# Comparison on mixtures of ethanol in water-saturated air

EURAMET TC-MC Project 1112

Physikalisch-Technische Bundesanstalt, Germany Braunschweig, November 2016

# **1** Summary

In many countries breath alcohol measuring instruments have to be calibrated and verified with mixtures of ethanol in water saturated air. For the preparation of such moist gases mainly a system proposed in OIML R 126 is used. Such a "bubble train", consists of a system of three or more flasks filled with an ethanol-water-solution of well known concentration. If air flows through the flasks, the concentration of ethanol in the resulting gas mixture depends on the solution concentration and the temperature.

Using the so-called Dubowski equation (OIML R 126, 1998) the ethanol concentration in the gas mixture can be calculated. Problematic is here that the used factors are ascertained from several empirically determined values. The uncertainty of these factors cannot be neglected, but for being comparable they are set to zero for this comparison. It should be part of later comparisons to include this influence.

To compare in a first step the technical realization of the preparation process (bubble train) only, it is proposed to use two different types of breath alcohol measuring instruments as monitoring devices sent around. Each of the collaborating laboratories will prepare gas mixtures with concentrations around 0,4 mg/l and 0,25 mg/l with its own equipment. The gas mixtures will be analysed with the monitoring devices and the results of the instruments will be compared at the pilot laboratory. Aim of the comparison will be to identify the critical points of the preparation process and in this way to increase the quality of mixture preparation.

# 2 Design of the comparison

## 2.1 Field of measurement

Amount-of-substance

## 2.2 Subject

EURAMET comparison in the field of legal measurements (ethanol in water-saturated air).

## 2.3 Participants

The following laboratories participated in the comparison: INM (Romania), GUM (Poland), BEV (Austria), LNE (France), METAS (Switzerland) and PTB (Germany, coordinating laboratory).

## 2.4 Measurement standards

Two breath alcohol analysers were chosen as comparators in a way that two different measuring principles and two different manufacturers were included. Both are accepted as satisfying the requirements of OIML R 126. This is important especially concerning the drift behavior and the accuracy. The two non-calibrated instruments were sent around as comparators, because it is impossible to compare the water-saturated gas mixtures directly.

The comparators were the following instruments:

• Alcotest 7110 Evidential, Type MK III, German version

This instrument measures in the standard mode the breath temperature and corrects the ethanol concentration of the analysed probe to a concentration according to 34 °C gas temperature. Additionally, it allows in the so-called "test mode" to display the results of the two independent sensors without temperature correction. This mode allows fast and subsequent measurements without the usually necessary test schedule for the official use. In the following this instrument is abbreviated with "Alcotest".

• Intox IR/EC II

This instrument as well allows fast and subsequent measurements without the test schedule for official measurements in a special calibration mode. Unfortunately it is impossible to get the individual results of the two sensors. In the following this instrument is abbreviated with "Intox".

Every laboratory prepares its own calibration gas mixtures that were analysed with the comparators. The mass concentration of the compared gas mixtures should have been around 0,25 mg/l ethanol in air and 0,4 mg/l ethanol in air. The gas mixtures had to be at app. 34°C according to the requirements of the OIML R 126. The mixture preparation systems and the respective methods of each lab are described below.

## 2.5 Conduct of the comparison

The participating laboratories used the preparation method described in OIML R 126. The ethanol mass concentrations of the gas mixtures were calculated using the so-called Dubowsky equation as it is described in the OIML recommendation. Because of this preparation method the ethanol concentration of the gas mixtures can differ from measurement to measurement. To be able to EURAMET TC-MC 1112 page 3 of 19

include this information into the validation of the results, it was asked for each measurement for the (target) mass concentration of the gas mixture and the respective gas temperature.

To get as much information as possible the two instruments were used in the following modes:

- 5 measurements with the Alcotest (temperature corrected results)
- 10 measurements in test mode with the Alcotest no temperature correction, individual results for the two sensors resulting in 30 results (10 target concentrations with the respective 10 results of the first sensor and the respective 10 results of the second sensor)
- 10 measurements in the calibration mode with the Intox no temperature correction, result determined form the results of two sensors.

Some of the participants did prepare gas mixtures containing ethanol, water and air but containing 5 % CO<sub>2</sub> as well. This could be partly taken into account by the instruments, where the test gas used in the test mode can be decided to be with or without CO2. An influence on the results of this comparison was not detected.

