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Second EC-JRC aromatic compounds intercomparison with automatic analyzer

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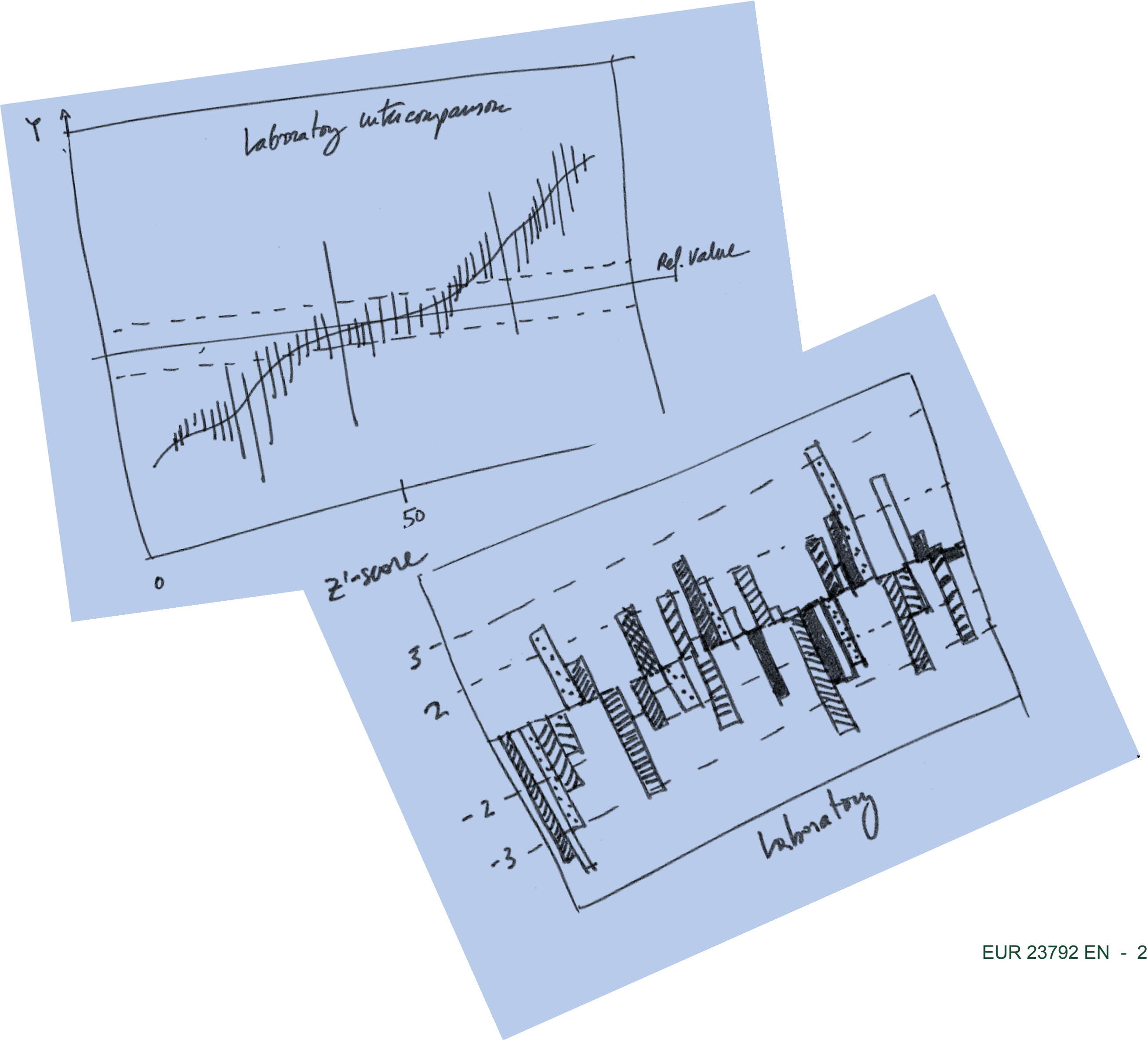

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Executive Summary

This report presents the results of the second intercomparison for BTEX automatic analysers carried out by the JRC on the 17-19 June 2008. Seven national reference laboratories participated in this exercise. Six concentrations levels were tested during the intercomparison, ranging from circa 3 to 50 µg/m^3, for benzene. With respect to the first intercomparison carried out in 2005, the reference value was assigned by ERLAP and the exercise was evaluated according to ISO 13528 methodologies for the evaluation of interlaboratory proficiency assessment and the recommendation of the protocol N37 of the AQUILA network. Participating laboratories are identified as requested by the AQUILA for further actions.

In general, the results of the exercise show no changes in the performance of the method with respect to the previous exercise. The robustness of the method is still an issue in particular for benzene. This is reflected in a relatively high inter-laboratory reproducibility standard deviation. As a consequence, the criterion for the standard deviation for proficiency assessment proposed in the AQUILA protocol seems to be very restrictive for the current performance of the methodology, this may require future harmonisation actions in the implemented methodology.

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Nomenclature and abbreviations

AEAT: AEA technology
AQUILA: air quality reference laboratories
BTEX: benzene, toluene, ethyl-benzene, xylene
CG: gas chromatograph
CHMI: Czech Hydrometorological Institute
D.D.: Dynamic Dilution
EEA; Executive environment Agency
EC: European Commission
ERLAP: European Reference Laboratory of Air Pollution
EU: European Union
FID: flame ionization detector
H.C.: hydrocarbons
ISCIII: Instituto de Salud Carlos III
ISO: International Standard Organisation
LV: limit value
QAQC: quality assurance quality control
NERI: Danmark Miljoundersogelser
n.p.: non provided information
NPL: National Physical Laboratory
NRL: National Reference Laboratory
PID: photo ionization detector
ppb (m/m): part per billion, molar fraction
Press. Cyl.: presssurised cylinder
RIVM: National Institute for Public Health and the Environment
Tr. Std.: travelling standard
UBA: Federal Environment Agency, Germany

$\overline{C}_i$: average concentration value of i measurements
$\overline{\overline{C}}$: interlaboratory average concentration
$\overline{C}_i^*$: robust average value
C_{ref}: reference concentration value
k_i: Mendel-k value for laboratory i
n: number of replicated analysis
p: number of participating laboratories
P(Z): probability function of the random variable Z.
R_c: residuals of the linear regression $\overline{C}_i$ vs C_{ref} at the evaluated concentration level, C
s^*: standard deviation of the robust average value $\overline{C}_i^*$
$S_{\bar{c}_i}$: standard deviation of the average inter-laboratory value
s_i: standard deviation of the sample i.
s_L^2: interlaboratory variance or between-laboratory variance

$s_{L_{N37}} = \sqrt{\hat{\sigma}_{N37}^2 - \frac{s_r^2}{n}}$: between laboratory standard deviation from the prescript conditions of proficiency assessment of AQUILA network.

s_r^2: repeatability variance or intra-laboratory variance
s_R^2: reproducibility variance
s_{bias}: standard deviation of the bias $\overline{C}_i^* - C_{ref}$
u: uncertainty of the method
u_{Cref}: uncertainty associated with the reference concentration value C_{ref}
Z : random variable $Z = \frac{\overline{C}_i^* - C_{ref}}{s_{bias}}$

$Z' - score = \frac{\overline{C}_i - C_{ref}}{\sqrt{\hat{\sigma}^2 + u_{C_{ref}}^2}}$

Z'-score(N37): Z'-score where the standard deviation is that prescript by AQUILA network
Z: random variable
µg/m^3: micrograms per cubic meter

α: level of significance
$\gamma = s_R/s_r$: gamma value
σ: standard deviation
$\hat{\sigma}$: standard deviation for proficiency assessment
$\hat{\sigma}_m = \sqrt{(0.5 \cdot s_L)^2 + \frac{s_r^2}{n}}$: minimum standard deviation of proficiency assessment coherent with method reproducibility
$\hat{\sigma}_{N37}$: standard deviation for proficiency assessment prescript by AQUILA network
(1-α): confidence level

Introduction

In accordance with the new EC directive 2008/50/EC and following on from the first EC-JRC aromatic BTEX intercomparison with automatic analysers [EUR 22523 EN], this intercomparison exercise follows the QAQC programme for the harmonization of air quality measurements in Europe and, in particular, for benzene.

