on ethanol-compressed gas was approved as the device for initial and subsequent verification.

The purpose of this work is to demonstrate the reliability of breath analysis in Portugal. The following parts can be identified in the system:

1) development of a suitable method to certify working standards;
2) establishment of a procedure to validate the reliability of instruments in situ;
3) definition of a realistic uncertainty budget; and
4) comparison of the results obtained during several subsequent verifications.

Certification of working standards

The validation of the composition attributed to the calibration gas mixtures can be achieved by comparison with appropriate reference gas mixtures. For this purpose, PRMs from the Nederlands Meetinstituut (NMi) have been used. These PRMs are prepared by gravimetric methods and directly linked to international standards of mass, pressure, temperature and amount of substance, which ensures traceability to international standards.

The composition of the ethanol in nitrogen working standards is verified by non-dispersive infrared spectroscopy (NDIR) in order to confirm the value of the preparations. The analysis is carried out by comparing the mixture to be certified with a set of PRMs of known composition and uncertainty.

The basic procedure can be summarized as follows:

1) Specify the analytical range of interest;
2) Specify the analytical method and measuring system to be used;
3) Design the calibration experiment;
4) Perform the calibration experiment;
5) Calculate the analysis function $x = G(y)$;
6) Determine the composition of the gas under verification (mole fraction and uncertainty); and
7) State the result of the entire analysis.

Three mixtures of ethanol in nitrogen are prepared, of nominal 217, 381, and 516 µmol/mol. A series of five primary reference materials is used for the calibration using NDIR spectroscopy. The composition of the PRMs is given in Table 1.

The NDIR spectrometer is connected to an automatic sampler, controlled by a computer program [5]. The sampler ensures the same analysis conditions for all cylinders, including pressure and mass flow control. The calibration is carried out in three runs. The NDIR-monitor is flushed 300 s before a measurement, a measurement consisting of 90 readings. The pressure is read 30 times and the mass flow is controlled during the measurement. The zero gas is nitrogen. The computer controls the measurement of the calibration mixtures and the sample cylinders.

The results have been fitted using a quadratic function of type [6]:

$$x = G(Y) = b_0 + b_1 y + b_2 y^2 \qquad (1)$$

Table 1 PRMs used for calibration

Cylinder	Composition µmol/mol	U µmol/mol
Standard 1	114.1	0.9
Standard 2	223.7	1.6
Standard 3	391.3	2.8
Standard 4	512.2	3.5
Standard 5	810.0	5.0

Table 2 Results from verification (in µmol/mol)

Cylinder	Nominal	Result
Sc 5800447	217	212.3
Sc 5800445	381	382.2
Sc 5800344	516	514.2

Table 3 Uncertainty evaluation of the verification (in µmol/mol)

	Uncertainty from the analysis function					
Cylinder	Run #1	Run #2	Run #3	s_r	u_c	U
Sc 5800447	0.50	0.50	0.50	0.20	0.89	1.8
Sc 5800445	0.88	0.89	0.87	0.31	1.56	3.1
Sc 5800344	0.98	0.99	1.010	0.29	1.75	3.5

Table 4 Composition of gas mixtures, expressed in blood alcohol units and range of tolerance

Cylinder	x_{EtOH} (ppm, mol/mol)	U (ppm, mol/mol)	c_{EtOH} (mg/L)	U (mg/L)	Certified value $X \pm u(x)$	Range of tolerance
Sc 5800447	212.3	1.8	0.383	0.003	[0.379; 0.386]	[0.352; 0.413]
Sc 5800445	382.2	3.1	0.689	0.006	[0.683; 0.694]	[0.634; 0.744]
Sc 5800344	514.2	3.5	0.927	0.006	[0.920; 0.933]	[0.853; 1.001]

The results of the fit of run #1 are shown in Fig. 1 (see next page). The results of the second and third runs are very similar and the results from the verification of the three mixtures prepared are given in Table 2.

The evaluation of the main sources of uncertainty from the verification process leads to an unequivocal confidence interval for the composition of the mixtures. The main sources of uncertainty are those associated with the repeatability of the response, and the quality of the fit. The results of the uncertainty evaluation are shown in Table 3.

The compositions and the expanded uncertainties of the three mixtures are tabulated in Table 4. In order to relate the composition of the gas mixtures to the commonly used unit for expressing alcohol levels in blood (mg/L), the formula used in [2] for this conversion is:

$$c_{EtOH} = 1\,000 \; \frac{x_{EtOH} M_{EtOH}}{M_{N2}} \rho_{N2} \qquad (2)$$

where:

x_{EtOH} = the mole fraction;
c_{EtOH} = the blood alcohol concentration;
M_{EtOH} = the molar mass of ethanol;
M_{N2} = the molar mass of nitrogen gas; and
ρ_{N2} = its density at 1 bar and 34 °C.