#### 2.5.1 Schedule

The schedule for this comparison reads as follows: September-December 2009 Check of the comparators, first measurements at PTB (Germany) January 2010 Measurements at INM (Romania) February 2010 Measurements at GUM (Poland) March 2010 Measurements at BEV (Austria) April and May 2010 Measurements at LNE (France) July 2010 Measurements at PTB (Germany) September 2010 Measurements at METAS (Switzerland) November 2010 Measurements at PTB February 2015 Draft A report (version 4)

# 2.6 Measurement equation

## 2.6.1 Gas temperature

One result of the comparison is the analysis of the gas temperatures. The Alcotest Evidential measures in the standard mode the gas temperature of the sample. The measured ethanol concentration will be recalculated according to a gas temperature of 34 °C basing on the Dubowski-equation. Because of this, even a "right" ethanol concentration will be displayed in this measuring mode far from the target value if the measured gas temperature is not near 34°C. The results are displayed in comparison with the theoretical curve basing on Dubowskis-equation. The theoretical curve was calculated as:

$$\beta_{theo}(\vartheta) = 0.4145 \cdot \beta_{solution} \cdot \exp(0.06583 \cdot 34^{\circ}C) \cdot \frac{\exp(0.06583 \cdot 34^{\circ}C)}{\exp(0.06583 \cdot \vartheta)}$$
(1)

With	$eta_{\scriptscriptstyle theo}(\mathcal{G})$	theoretical curve of "wrong temperature corrected" values in mg/l
	$eta_{\scriptscriptstyle solution}$	concentration of the ethanol-water solution in g/l
	9	gas temperature measured by the Alcotest Evidential in °C

If there is no deviation in the gas concentration the results should be near the theoretical curve. Because the temperature measurement of the monitoring instrument is not very accurate, the presented deviations are more qualitative results than quantitative deviations.

#### 2.6.2 Ethanol concentration

The Results of the measurements were calculated as the relative deviations of the target values from the values displayed at the monitoring instruments:

$$a_{j,k,i} = \frac{\beta_{monitor_{k,i}}}{\beta_{calculated_{j,k,i}}}$$
(2)

with

$\beta_{calculated_{k,i}}$	target mass concentration in mg/l as determined by the lab $k$ for
	measurement $i$ in the cycle of 10 single measurements
$\beta_{monitor_{j,k,i}}$	mass concentration in mg/l as displayed at the monitoring instrument $j$ for
	measurement $i$ in lab $k$ in the cycle of 10 single measurements
$a_{j,k,i}$	the result of measurement $i$ at lab $k$ with monitor $j$

The mean values  $A_{j,k}$  for each monitoring system j (two of the Alcotest Evidential, one of the Intox) of lab k are determined as:

$$A_{j,k} = \frac{1}{10} \sum_{i=1}^{10} a_{j,k,i} \qquad \text{with } j \in 1,2,3$$
(3)

The uncertainties of the values (within one lab) were calculated as:

$$u(A_{j,k}) = |A_{j,k}| \cdot \sqrt{u_{rel}^{2}(A_{j,k})_{\text{variation}} + u_{rel}^{2}(\beta_{\text{display}})_{\text{resolution}} + u_{rel}^{2}(\beta_{\text{target}})_{gas}}$$

#### 2.6.3 Calculation of the reference values

The (interlaboratory) mean out of the  $A_{j,k}$  of the labs could be used as reference value for the respective monitoring system. For a weighted mean of measurement results the following is proposed at the website of JCRB if the variability of the lab to lab values are known. The lab to lab variability was determined as the standard deviation of the  $A_{j,k}$  of one analyzing system:

 $u(A_i) = s(A_{i,k})$  with  $A_j$  being the simple mean of the  $A_{j,k}$ 

The weights,  $w_{j,k}$ , for the calculation of the weighted means are determined as the square root of the square sum of uncertainties "within" each lab ( $u(A_{j,k})$ ) and "between" the labs ( $u(A_j)$ ):

$$w_{j,k} = \sqrt{u^2(A_{j,k}) + u^2(A_j)}$$
(4)

The weighted mean,  $m_j$ , for the monitoring system j follows as:

$$m_{j} = \frac{\sum_{k=1}^{N} A_{j,k} / w_{j,k}}{\sum_{k=1}^{N} 1 / w_{j,k}}$$
(5)

With its uncertainty

$$u(m_j) = \frac{1}{\sum_{k=1}^{N} 1/w_{j,k}}$$
(6)

#### 2.7 Degrees-of-equivalence

A unilateral degree of equivalence in comparisons is the deviation from a reference value, defined as

$$D_{j,k} = A_{j,k} - m_j \tag{7}$$

and  $U(D_{j,k})$  the uncertainty of the difference  $D_{j,k}$  at 95% level of confidence.

Here  $m_j$ , the weighted mean of the measurement results of monitoring device j, denotes the comparison reference value of the respective results, and  $A_{j,k}$  the mean of the results of laboratory k with monitor j.