In contrast to the first intercomparison organised in October 2005, this exercise only focused on a laboratory's capacity to quantify the analyte of interest over a pre-defined range of concentrations. The duration of the exercise was consequently reduced with respect to the previous intercomparison and any effect from possible interferences, such as humidity or ozone was not considered. This report applies the criteria of proficiency agreed on by the AQUILA network for the organization of intercomparison exercises in the framework of the EU National Air Quality Laboratories (NRLs) and those from the WHO Euro region. AQUILA requested that the laboratories be identified in the report for further actions.

Intercomparison strategy

The intercomparison was carried out at the JRC Ispra site bench facilities from 17th to 19th June 2008. Registration of the participants was closed on the 31st March 2008.
The exercise was performed according to the working agenda given in the Annex. After a zero air check, six concentration levels were tested at the increasing and decreasing concentration. Time for calibration of the instruments was given at the beginning and at the end of the concentration test. Laboratories were asked to perform 6 measurements for each concentration level on the basis of 15 minute analysis, the first measurement at each concentration level being excluded from the data analysis. Data were reported according to a predefined format.

Participating laboratories and instrumentation

Seven NRLs participated in the intercomparison exercise. Table 1 shows the name of the participating laboratories. RIVM participated with two instruments.

Table 2 identifies the type of instrumentation used by each laboratory, with the exception of one instrument that had a flame ionization detector (FID), the instruments used a photo ionization detector (PID). Table 3 shows the reference material or travelling standard used by each laboratory to calibrate the analyser.

Table 1.- List of participating laboratories

Acronym	**Laboratory**	**Country**	**Contact**
ISCIII	Instituto de Salud Carlos III	Spain	Rosalia Fernandez Patier, Pilar Morillo, Oscar Gonzalez
EEA	Executive Environment Agency	Bulgaria	Nikolay Panayotov
NERI	Danmark Miljoundersogelser, National Environmental Research Institute	Denmark	Henrik Skov, Hans Nielsen, Hans Ahleson
UBA	EU-Reference Laboratory for Air Quality (Federal Environment Agency)	Germany	Stephan Rutschewski Alexandrina Schuster
CHMI	Czech Hydrometorological Institute	Czech Republic	Jiri Novak, Miroslav Vokoun
RIVM	National Institute for Public Health and the Environment	The Netherland	Camelia van Zwol, Hans Verboom
AEAT	AEA Technology	United Kingdom	Peter Dumitrean, Steve Telling

Table 2.- Instrumentation used by the participating laboratories during the intercomparison exercise

Code	**Analyser**	**Detector**	**Column:** Length, i.d.*, film tickness Operational conditions	**Adsorbent** Desorption conditions
Carlos III	SYNTECH SPECTRAS Analyser GC 955, 2004	PID	**AT-624:** 13 m, 0.32 mm, 1.8 µm 50°C (3’),6.6°C/min,70°C (5’) 6.6°C/min 90°C	**Tenax GR** 180°C for 40 s, 1.5 ml/min
EEA	SYNTECH SPECTRAS GC 855, 2004	PID	**AT-5:** 13 m, 0.32 mm, 1 µm --°C (--),---°C/min,---°C	**Tenax GR** 180°C for 30 s, 0.5 ml/min
NERI	Airmotec airmoBTX HC 1000, 2004	FID	**DB-624:** 12 m, 0.20 mm, 1.12 µm 40°C, ---°C/min, 140°C	**Carbotrap-B** 350°C for 180 s, 2 ml/min
UBA	SYNTECH SPECTRAS Analyser GC 955, 2005	PID	**AT-624:** 13 m, 0.32 mm, 1.8 µm 60°C (3’),6.6°C/min,80°C (5’)	**Tenax GR** 180°C for 54 s, 1.5 ml/min
CHMI	SYNTECH SPECTRAS GC 855	PID	**AT-624:** 13 m, 0.32 mm, 1.8 µm 50°C (240 s),10°C/min,70°C	**Tenax GR** 180°C for 40 s, 1.8 ml/min
RIVM-1	SYNTECH SPECTRAS Analyser GC 955, 2007	PID	**AT-5:** 13 m, 0.32 mm, 1 µm 50°C , 10 °C/min,70°C (7’)	**Tenax GR** 180°C for 30 s, 1.5 ml/min
RIVM-2	SYNTECH SPECTRAS Analyser GC 955, 2007	PID	**AT-5:** 13 m, 0.32 mm, 1 µm 50°C , 10 °C/min,70°C (7’)	**Tenax GR** 180°C for 30 s, 1.5 ml/min
AEAT	Environnement SA.VOC 71M	PID	**SPB-624:** 13 m, 0.32 mm, 1.8 µm 34°C (115 s),20°C/min,150°C (155 s)	**Carbotrap/Carbopak-X** 350°C for 180 s, 1 ml/min

Table 3.- Reference material used by the participating laboratories

Laboratory	**Reference Material**	**Benzene** ppb(m/m)*	**Toluene** ppb(m/m)*	**Ethyl-benzene** ppb(m/m)*	**m-Xylene** ppb(m/m)*	**p-Xylene** ppb(m/m)*	**o-Xylene** ppb(m/m)*	**Other compounds**	**Producer**	**Certified by**	**Certification date**
ISCIII	Press. Cyl. **D.D.** (API model 700)	500 ± 15	487 ± 15	254 ± 7	128 ± 4	124 ± 4	243 ± 7	_	NMI	NMI	14/01/2008
EEA	Press. Cyl. **D.D.**	150 ± 4.5	_	_	_	_	_	_	Linde Gas	NPL	n.p.
NERI	Press. Cyl.	18 ±1	22 ± 2	_	_	_	20 ± 2	_	Air Liquid	Air Liquid	19/12/2005
UBA	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	n.p.	By own laboratory. Static Volumetric method	n.p.
CHMI	Press. Cyl. **Tr. Std.:** (Canister Silcosteel)	10.22 ± 0.36	10.14 ± 0.56	10.64 ± 0.64	21.1 ± 1.3		10.36 ± .65	_	NPL	By own laboratory	11/06/2008
RIVM	Press. Cyl. **D.D.** (Sonimix 6000 C)	100 ± 5	_	_	_	_	_	_	Lindegas Benelux	By own laboratory	n.p.
AEAT	Press. Cyl.	3.76 ± 0.08	3.78 ± 0.08	3.81 ± 0.08	3.78 ± 0.08	3.80 ± 0.08	3.80 ± 0.08	30 H.C. mixture.	NPL	NPL	n.p.

Press. Cyl.: Pressurised cylinder; D.D.: Dynamic Dilution; Tr. Std.: Travelling Standard; H.C.: Hydrocarbons; n.p.: non provided information

**: ppb(m/m): concentration in part per billion with respect to molar fraction ± its expanded uncertainty.*

Reference value

In accordance with AQUILA document N37 “Protocol for intercomparison exercise”, the measurements performed by The European Reference Laboratory of Air Pollution (ERLAP) were taken as the reference value. These measurements were traceable to gravimetric international standards (NPL), which were also in agreement with concentrations generated by in-house primary reference material based on the dynamic and static dilution of permeation and volumetric injection.

Two instruments, a BTEX Chrompack mod. 7001 and a GC Agilent 6890 Series II coupled with an on-line sampling Turbomatrix Perkin Elmer thermal desorption system, were used by ERLAP to provide the reference value. A multipoint calibration over the operative range of the intercomparison was used to calibrate both instruments. Due to an important source of uncertainty over the calibration range being attributed to the linearity of the instrument, linear and log-linear calibration curves were applied to each pollutant according to the best correlation and the lower uncertainty calculated for the estimated reference value, thus avoiding the use of response factor. Uncertainties for the estimated concentrations for each instrument were calculated according to ISO 6143 and the final uncertainty for the average concentration was combined according to ISO GUM.