The maximum permissible errors accepted by Portuguese legislation, for instance for periodical verification, for each of the three gas mixtures are 0.032 mg/L in absolute error for the concentration in cylinder Sc 5800447 and 8 % in relative error for the concentrations in cylinders Sc 5800445 and Sc 5800344. As can readily be seen, the confidence interval provided by the expanded uncertainty is much smaller than the range of tolerance of the breath analyzers, as it should be!

Reliability of the instruments on site

The quality control of the instruments on site must be guaranteed in order to avoid the risk of inaccurate results. The metrological features are more or less rigorous and include accuracy, linearity, hysteresis and short-term drift. Under reference conditions five concentrations are used within the range 0–800 ppm. In this case, reference gas mixtures with an uncertainty better than 1 % should be used. In the subsequent verification, the working standards with alcohol concentrations of 0, 220, 440, 660, and 800 ppm (µmol/mol) are applied for verifying linearity. For accuracy, 220 ppm and 660 ppm mixtures are used. At least 10 measurements of each gas mixture are used for repeatability. The memory effect and short-term drift are checked with the same concentration gases.

Uncertainty evaluation

Although the uncertainty concept as used in the "Guide to the expression of uncertainty in measurement" (GUM) [7] is not mentioned in OIML R 126 [1], it was

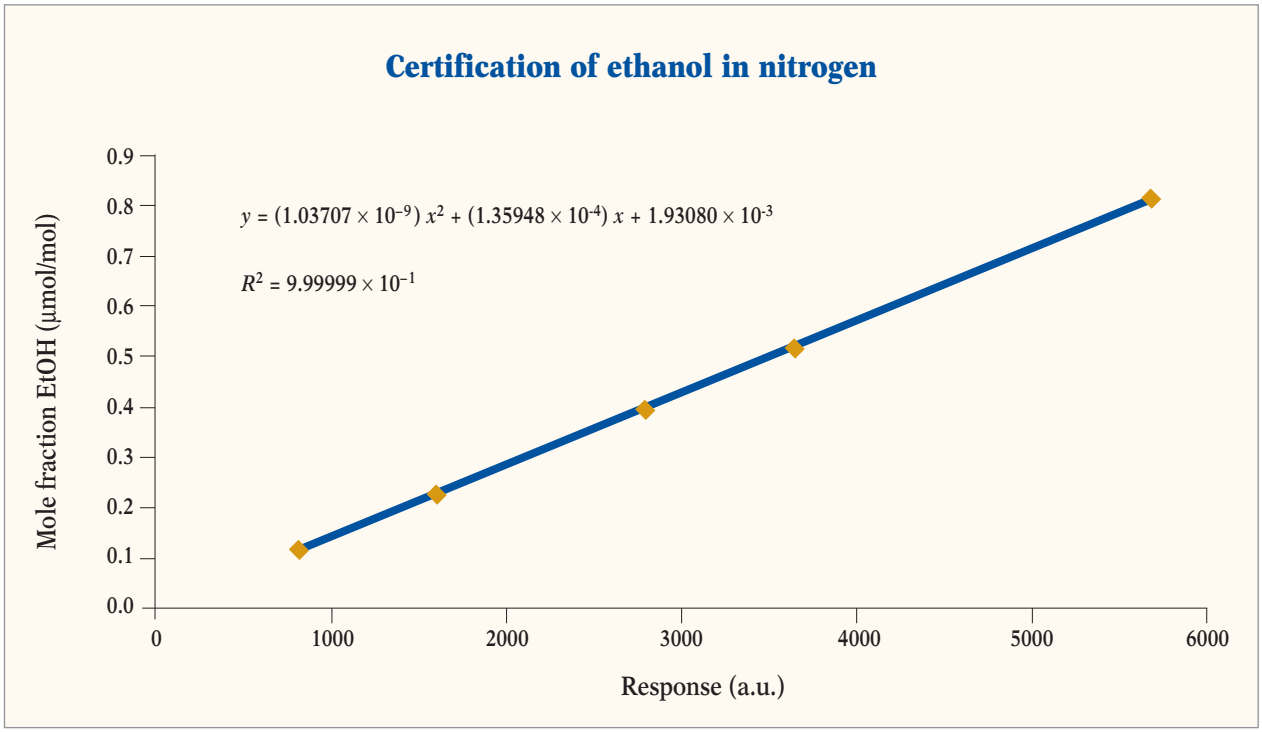

Fig. 1 Fitting results of run #1

decided to apply it just as an evaluation so that the instrument should not be rejected based on the uncertainty results. The measurement uncertainty resulting from the legal procedure was evaluated in accordance with the methodology described in the GUM, the Eurachem Guide [8] and the methodology described by ISO/TC158 [6] working groups. The expanded uncertainty U was obtained when a coverage factor k = 2 was applied. A typical excerpt of the uncertainty evaluation is shown in Table 5.

Hysteresis is assessed separately. Linearity of the device is checked by means of linear regression. The contribution from the working standard is ascertained from the uncertainty marked on the certificate.