Because the uncertainty of  $A_{j,k}$  is part of the determination of  $u(m_j)$  and  $u(m_j)$  is more than one decade smaller than  $A_{j,k}$  the uncertainty of  $D_{j,k}$  is expressed (with k = 2) as

$$U(D_{j,k}) = u(A_{j,k}) \cdot 2$$
(8)

Where  $u(A_{j,k})$  is the uncertainty of the mean value of lab k at monitor j consisting of the variation of the single measurements, the resolution of the monitoring device and the uncertainty of the ethanol mass concentration in the gas as determined by the laboratory.

## **3 Results**

#### 3.1 Mixture Generating Systems

The mixture generating systems of the labs except LNE follow in general OIML R 126 (1998), annex G [2]. The preparation of "wet gas" is described there by the use of a "bubble train". A bubble train is a combination of two or more glass flasks filled with ethanol-water solution where the carrier gas is bubbled through. The specialties of the individual mixture generators are listed in table 2.

LNE uses for the mixture generation a system of mass flow controllers (gaseous and liquid) linked to an FID. Thus, by the mass flow controllers the ethanol and CO<sub>2</sub> concentration of the gas can be controlled in some limits and is checked by the FID. The FID itself is calibrated with gas mixtures prepared with a bubble train. The facts about this bubble train are listed in table 2. The uncertainties due to calibration and stability of the FID are included in the uncertainty budget of the measurement results.

At PTB a fundamental gravimetrical mixture generator was set up, to prepare gas mixtures like the mixtures within this comparison without the empirical determined Dubowsky-equation. The system is described in detail in [1]. The values realized with that system were not included into the determination of the weighted mean values, but they are included into the diagrams to get an imagination about the agreement between the "Dubowsky"-systems and the new fundamental system. In the tables and diagrams these results are marked as "PTB grav.".

## 3.2 Consequences concerning INM Results

Because INM has delivered all results of the Alcotest with the temperature correction of the instrument in the standard mode, the respective results for the comparison of the ethanol measurement were recalculated with the following equation:

$$\beta_{INM\_recalc} = \beta_{INM\_display} \cdot \frac{\exp(0,06583 \cdot \mathcal{G}_{display})}{\exp(0,06583 \cdot \mathcal{G}_{stated})}$$
(9)

For the further calculations only the recalculated values were used. For the determination of the reference values for monitoring systems the results of INM were not taken into account, but the respective deviations are tabled.

For the determination of the reference values only the results of GUM, BEV, METAS, the result of LNE at 0,35 l/s and the first result of PTB were used. The deviations of all results with respect to the calculated mean value were determined and presented in the diagrams 3 and 5.

## 3.3 Temperatures of the calibration gases

Diagram 1 shows the results as described in 2.6.2. As can be seen there are partly great deviations of the measured and stated gas temperatures (figures out by the "error bars"). But all the results follow in general the "theoretical value" (grey line). This leads to the assumption that the temperature changes occurred after the generation process of the calibration gases.

		0,25 mg/l		0,4 mg/l		
		mean gas	mean gas	mean gas	mean gas	
		temperature	temperature	temperature	temperature	
		stated by the	measured by	stated by the	measured by	
Month/Year	Institute	lab in °C	Alcotest in °C	lab in °C	Alcotest in °C	
11 2009	PTB	34	33,7	34	33,52	
11 2009	PTB grav	34,03	34,23	34,03	34,16	
12 2009	PTB	34	34	34	33,55	
01 2010	INM	34	30,77	34	30,58	
02 2010	GUM	33,9789	35,46	33,9879	35,36	
03 2010	BEV	33,966	33,92	34,005	33,64	
04 2010	LNE	34	31,21	34	31,5	
05 2010	LNE	34	31,51	34	31,35	
07 2010	PTB	34	33,76	34,02	33,71	
09 2010	METAS	37,388	36,53	37,699	36,85	
11 2010	PTB	34	34,035	34	34,18	

Table 1: Stated temperatures against temperatures measured by the Alcotest instrument