Figure 1 represents the associated uncertainties calculated for three different calibration modes (log-linear, linear and based on an average response factor), as well as the bias of the estimated value with respect to the lower uncertainty calibration method. These biases did not, however, represent significant differences.

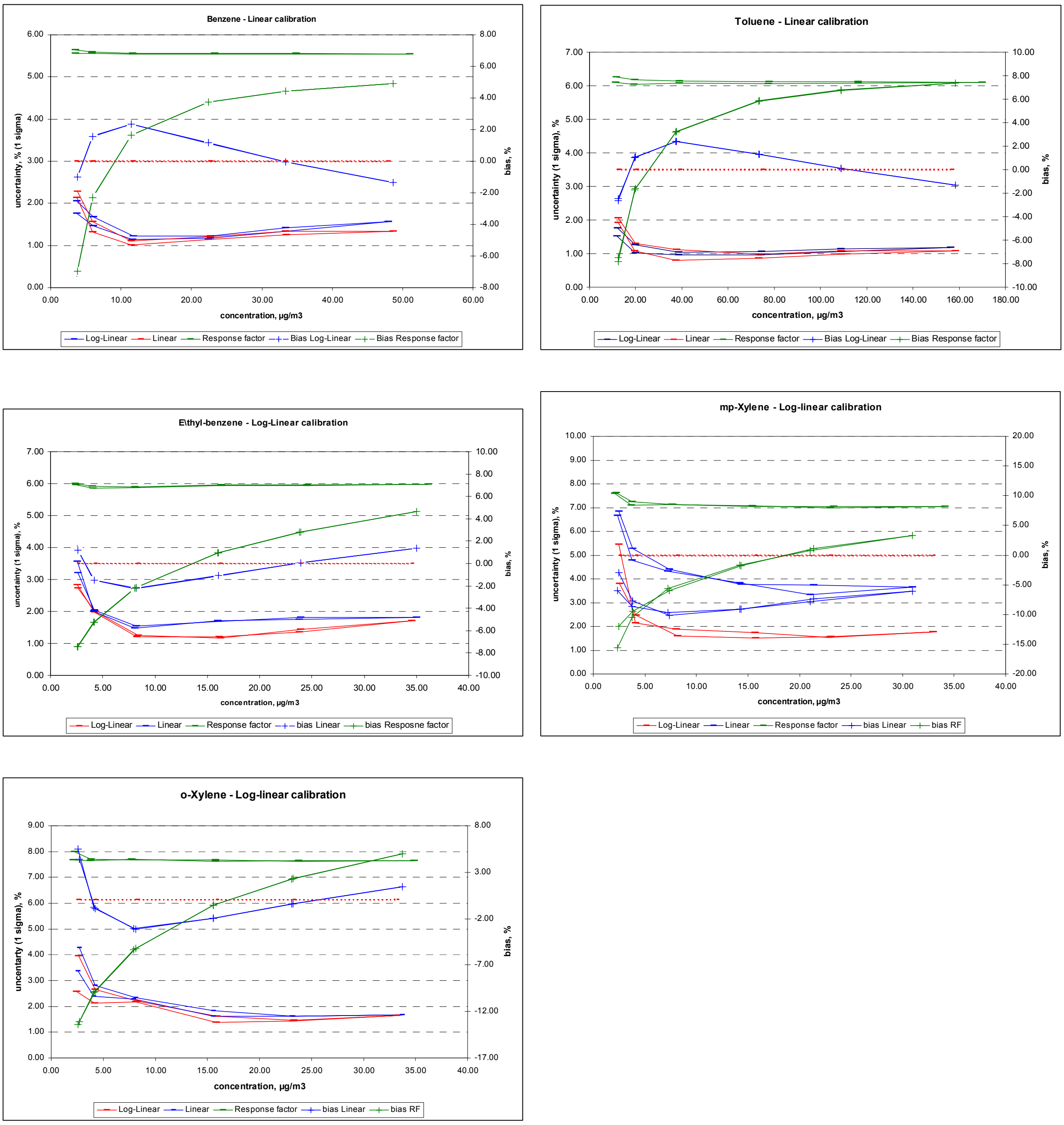


Figure 1.- Uncertainty of the different calibration modes (linear, Log-linear and response factor)

Testing concentration levels

Following the guidelines set out by the N37 AQUILA protocol, concentrations of benzene were tested in the range from 0 to 50 µg/m^3 at six different levels. The remaining aromatic compounds were related to benzene according to the following ratios: toluene/benzene: 3/1 and ethyl-benzene/benzene, mp-xylene/benzene and o-xylene/benzene: 2/3.

Table 4 shows the reference values and associated uncertainties for the different concentration levels of the exercise

Table 4.– Reference value and associated uncertainties

Level	*benzene*	*uncertainty (1σ), %*	*toluene*	*uncertainty (1σ), %*
1ST-A	3.75	2.14	12.32	1.92
2ND-A	5.99	1.33	19.65	1.08
3RD-A	11.42	1.02	37.51	0.80
4TH-A	22.44	1.15	73.21	0.87
5TH-A	33.43	1.25	108.88	0.98
6TH-A	48.60	1.33	158.35	1.08
5TH-B	33.37	1.34	108.83	1.07
4TH-B	22.43	1.20	73.41	0.99
3RTD-B	11.45	1.11	37.70	1.12
2ND-B	5.96	1.56	19.79	1.29
1ST-B	3.80	2.29	12.56	2.05

Level	*ethylbenzene*	*uncertainty (1σ), %*	*mp-xylene*	*uncertainty (1σ), %*
1ST-A	2.56	3.57	2.50	5.44
2ND-A	4.15	1.99	4.09	2.14
3RD-A	8.07	1.47	8.01	1.87
4TH-A	15.97	1.70	15.65	1.73
5TH-A	23.83	1.75	22.84	1.52
6TH-A	35.03	1.81	32.97	1.78
5TH-B	23.94	1.81	23.05	1.56
4TH-B	16.06	1.68	15.75	1.52
3RTD-B	8.18	1.55	8.18	1.59
2ND-B	4.19	2.04	4.14	2.45
1ST-B	2.63	3.21	2.53	3.79

Level	*o-xylene*	*uncertainty (1σ), %*
1ST-A	2.58	3.37
2ND-A	4.12	2.38
3RD-A	7.89	2.28
4TH-A	15.55	1.63
5TH-A	23.11	1.61
6TH-A	33.71	1.68
5TH-B	23.23	1.63
4TH-B	15.57	1.83
3RTD-B	8.09	2.33
2ND-B	4.20	2.82
1ST-B	2.72	4.27

Statistical considerations

Linearity test

Linearity of the analysers was tested according to EN14662-3 by comparing the average value of the reported results at each level and instrument, $\overline{C}_i$, with its respective reference value, C_{ref}, at this level. Residual, R_c, is calculated according to the following expression:

$$R_c = \overline{C}_i - (a + b \cdot C_{ref}) \qquad (1)$$

where *a* and *b* are the correlation coefficients of the corresponding linear regression ($\overline{C}_i$ vs C_{ref}). As a criterion of linearity, the maximum accepted value as residual is 5%.

Repeatability, reproducibility and robustness of the method

The repeatability and reproducibility derived from the intercomparison exercise results were calculated after the elimination of outliers identified by Mandel's h and k statistic:

The ***inter-laboratory consistency*** is determined by the statistic***, h,*** which represents the ratio between the bias of the measure with respect to the average value, $\overline{C_i}$, and the standard deviation of the average inter-laboratory values, $S_{\overline{C}_i}$.

The ***intra-laboratory consistency*** is determined by the statistic, ***k***, which is defined by the ratio between the laboratory standard deviation of the sample, **s_i**, and the pooled within-laboratory standard deviations:

$$k_i = \frac{s_i}{\sqrt{\frac{\sum s_i^2}{p}}} \qquad (2)$$

Indicators for Mandel's statistics at the 1 and 5 % of significance level are given in Annex. These values determine the outliers and stragglers, respectively.