The contributions from instrument's scale resolution and zero-setting are based on the manufacturer's specifications and a rectangular distribution is assumed. They are entered as "instrument" in Table 5. In Table 6 the measurement uncertainty at different concentrations is presented for a typical breath analyzer; these results can be regarded as representative of more than 400 instruments.

Comparison of the results obtained over several subsequent verifications

Using the same standard operational procedure during four years, all the devices were tested and the results were stored and compared in order to verify that no long-term drift can be observed. Table 7 shows the results.

Table 5 Uncertainty evaluation of an on-site tester

Variable X_i	Estimate x_i	Uncertainty	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution to standard uncertainty $u_i(y)$
Test	0.376	8.7×10^{-5}	Normal	8.7×10^{-5}	1	8.7×10^{-5}
CRM	0	0.004	Normal	0.0023	1	0.0023
Instrument	0	0.004	Rectangular	0.0025	1	0.0025
Result	0.376					0.007

Table 6 Results from verifying an on-site breath analyzer

Scale point (mg/L)	Maximum permissible error	Uncertainty	Scale point + observed error + *U*	Compliance lower limit	Compliance higher limit
0.200	± 0.032 (mg/L)	0.006 (mg/L)	0.224 (mg/L)	0.168 (mg/L)	0.232 (mg/L)
0.400	± 0.032 (mg/L)	0.007 (mg/L)	0.402 (mg/L)	0.368 (mg/L)	0.432 (mg/L)
0.678	± 8 %	0.022 (%)	0.687 (mg/L)	0.624 (mg/L)	0.733 (mg/L)
0.978	± 8 %	0.030 (%)	1.065 (mg/L)	0.900 (mg/L)	1.057 (mg/L)
1.457	± 8 %	0.050 (%)	1.457 (mg/L)	1.340 (mg/L)	1.573 (mg/L)

Table 7 Values of uncertainty during four years for the same instrument and in the same points

Scale point	1996	1997	1998	1999
0.200 mg/L	0.009 (mg/L)	0.008 (mg/L)	0.007 (mg/L)	0.010 (mg/L)
0.417 mg/L	0.007 (mg/L)	0.008 (mg/L)	0.011 (mg/L)	0.010 (mg/L)
0.700 mg/L	0.021 (%)	0.023 (%)	0.024 (%)	0.026 (%)
0.950 mg/L	0.034 (%)	0.040 (%)	0.038 (%)	0.043 (%)
1.500 mg/L	0.045 (%)	0.045 (%)	0.042 (%)	0.044 (%)

Conclusions

The methodology presented allows for transparency and validation of the methods used in legal verification. These concepts allow laboratory quality assurance and quality control to be improved without spending extra time, and is a set of tools that ensures the reliability of the measurements and provides the jurisdiction with clear evidence of reliability.

This traceability is provided through an unbroken chain of calibrations linking measurements made in one laboratory with measurements made in other places at different times. The link to other countries is established through IPQ's working standards, which are made traceable to international PRMs.

Another important consideration is the appreciation of the results for setting up compliance limits using the GUM uncertainty concept. ■

Bibliography

[1] OIML Recommendation R 126 *Evidential Breath Analyzers*

[2] Jones A.W., *Enforcement of drink-driving laws by use of "per se" legal limits; Blood and/or breath concentration of impairment, Alcohol, Drugs and Driving*, 99 (4) 1988

[3] Dubowski K.M., Essary N.A., *Vapor-Alcohol Control Tests with Compressed Ethanol Gas Mixtures: Scientific Bases and Actual Performance*, Journal of Analytical Toxicology, 20, pp. 484–491, 1996

[4] Silverman L.D., Wong K., Miller S., *Confirmation of Ethanol Compressed Gas Standards Concentrations by a NIST Traceable absolute Chemical Method and Comparison to Wet Breath Alcohol Simulators*, ICMT, 1997

[5] Alink A., Castanheira I., *GAMIFAC phase 2, 3 and 5- Final Report*, Instituto Português da Qualidade, 1999

[6] ISO/DIS 6143-2: 1999 *Gas analysis - Determination of the composition of calibration gas mixtures - Comparison methods*

[7] *Guide to the expression of uncertainty in measurement*, first edition, second print, BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML - ISO Geneva, 1995

[8] Eurachem/CITAC, *Guide for Quantifying Uncertainty in Analytical Measurement*, 2nd edition, 2000

AUTHOR CONTACT DETAILS:

DANIELA VAZ & ISABEL CASTANHEIRA
Instituto Portugues da Qualidade,
Rua C. à Av. dos três Vales, 2825 Monte de Caparica, Portugal
dvaz@mail.ipq.pt icastanheira@mail.ipq.pt

HELENA FINO - UNINOVA, Monte de Caparica, Portugal
hf@uninova.pt

ADRIAAN M.H. VAN DER VEEN
Nederlands Meetinstituut,
Schoemakerstraat 97, 2628 VK Delft, Netherlands
avdveen@nmi.nl