Institute	Num.	volume of	Source of the solution	Temperature stabilisation	Temperature	Approximate flow	Carrier gas
	of	solution in			measurement	used for the	or gases
	flasks	each flask in				measurement	within the
		ml					mixture
INM/BRML	3	500	Prepared by NMR(INM)	Each flask is thermostated		0,3 l/s	Cleaned air
				by its own heating system			
GUM	3	500	GUM gravimetric	±0,01°C	In the solution of	0,3 l/s	Synthetic air
			method/solution validated		the last flask		with 5% vol
			by density meter DMA				CO <sub>2</sub>
			5000				
BEV	2	about 500 ml	Prepared by BEV	Each flask is thermostated	In the solution of	One cycle with 0,2	Cleaned air
			(Gravimetric, and density)	by its own system	the last flask	l/s other cycles	
						with 0,33 l/s	
LNE (for the	3	250	LNE	The flasks are introduced	At different	First cycle with	Air with 5%
calibration of				into a thermo-stabilized	places of the	0,6 l/s, second	CO2
the FID only)				enclosure with a	system; finally in	cycle with 0,35 l/s	002
				temperature-controlled bath	the solution of		
					the last flask		
METAS	3	500	Prepared by METAS	Whole system in a liquid	Solution of the	0,25 l/s	Cleaned
				thermostat ±0,03°C;	last flask;		natural air
				individual thermostat for	temperature of		
				each flask ±0,01°C	produced gas		
					mixture at outlet		
РТВ	3	Ca. 700	Prepared by PTB	Whole system in a liquid	In the solution of	0,3 l/s	Cleaned air
				thermostat; ±0,01°C	the last flask		

**Table 2:** Specialties of the mixture generators of the different laboratories (from NMR no further information was delivered)

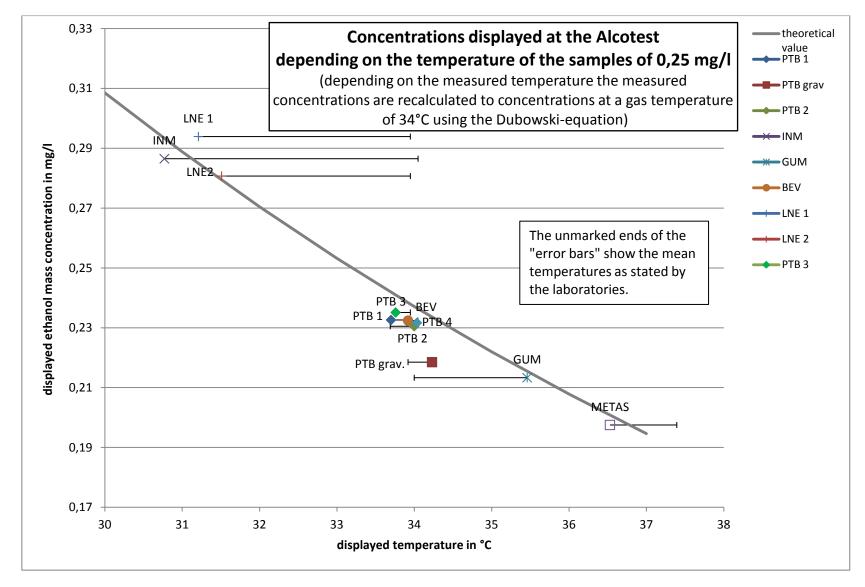


Diagram 1 Deviations of the stated and observed gas temperatures at 0,25 mg/l

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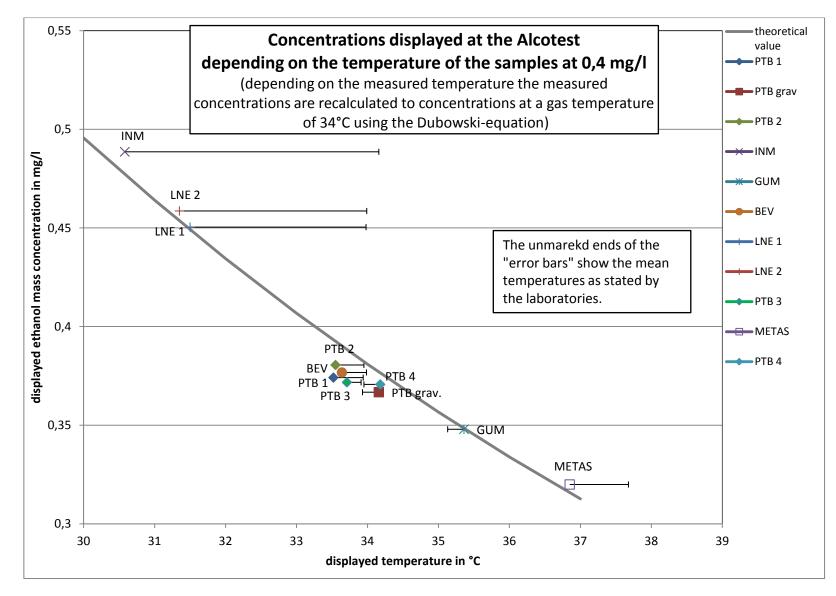


Diagram 2 Deviations of the stated and observed gas temperatures at 0,4 mg/l

## 3.4 Ethanol mass concentration

The dark colored lines of the first six columns contain the values considered in the mean values shown in the diagrams 3 and 4. The dark colored lines in the last two columns show deviations from the weighted mean larger than the respective uncertainties.