Therefore, the uncertainty of the inter-laboratory average value, $\overline{\overline{C}}$, is determined by the combination of the inter-laboratory variance, s_L^2, and the intra-laboratory variance (repeatability variance), s_r^2. The addition of both variances represents the reproducibility variance, s_R^2, being in this case the variance associated with the uncertainty of the method [ISO 5725 Part 1, Part 2, 1994]:

$$u = \sqrt{s_L^2 + s_r^2} = s_R \qquad (3)$$

being

$$s_r^2 = \frac{1}{p}\sum_i^p s_i^2 \qquad (4)$$

$$s_R^2 = \frac{1}{p-1}\sum_i^p \left(\overline{C}_i - \overline{\overline{C}}\right)^2 + \left(1-\frac{1}{n}\right)\cdot s_r^2 \qquad (5)$$

where 'p' is the number of laboratories; 'n' is the number of replicated analyses done by each laboratory; 's_i' and '$\overline{C_i}$' are the standard deviation and average value corresponding to the laboratory 'i'.

The null hypothesis for equivalence between the inter-laboratory averages can be used as a criterion for the robustness of the method tested. Such an hypothesis assumes a F-distribution with p-1 and p(n-1) degrees of freedom for the statistic F defined by the ratio: $\frac{s_L^2}{s_r^2}$.

This unilateral test for the F-distribution statistic depends on the degrees of freedom (experimental design: number of participating laboratories and replicated samples) and the accepted significance level. As a conservative approach, methods with F-values lower than 3 can be considered as robust methods. This criterion expressed as a ratio between reproducibility and repeatability standard deviations implies gamma values, γ, lower than 2, being $\gamma = s_R/s_r$ [P. Pérez Ballesta et al., 2001].

Z’-score and repeatability score

Z’-score is used as an indication of the laboratory performance, which as described by ISO 13528 is calculated by the equation:

$$Z'\text{–}score = \frac{\overline{C}_i - C_{ref}}{\sqrt{\hat{\sigma}^2 + u_{C_{ref}}^2}} \tag{6}$$

where u_{Cref} is the uncertainty associated with the reference value and $\hat{\sigma}$ the standard deviation for proficiency assessment:

$$\hat{\sigma} = \sqrt{s_L^2 + \frac{s_r^2}{n}} = \sqrt{\frac{1}{p-1}\sum_{i}^{p}\left(\overline{C}_i - \overline{\overline{C}}\right)^2} \tag{7}$$

When the uncertainty of the reference value is negligible in comparison to the standard deviation of the proficiency assessement, the “Z’-score” becomes “Z-score” and equation (6) provides similar results to the k-value statistic. In this case, the critical values are, however, 2 and 3 for giving a warning and an action signal.

On the other hand, if the “standard deviation for proficiency assessment” is defined (for benzene) according to the AQUILA N37 recommendation, this, $\hat{\sigma}_{N37}$ is calculated as a function of the concentration level in µg/m^3, C, by the following equation:

$$\hat{\sigma}_{N37} = 0.128 + 0.057 \cdot C \tag{8}$$

The Z’-score calculated with the new $\hat{\sigma}_{N37}$ implies a more restrictive condition for acceptance of the results. Nevertheless, the Z’-score(N37) becomes, in this way, independent from the number of participating laboratories.

A repeatability score has been derived from the k-statistic in order to evaluate the performance criterion as established by EN 14662-3 for benzene automatic analysers, i.e. 5 % at the limit value and 0.3 % for values lower than 0.1 x LV. In this case the pooled-within-laboratory standard deviation is replaced by the corresponding maximum accepted repeatability value or, alternatively by the associated uncertainty of the reference value, when this value is limiting the repeatability test. Repeatability scores values lower than $\sqrt{2}$ are considered acceptable, between $\sqrt{2}$ and $\sqrt{3}$ are questionable and higher than $\sqrt{3}$, i.e. out of the 99 % confidence level, are considered as poor performance.

Results and discussion

Not all laboratories provided results for all the tested compounds: EEA only provided results for benzene; NERI did not report ethyl benzene and mp-xylene.

Linearity test

Table 5 shows the results of the lineary test for the correlation between reported and reference value. Residuals were calculated by equation (1). In this table the percentage of residual was indicated for those values higher thant 5 %. Values were highlighted in red when this was higher than 10 %. In general, linearity was better for benzene when compared to other aromatic compounds.

Table 5.- Results of the linearity test in percent of residual value

BENZENE	Carlos III	EEA	NERI	UBA	CHMI	RIVM1	RIVM2	AEAT
1st –A	OK	-7	OK	OK	-11	-9	32	26
2nd –A	OK	OK	OK	OK	OK	-6	OK	OK
3rd -A	OK	OK	OK	OK	OK	OK	-9	-16
4th -A	OK	OK	OK	OK	OK	OK	-6	-34
5th -A	-5	OK	OK	OK	OK	OK	OK	-19
6th	OK	OK	OK	OK	OK	OK	OK	8
5th -B	OK	OK	OK	OK	OK	OK	OK	OK
4th -B	OK	OK	OK	OK	OK	OK	OK	27
3rd -B	OK	OK	OK	OK	OK	5	-6	OK
2nd -B	8	OK	OK	OK	OK	OK	6	25
1st -B	7	OK	OK	OK	-7	-6	30	41
TOLUENE	**Carlos III**	**EEA**	**NERI**	**UBA**	**CHMI**	**RIVM1**	**RIVM2**	**AEAT**
1st -A	OK	-	-38	-38	OK	19	OK	-102
2nd -A	OK	-	-15	-12	-11	6	OK	-27
3rd -A	OK	-	OK	13	-10	-7	OK	25
4th -A	-	-	10	16	OK	-11	OK	19
5th -A	-	-	6	-7	OK	-6	OK	OK
6th	-	-	-9	-	OK	6	OK	-9
5th -B	-	-	6	-7	OK	OK	OK	6
4th -B	-	-	11	15	OK	-6	OK	10
3rd -B	OK	-	OK	10	OK	OK	OK	32
2nd -B	OK	-	-14	-15	OK	17	OK	-17
1st -B	OK	-	-33	-40	7	33	OK	-85
ETHYLBENZENE	**Carlos III**	**EEA**	**NERI**	**UBA**	**CHMI**	**RIVM1**	**RIVM2**	**AEAT**
1st -A	29	-	-	-40	20	-12	-17	OK
2nd -A	OK	-	-	-5	9	OK	OK	OK
3rd -A	-8	-	-	11	-7	OK	OK	OK
4th -A	-7	-	-	-	-6	OK	OK	-7
5th -A	OK	-	-	OK	OK	OK	OK	OK
6th	OK	-	-	OK	OK	OK	OK	OK
5th -B	OK	-	-	OK	OK	OK	OK	OK
4th -B	OK	-	-	OK	OK	OK	OK	6
3rd -B	OK	-	-	9	OK	OK	7	OK
2nd -B	15	-	-	-6	13	6	7	12
1st –B	40	-	-	-37	28	OK	-7	16
MP-XYLENE	**Carlos III**	**EEA**	**NERI**	**UBA**	**CHMI**	**RIVM1**	**RIVM2**	**AEAT**
1st –A	OK	-	-	-12	13	OK	OK	OK
2nd –A	-7	-	-	5	8	OK	7	OK
3rd –A	-8	-	-	10	-15	-6	OK	-5
4th –A	OK	-	-	OK	OK	-8	-6	-10
5th –A	OK	-	-	OK	OK	OK	OK	-6
6th	OK	-	-	OK	OK	OK	OK	OK
5th –B	OK	-	-	OK	OK	OK	OK	OK
4th –B	OK	-	-	OK	OK	OK	OK	OK
3rd –B	OK	-	-	5	OK	OK	OK	OK
2nd –B	8	-	-	OK	14	14	10	15
1st –B	18	-	-	-21	25	17	10	28
O-XYLENE	**Carlos III**	**EEA**	**NERI**	**UBA**	**CHMI**	**RIVM1**	**RIVM2**	**AEAT**
1st –A	27	-	11	-38	OK	-27	-24	OK
2nd –A	OK	-	OK	-8	8	OK	OK	-5
3rd –A	-10	-	OK	13	-6	OK	8	OK
4th –A	-8	-	OK	11	-6	OK	OK	-9
5th –A	OK	-	OK	OK	OK	OK	OK	-6
6th	OK	-	OK	OK	OK	OK	OK	OK
5th –B	OK	-	OK	OK	OK	OK	OK	OK
4th –B	OK	-	OK	7	OK	OK	OK	5
3rd –B	OK	-	OK	8	OK	10	8	8
2nd –B	11	-	OK	-14	9	5	OK	10
1st –B	32	-	OK	-45	12	-15	-19	10

OK: Residual < 5 %,   -: result not provided by the participant

Comparison between reference and robust average value

Assigned values acting as reference can be compared to the robust average derived from the results of the interlaboratory round. The robust average value, $\overline{C}_i^*$, and its standard deviation, s^*, is calculated according to ISO 13528 (robust analysis in the Annex).