Month/year	Institute (k)	mean of the target values in mg/l	$A_{1,k}$	u_rel(A <sub>1,k</sub> )	u(A <sub>1,k</sub> ) calc. as SSR (b) or given by lab(a)	D <sub>1,k</sub>	U(D <sub>1,j</sub> ) (cov. factor k=2)
11/2009	PTB	0,249	0,9390	4,834E-03	b	1,471E-03	1,528E-02
11/2009	PTB grav	0,247	0,8976	4,671E-03	b	-4,000E-02	1,507E-02
12/2009	PTB	0,246	0,9236	4,873E-03	b	-1,397E-02	1,533E-02
01/2010	INM	0,252	0,9112	4,662E-03	а	-2,635E-02	1,506E-02
02/2010	GUM	0,250	0,9337	5,869E-03	b	-3,859E-03	1,667E-02
03/2010	BEV	0,250	0,9332	1,680E-02	а	-4,353E-03	3,562E-02
04/2010	LNE	0,250	0,9620	1,408E-02	b	2,443E-02	3,054E-02
05/2010	LNE	0,250	0,9312	1,429E-02	b	-6,374E-03	3,093E-02
07/2010	PTB	0,249	0,9380	4,680E-03	b	4,259E-04	1,509E-02
09/2010	METAS	0,251	0,9450	5,535E-03	b	7,377E-03	1,620E-02
11/2010	PTB	0,250	0,9276	4,740E-03	b	-9,974E-03	1,516E-02

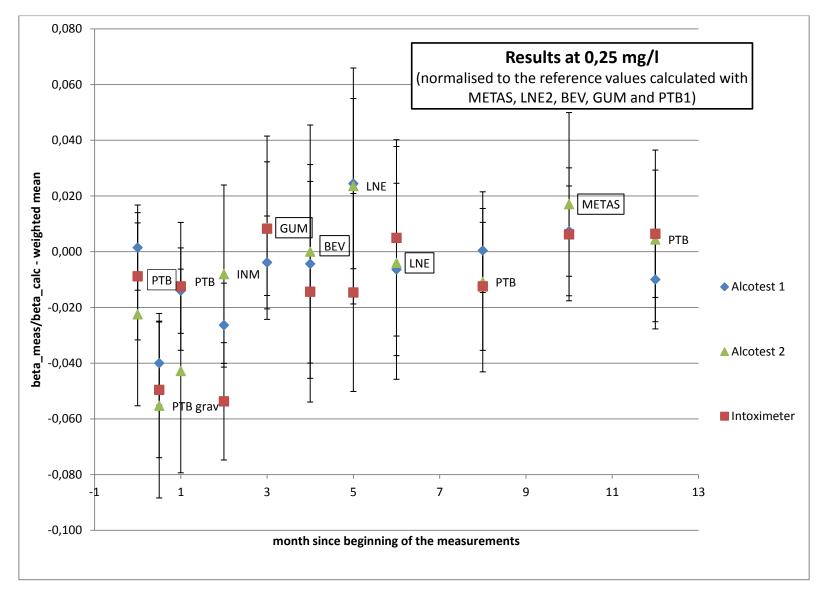
**Table3:** Data for 0,25 mg/l at analyzing system 1 of Alcotest– weighted mean out of the results of GUM, BEV, LNE2, METAS and PTB1: 0,9376

Month/year	Institute (k)	mean of the target values in mg/l	$A_{2,k}$	u_rel(A <sub>2,k</sub> )	u(A <sub>2,k</sub> ) calc. as SSR (b) or given by lab(a)	D <sub>2,k</sub>	U(D <sub>2,j</sub> ) (cov.factor k=2)
11/2009	PTB	0,249	0,9607	5,901E-03	b	-2,249E-02	3,282E-02
11/2009	PTB grav	0,247	0,9279	6,298E-03	b	-5,528E-02	3,311E-02
12/2009	PTB	0,246	0,9404	9,978E-03	b	-4,282E-02	3,655E-02
01/2010	INM	0,252	0,9751	4,662E-03	а	-8,072E-03	3,201E-02
02/2010	GUM	0,250	0,9918	6,012E-03	b	8,603E-03	3,290E-02
03/2010	BEV	0,250	0,9832	1,680E-02	а	6,049E-06	4,546E-02
04/2010	LNE	0,250	1,0068	1,462E-02	b	2,358E-02	4,234E-02
05/2010	LNE	0,250	0,9792	1,422E-02	b	-4,019E-03	4,178E-02
07/2010	PTB	0,249	0,9724	5,164E-03	b	-1,082E-02	3,231E-02
09/2010	METAS	0,251	1,0003	5,981E-03	b	1,706E-02	3,287E-02
11/2010	PTB	0,250	0,9876	4,811E-03	b	4,381E-03	3,210E-02

**Table 4:** Data for 0,25 mg/l at analyzing system 2 of Alcotest– weighted mean out of the results of GUM, BEV, LNE2, METAS and PTB1: 0,9832

Month/year	Institute (k)	mean of the target values in mg/l	A <sub>3,k</sub>	u_rel(A <sub>3,k</sub> )	u(A <sub>3,k</sub> ) calc. as SSR (b) or given by lab(a)	$D_{3,k}$	U(D <sub>3,j</sub> ) (cov. factor k=2)
11/2009	PTB	0,247	1,0278	4,451E-03	b	-8,830E-03	2,284E-02
11/2009	PTB grav	0,247	0,9870	6,127E-03	b	-4,959E-02	2,434E-02
12/2009	PTB	0,246	1,0242	4,586E-03	b	-1,244E-02	2,295E-02
01/2010	INM	0,252	0,9829	5,040E-04	а	-5,370E-02	2,106E-02
02/2010	GUM	0,250	1,0449	5,763E-03	b	8,261E-03	2,398E-02
03/2010	BEV	0,250	1,0223	1,677E-02	а	-1,437E-02	3,959E-02
04/2010	LNE	0,250	1,0220	1,431E-02	b	-1,464E-02	3,553E-02
05/2010	LNE	0,250	1,0416	1,413E-02	b	4,962E-03	3,523E-02
07/2010	PTB	0,249	1,0242	4,614E-03	b	-1,244E-02	2,297E-02
09/2010	METAS	0,251	1,0429	5,631E-03	b	6,231E-03	2,386E-02
11/2010	PTB	0,250	1,0431	4,471E-03	b	6,433E-03	2,286E-02

**Table 5:** Data for 0,25 mg/l at analyzing system 3 of Intox – weighted mean out of the results of GUM, BEV, LNE2, METAS and PTB1: 1,037



*Diagram 3* Deviations of calculated relative measurement results from the weighted mean at 0,25 mg/l (all results)

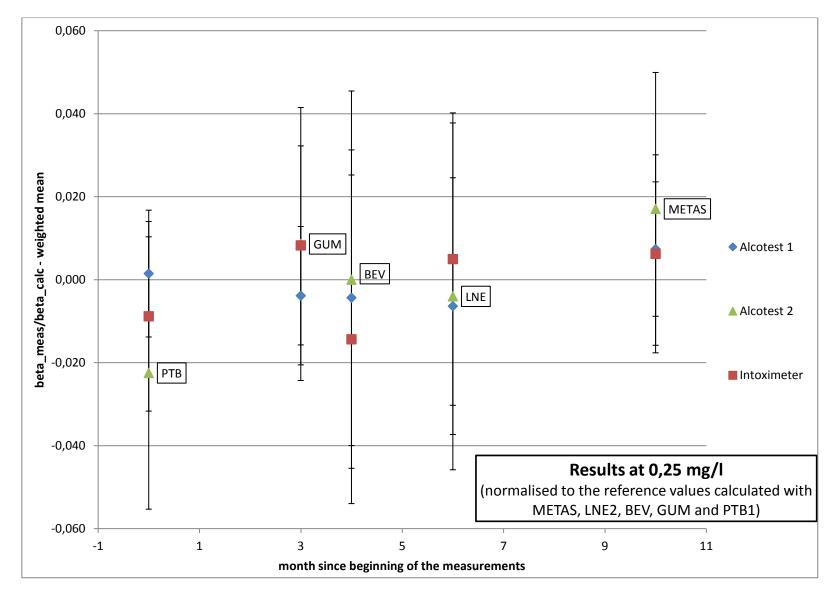


Diagram 4 Deviations of calculated relative measurement results from the weighted mean at 0,25 mg/l