Assuming a normal distribution for the bias, $\overline{C}_i^* - C_{ref}$, the associated standard uncertainty is estimated as:

$$s_{bias} = \sqrt{\frac{(1.25 \cdot s^*)^2}{p} + u_{C_{ref}}^2} \tag{9}$$

where p is the number of participating laboratories.

The null hypothesis for a bias equal to zero can be evaluated using the two tails statistical test of normal distribution of the random variable, Z, defined as:

$$Z = \frac{\overline{C}_i^* - C_{ref}}{s_{bias}} \tag{10}$$

which defines the probability function of the distribution for a confidence level of $(1-\alpha)$:

$$P(-Z_{1-\alpha/2} < Z < -Z_{1-\alpha/2}) = 1 - \alpha \tag{11}$$

α represent the level of significance of the test. P values lower than 0.95 imply no significant bias and the bias becomes significant with the increase of the P value.

Table 6 shows the results of the statistical test. Significant biases with α values lower than 0.01 were detected at the beginning of the exercise for the first and second levels for toluene, where the robust average seems to underestimate the reference concentration, such a bias becoming negligible for similar concentrations levels during the decreasing concentration stage of the exercise. These differences could be attributed to the general need for a longer warming up period. A significant overestimation of the lowest levels of concentration for o-xylene was also noted. This could be due to the high blank level, which characterises the analysis of the heaviest aromatic compounds. In a similar way, a significant positive bias was also identified for the second level of decreasing concentrations, (2ND-B) of mp-xylene.

In general, these results confirm the reference value and associated uncertainty as coherent with the robust average value of the intercomparison.

Table 6.- Level of significant of the bias between the reference and robust average value

Level	Benzene	α	Bias, %	Toluene	α	Bias, %
1ST-A	3.75	0.424	4.61	12.32	**7.38E-05▪**	-11.14
2ND-A	5.99	0.095	7.73	19.65	**5.42E-05▪**	-5.43
3RD-A	11.42	0.072	11.41	37.51	0.391	2.42
4TH-A	22.44	0.168	12.46	73.21	0.349	3.73
5TH-A	33.43	0.211	15.09	108.88	0.764	-3.43
6TH-A	48.6	0.126	18.00	158.35	0.474	-14.17
5TH-B	33.37	0.172	16.25	108.83	0.859	-2.19
4TH-B	22.43	0.126	15.67	73.41	0.228	5.61
3RD-B	11.45	0.052	14.28	37.7	0.023*	7.10
2ND-B	5.96	0.035*	12.20	19.79	0.980	-0.10
1ST-B	3.8	0.168	7.36	12.56	0.879	2.05

Level	Ethyl-benzene	α	Bias, %	mp-Xylene	α	Bias, %
1ST-A	2.56	0.089	-11.97	2.5	0.540	5.44
2ND-A	4.15	0.050	-5.98	4.09	0.581	2.14
3RD-A	8.07	0.507	-1.36	8.01	0.157	1.87
4TH-A	15.97	0.374	-4.28	15.65	0.672	1.73
5TH-A	23.83	0.852	0.85	22.84	0.264	1.52
6TH-A	35.03	0.637	1.98	32.97	0.080	1.78
5TH-B	23.94	0.562	2.65	23.05	0.128	1.56
4TH-B	16.06	0.646	2.29	15.75	0.271	1.52
3RD-B	8.18	0.087	3.77	8.18	0.165	1.59
2ND-B	4.19	0.345	4.80	4.14	**5.06E-07▪**	2.45
1ST-B	2.63	0.828	-1.38	2.53	0.279	3.79

Level	o-Xylene	α	Bias, %
1ST-A	2.58	**0.001▪**	3.37
2ND-A	4.12	0.389	2.38
3RD-A	7.89	0.573	2.28
4TH-A	15.55	0.408	1.63
5TH-A	23.11	0.273	1.61
6TH-A	33.71	0.562	1.68
5TH-B	23.23	0.600	1.63
4TH-B	15.57	0.811	1.83
3RD-B	8.09	0.961	2.33
2ND-B	4.2	0.673	2.82
1ST-B	2.72	0.010*	4.27

*: 95-99 % confidence level, (1- α)
▪ : > 99% confidence level, (1- α)

Repeatability, reproducibility and robustness of the method

As indicated in the previous section, repeatability and reproducibility standard deviation were calculated after elimination of the outliers identified by the k and h statistics. The results of these statistics are shown in the Annex. The values of repeatability and reproducibility standard deviation and associated uncertainties are represented in Figure 2 for each compound and tested concentration.

The values of repeatability and reproducibility from Figure 2 have a relatively high uncertainty because of the limited number of participants. Although those values generally agree with the results from the previous exercise (EUR 22523EN). It is important to note the increase of the reproducibility value for toluene at the higher levels of concentration, which was out of the calibration range for most of the participants. Table 7 shows the average values of repeatability, reproducibility and gamma over the tested concentration range for each analyte. It is noted that all the gamma values are higher than two (limit for the criterion for robustness). This confirms the observation of the last intercomparison, where problems of robustness in the methodology were associated with a combination of factors such as lack of linear response of instruments, differences between reference standards, malfunctioning of instrumentation, etc. In this exercise, the limited number of participants influenced the uncertainty of these values, which show in particular relatively high values of reproducibility for benzene and o-xylene. The higher repeatability of m-xylene is probably linked to poor integration.

Table 7.- Average repeatability, reproducibility and gamma values of the exercise

	Repeatability, %	**Reproducibility, %**	γ
Benzene	1.4	**17.8**	**17.2**
Toluene	1.8	10.0	7.1
ethyl-benzene	2.2	9.7	6.1
mp-xylene	**4.2**	8.0	2.1
o-xylene	3.1	**16.5**	6.7