Month/year	Institute (k)	mean of the target values in mg/l	$A_{1,k}$	u_rel(A <sub>1,k</sub> )	u(A <sub>1,k</sub> ) calc. as SSR (b) or given by lab(a)	$D_{1,k}$	U(D <sub>1,j</sub> ) (k=2)
11/2009	PTB	0,398	0,9717	1,028E-02	b	-1,107E-02	3,749E-02
11/2009	PTB grav	0,409	0,9112	6,452E-03	b	-7,152E-02	3,390E-02
12/2009	PTB	0,398	0,9835	1,014E-02	b	7,256E-04	3,734E-02
01/2010	INM	0,408	0,9769	6,120E-03	а	-5,853E-03	3,366E-02
02/2010	GUM	0,400	0,9897	5,967E-03	b	6,889E-03	3,355E-02
03/2010	BEV	0,400	0,9601	1,050E-02	а	-2,271E-02	3,774E-02
04/2010	LNE	0,400	1,0102	5,085E-03	b	2,748E-02	3,296E-02
05/2010	LNE	0,401	0,9925	5,125E-03	b	9,740E-03	3,299E-02
07/2010	PTB	0,399	0,9616	1,022E-02	b	-2,112E-02	3,743E-02
09/2010	METAS	0,402	0,9954	3,929E-03	b	1,266E-02	3,232E-02
11/2010	PTB	0,398	0,9875	1,015E-02	b	4,742E-03	3,735E-02

**Table 6:** Data for 0,4 mg/l at analyzing system 1 of Alcotest– weighted mean out of the results of GUM, BEV, LNE2, METAS, PTB1( marked values): 0,9828

Month/year	Institute (k)	mean of the target values in mg/l	$A_{2,k}$	u_rel(A <sub>2,k</sub> )	u(A <sub>2,k</sub> ) calc. as SSR (b) or given by lab(a)	$D_{2,k}$	U(D <sub>2,j</sub> ) (k=2)
11/2009	PTB	0,398	0,9438	1,014E-02	b	2,998E-03	3,176E-02
11/2009	PTB grav	0,409	0,9054	6,188E-03	b	-3,545E-02	2,739E-02
12/2009	PTB	0,398	0,9442	1,014E-02	b	3,400E-03	3,176E-02
01/2010	INM	0,408	0,9218	6,120E-03	а	-1,899E-02	2,733E-02
02/2010	GUM	0,400	0,9372	5,848E-03	b	-3,660E-03	2,709E-02
03/2010	BEV	0,400	0,9213	1,050E-02	а	-1,953E-02	3,222E-02
04/2010	LNE	0,400	0,9683	5,074E-03	b	2,743E-02	2,646E-02
05/2010	LNE	0,401	0,9453	4,983E-03	b	4,485E-03	2,639E-02
07/2010	PTB	0,399	0,9208	1,016E-02	b	-2,005E-02	3,178E-02
09/2010	METAS	0,402	0,9529	3,688E-03	b	1,205E-02	2,553E-02
11/2010	PTB	0,398	0,9308	1,010E-02	b	-1,005E-02	3,170E-02

**Table 7:** Data for 0,4 mg/l at analyzing system 2 of Alcotest– weighted mean out of the results of GUM, BEV, LNE2, METAS, PTB1: 0,9408

Month/year	Institute (k)	mean of the target values in mg/l	$A_{3,k}$	u_rel(A <sub>3,k</sub> )	u(A <sub>3,k</sub> ) calc. as SSR (b) or given by lab(a)	$D_{3,k}$	U(D <sub>3,j</sub> ) (k=2)
11/2009	PTB	0,398	1,0277	1,074E-02	b	-1,683E-03	2,889E-02
11/2009	PTB grav	0,409	0,9817	7,257E-03	b	-4,769E-02	2,416E-02
12/2009	PTB	0,398	1,0279	1,078E-02	b	-1,432E-03	2,894E-02
01/2010	INM	0,408	0,9956	1,471E-02	а	-3,376E-02	3,518E-02
02/2010	GUM	0,400	1,0357	6,044E-03	b	6,316E-03	2,278E-02
03/2010	BEV	0,400	1,0156	4,200E-03	а	-1,375E-02	2,106E-02
04/2010	LNE	0,400	1,0143	5,215E-03	b	-1,510E-02	2,195E-02
05/2010	LNE	0,400	1,0275	5,170E-03	b	-1,858E-03	2,190E-02
07/2010	PTB	0,398	1,0081	1,074E-02	b	-2,126E-02	2,888E-02
09/2010	METAS	0,402	1,0402	4,034E-03	b	1,085E-02	2,093E-02
11/2010	PTB	0,398	1,0159	1,076E-02	b	-1,348E-02	2,892E-02

**Table 8:** Data for 0,4 mg/l at analyzing system 3 of Intox – weighted mean out of the results of GUM, BEV, LNE2, METAS and PTB1: 1,029