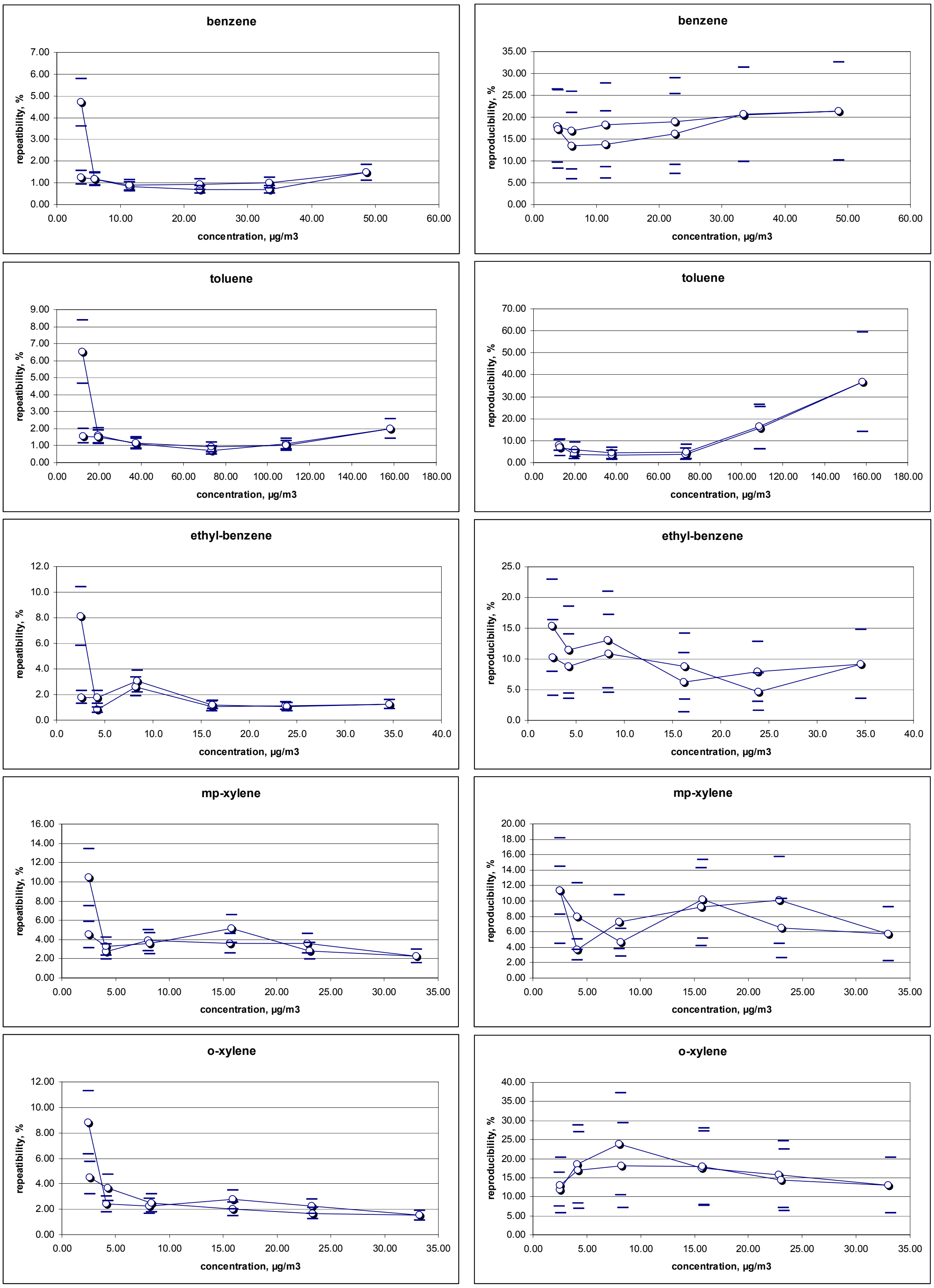


Figure 2.- Repeatability and reproducibility standard deviation values over the intercomparison concentration range

Repeatability and Z'-scores for proficiency testing

In order to evaluate the laboratory proficiency for the analysis of aromatic compounds under a common criterion, the Z'-score was calculated by means of the standard deviation for proficiency testing, equation (8), recommended in the document N37 protocol from AQUILA network. The results of these tests are shown in Figure 3.

In light of these results, the following observations can be drawn:

By observing the individual behaviours of the instrumentation over the different runs, a slight trend from sub-estimate concentrations at the beginning of the exercise, when concentrations are increasing, towards an over-estimation, when concentrations are decreasing, is noted. This is more clearly shown in Figure 4, which represents the logarithm of the ratio between the average interlaboratory concentration of the "i" consecutive analysis carried out by each participant and the average concentration value for this level, versus the "i" consecutive analysis. In this Figure it is noted that there is a trend from negative to positive values of the logarithm for the increasing concentration runs (A-series), and a trend from positive to negative for the decreasing ones (B-series). Such an effect was still noted in spite of the fact that the first measurement carried out at each level was rejected, i.e. the Figure 4 shows the five consecutive measurements reported.

In principle, whatever effect due to the non-steady state conditions in the bench during the test is minimised after the first 15 minutes of operation. The working flows in the bench were high enough to consider that the concentration was as a minimum 96 % of the one theoretically implemented. Therefore, subsequent runs were represented 98 % of the steady state concentration. This effect should not be significant in the overall results as such a variation is covered by the measurement uncertainty. Therefore, what is visible in the results is more the response time of the instrument, the conditioning of the sampling line and the stabilization of the operative conditions of the instrument. This is supported by the fact that the repeatability of the instrumentation is generally improved during the course of the intercomparison.

AEAT was systematically failing in the repeatability score tests, where the differences in response of the adsorbent tubes from the sampling carrousel significantly increased the repeatability standard deviation of the replicated measurements at each level.

The outlier of the reproducibility value for NERI at the higher concentration level for benzene was due to one value from their five measurements, which increased the repeatability of the series. Its elimination from the average did not, however, imply to satisfy the Z'-score(N37) test.

In light of the Z'-score(N37) values calculated for the different laboratories, CHMI was considered to generally underestimate the benzene concentrations. This may be due to the fact that they were using a canister (prepared from a gravimetric standard) as a travelling standard during calibration.