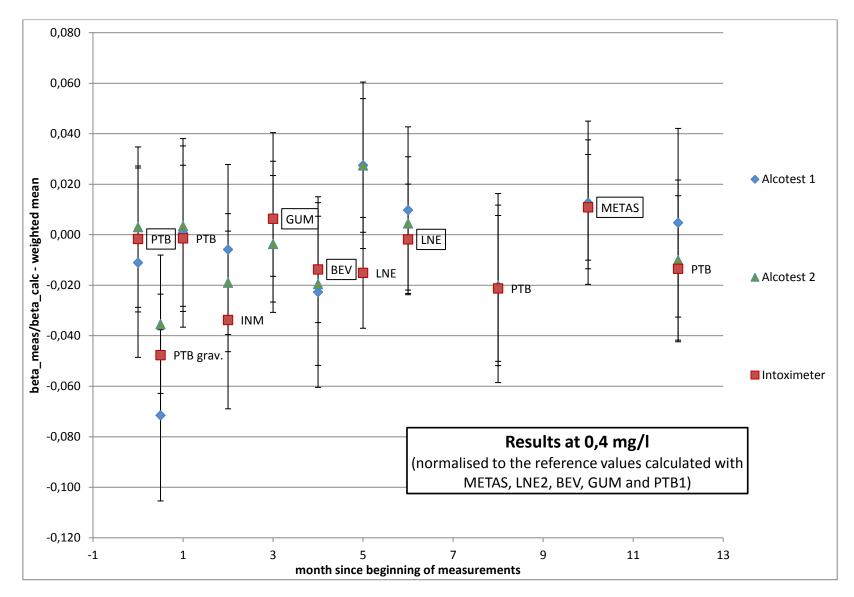


Diagram 5 Deviations of calculated relative measurement results from the weighted mean at 0,4 mg/l (all results)

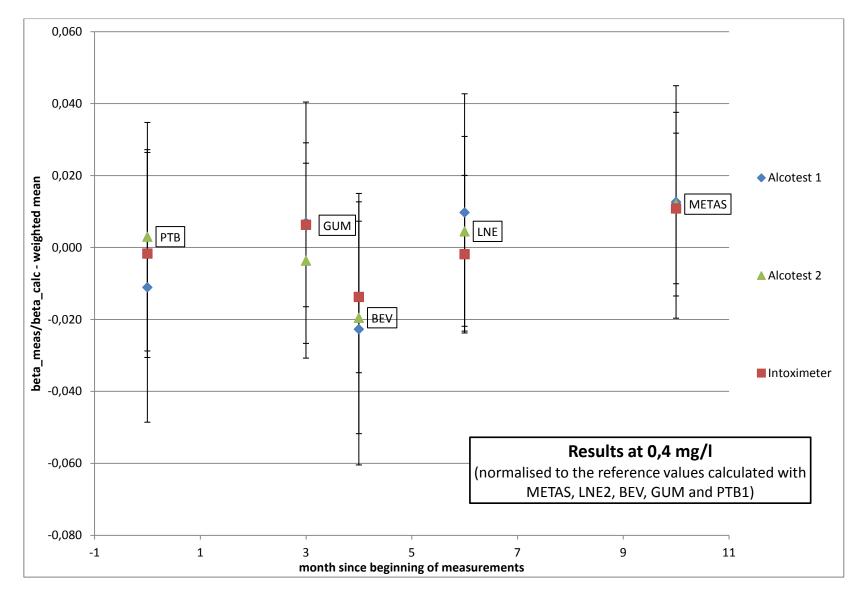


Diagram 6 Deviations of calculated relative measurement results from the weighted mean at 0,4 mg/l

## 3.5 Conclusion

The results at both ethanol mass concentrations show, that the calibration gas generators used within this comparison agree better than  $\pm 2,5$  %. Main contribution of the uncertainty is the variation of the results between the laboratories. The results of the test instruments of the pilot lab show variations within the size of the comparison results over the meantime of the comparison. As the measurements were prepared by different persons, probably the influences of the generator/instrument handling seem to be larger than the drift of the instruments. If one wants to interpret the quality of the used transfer instruments it has to be taken into account, that the Alcotest was not used in the usual measurement mode. The final result of it is calculated from the two measurement values generated by the two sensor systems. Thus the final results are usually more stable.

It is expected that the influences of the temperature and pressure within the mixture generators and within the instruments are not recognized adequately. The two results of LNE promote the idea of pressure influences because the measurements with hardly different flows show, as expected, very divergent results. For the preparation of these gas mixtures at LNE no bubble-train was used. Thus, systematic influences of the generators can be excluded here. Future comparisons in this field should take such aspects more into account.

It would be scientifically interesting to find out the reasons for the difference between the "absolute" gravimetric generation system and the "usual" bubble-trains basing on Henrys Law. Influences of temperature and pressure are here expected as well to play a key role in this explanation.

## 4 References

- [1] Sonja Pratzler *et al* 2010 *J. Breath Res.* **4** 036004, Preparation of calibration gas mixtures for the measurement of breath alcohol concentration
- [2] OIML R126:1998, Evidential breath analyzers