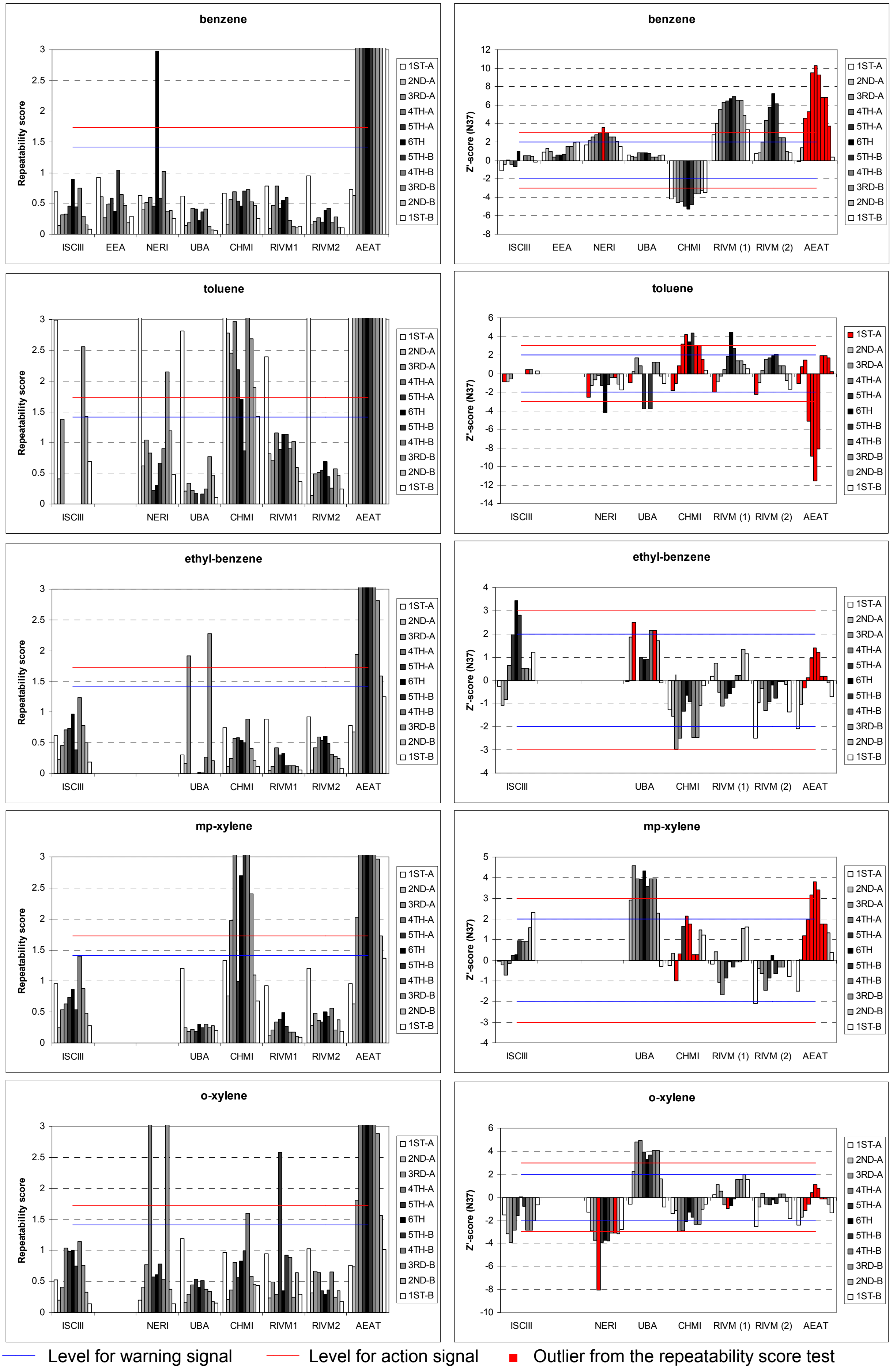


Figure 3.- Repeatability and Z'-scores (N37) for the intercomparison exercise

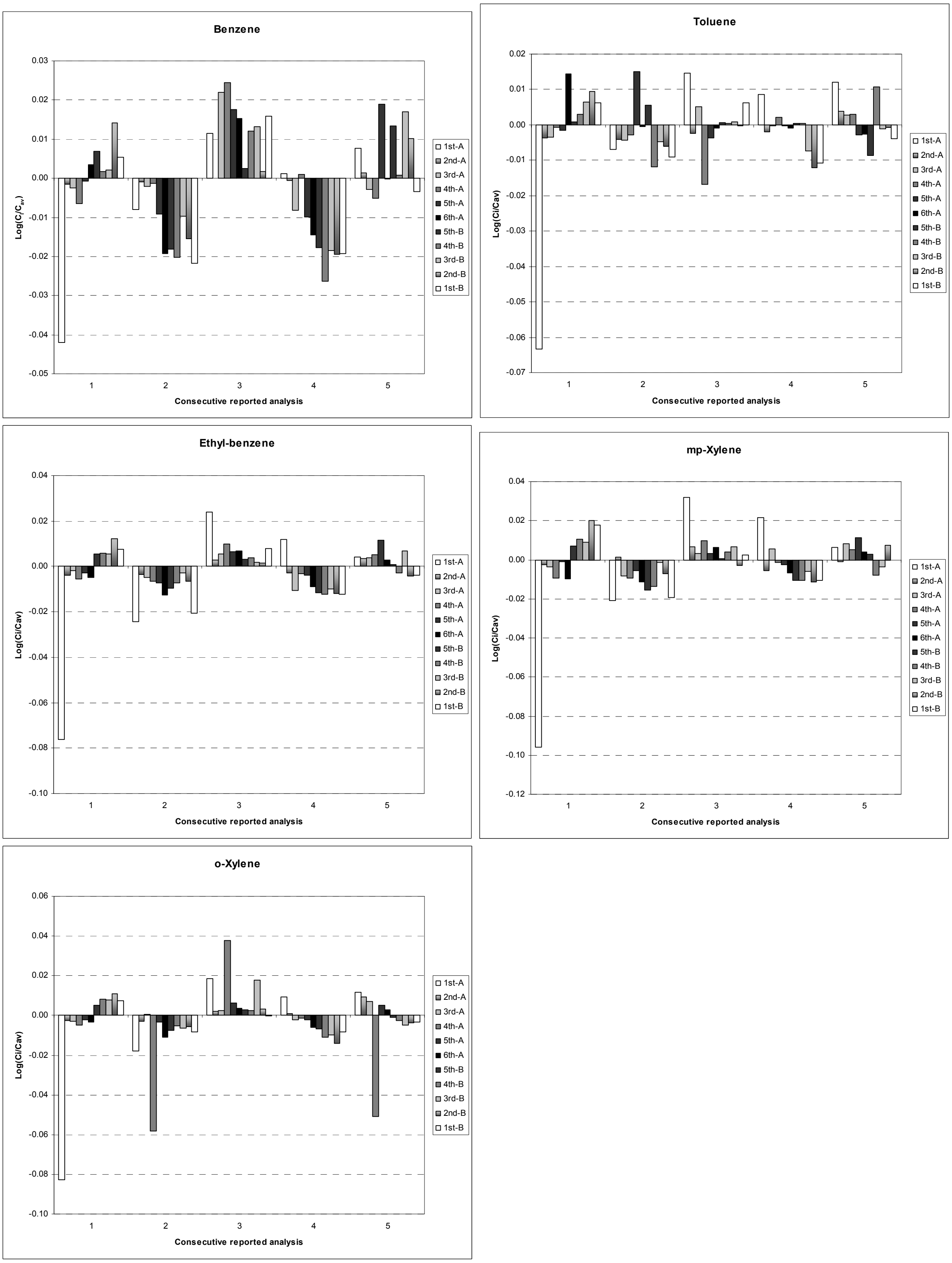


Figure 4.- Average concentration trend of the five consecutive measurements for each concentration tested in the exercise.

On the other hand, RIVM showed a clear overestimation of benzene concentrations for both instruments, although for the second instrument this was only observed for the higher concentration levels.

The other three laboratories ISCIII, EEA and UBA reported values below the limit of warning of the Z'-score(N37), showing for benzene a good performance over the operative concentration range of the exercise.

The repeatability scores for toluene over the different concentration levels reflect the longer stabilisation time needed by the instrumentation for this compound, which is also increased by the higher concentration when compared to the other pollutants. This effect was not relevant for the other aromatic compounds.

In general, for toluene, Z'-scores(N37) were mainly reporting outliers for the higher concentration levels tested during the exercise, which probably was out of the calibration range.

As a general observation, for the other tested compounds, trends of the instrument to increase or decrease the Z'-score with the concentration level were in some way an indication of linearity problems, outliers were appeared at a certain level of concentration, which was the case for ethyl-benzene and o-xylene for Carlos III. CHMI showed problems of reproducibility for mp-xylene. UBA over-estimated xylenes and NERI under-estimated o-xylene.

Fitness of the N37 standard deviation for proficiency assessment

The choice by prescription of a standard deviation for proficiency assessment may not be realistic in relation to the reproducibility of the measurement method. According to ISO 13528, the ratio between the between-laboratory standard deviation of the intercomparison, s_L, and that derived from the prescript standard deviation for the proficiency assessment, $s_{L_{N37}}$, should be lower than 2 to represent a realistic choice.

The between-laboratory standard deviation from prescript conditions of proficiency assessment is calculated according to the following expression:

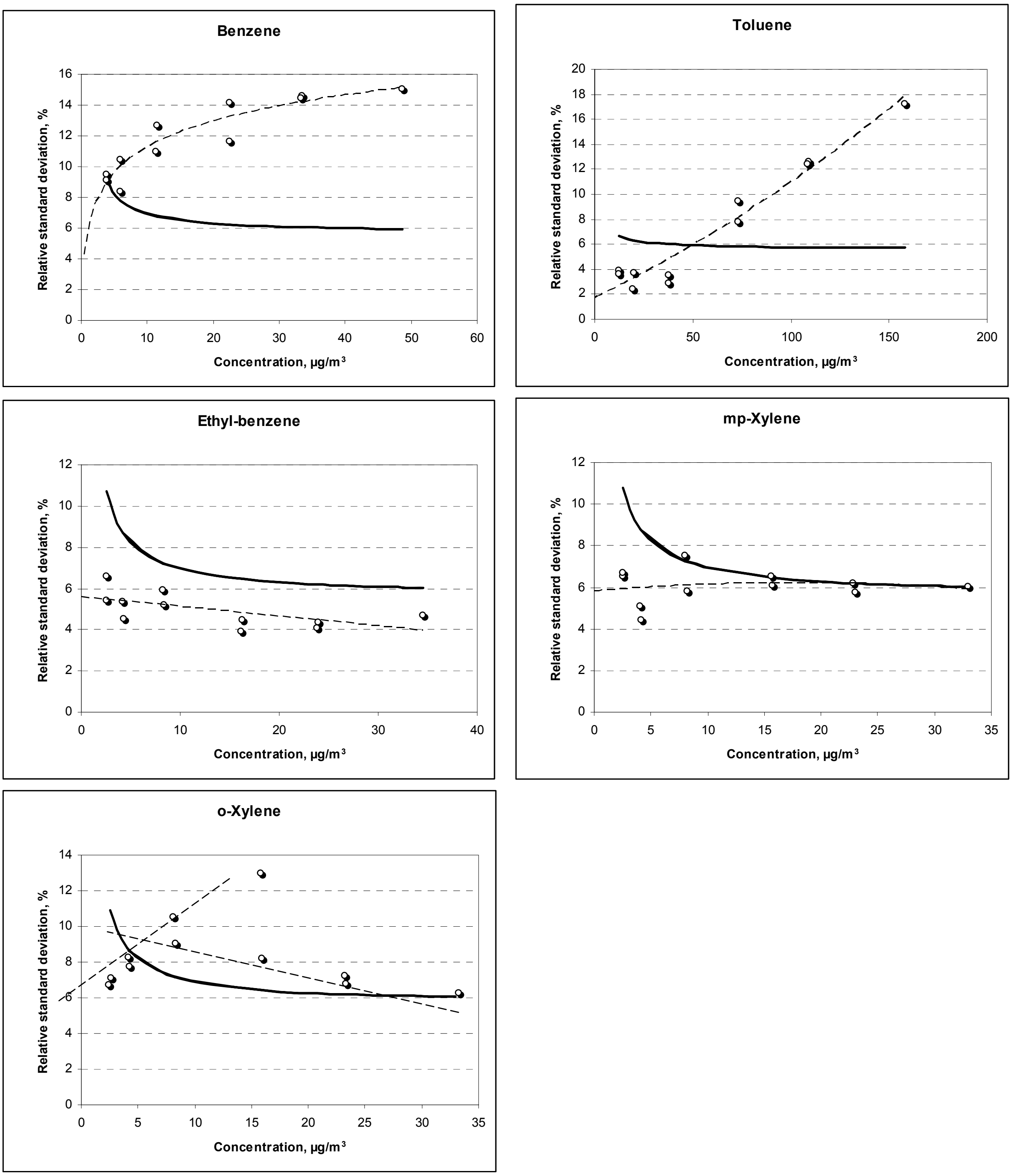
$$s_{L_{N37}} = \sqrt{\hat{\sigma}^2_{N37} - \frac{s_r^2}{n}} \qquad (12)$$

In agreement with ISO 13528, the minimum standard deviation of proficiency assessment coherent with method reproducibility, $\hat{\sigma}_m$, can be calculated by the following equation:

$$\hat{\sigma}_m = \sqrt{(0.5 \cdot s_L)^2 + \frac{s_r^2}{n}} \qquad (13)$$

Therefore, when $\hat{\sigma}_{N37}$ is higher than $\hat{\sigma}_M$ the AQUILA N37 proposed value for the standard deviation for proficiency assessment is coherent with the reproducibility of the measurements in the exercise. Otherwise, the corresponding expected reproducibility standard deviations cannot be achieved in practice.

Figure 5 represents the prescript N37 and the minimum acceptable relative standard deviation coherent with the reproducibility of the exercise for the different concentration level of the intercomparison. When the N37 standard deviation is lower than the minimum acceptable, the prescript value is not achievable and needs to be explained.



—— Relative standard deviation from AQUILA N37 proposal, $\hat{\sigma}_{N37}/C_{ref}\cdot 100$

----O--- Minimum relative standard deviation compatible with the reproducibility of the exercise, $\hat{\sigma}_{m}/C_{ref}\cdot 100$

Figure 5.- Prescript and minimum acceptable relative standard deviation for proficiency assessment

The benzene graph in Figure 3 shows that the AQUILA N37 proposal is too restrictive for the reproducibility of the method. This is in agreement with the lack of robustness of the methodology for the analysis of benzene. The same criterion for toluene seems to fail for the higher concentrations. This can be explained by the fact that instruments were probably operating out of the calibration range at those concentration levels. The AQUILA N37 criterion was also partially restrictive for the results obtained with o-xylene. This is in line with the relatively high reproducibility standard deviation observed for this compound.

Conclusions

For benzene, the average reproducibility standard deviation for the exercise (about 18 %) is in contrast with the relatively low repeatability standard deviation (1.4 %). This lack of robustness (γ ~ 17) is an indication of the need for traceability in the calibration process and improvement of the instrument linearity.

Benzene reproducibility standard deviation values of about 15 % at the limit value (5 $\mu g/m^3$) are very close to the reproducibility value obtained in the last intercomparison (12.5%). Considering the higher associated uncertainty due to the limited number of participating laboratories, no changes in the performance of the method can be derived from this intercomparison with respect to the last exercise.

Z'-score is revealed as an appropriate criterion for the evaluation of laboratory performance when a limited number of participating laboratories are involved. Nevertheless, the N37 proposal for the reproducibility standard deviation for proficiency assessment seems to be very restrictive for the method. In spite of that, almost half of the participants passed the Z'-score (N37) test for benzene measurement proficiency testing.

Further harmonisation actions need to be implemented in order to obtain reproducibility values, which can satisfy the N37 criterion for benzene. Otherwise, the proposed N37 standard deviation needs to be reconsidered to fit to the method performance limits.

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ISO 5725-2: 1994. Accuracy (trueness and precision) of measurment methods and results. Part 2. Basic method for the determination of repeatability and reproducibility of a standard measurement method.

ISO 6143 : 1999. Gas analysis – Détermination of the composition of calibration gas mixtures – Comparison methods.

ISO 13528: 2005. Statistical methods for use in proficiency testing by interlaboratory comparison.

Annex

Agenda of the Intercomparison Exercise

BTEX Intercomparison Exercise

Ispra 17-19 June 2008

Day	Starting Date	Time	Ending Date	Time	Event
Tuesday	17/6/08	14:00		15:00	Reception of the participants
		15:00		15:30	Welcome to ERLAP and description of the exercise
		15:30		17:30	Installation and set-up of Instrument
Wednesday	18/6/08	9:00		13:30	Calibration of Instruments
		13:30		14:00	Synchronisation of all the BTEX analysers
	18/6/08	14:00	19/6/08	10:00	Measuring 6 Concentration levels
Thursday	19/6/08	10:00		12:00	Calibration check
		12:00		17:30	Collection and data processing Reporting preliminary data to JRC

Participants are requested to report 5 measurements per level and each BTEX compound.
It is the responsibility of the participating laboratories to ensure the traceability and validity of their CRM.

Indicators of Mandel's statistic

Number of Laboratories, p	k values at* of s.l. 1 %	5 % **	h values at s.l. 1 %	5 % **
3	1.53	1.40	1.15	1.15
4	1.60	1.44	1.49	1.42
5	1.65	1.46	1.72	1.57
6	1.68	1.48	1.87	1.66
7	1.70	1.49	1.98	1.71
8	1.71	1.50	2.06	1.75
9	1.73	1.50	2.13	1.78
10	1.74	1.50	2.18	1.80
11	1.74	1.51	2.22	1.82
12	1.75	1.51	2.25	1.83
13	1.76	1.51	2.27	1.84
14	1.76	1.52	2.30	1.85
15	1.76	1.52	2.32	1.86
16	1.77	1.52	2.33	1.86
17	1.77	1.52	2.35	1.87
18	1.77	1.52	2.36	1.88
19	1.78	1.52	2.37	1.88
20	1.78	1.52	2.39	1.89
21	1.78	1.52	2.39	1.89
22	1.78	1.52	2.40	1.89
23	1.78	1.53	2.41	1.90
24	1.79	1.53	2.42	1.90
25	1.79	1.53	2.42	1.90
26	1.79	1.53	2.43	1.90
27	1.79	1.53	2.44	1.91

* for 5 replicated values. ** s.l. : significance level

Robust Analysis for the estimation of robust values of the average and standard deviation of a number of interlaboratory measurements

The robust estimation of an average value, $\overline{C_i}^*$, and standard deviation, s^*, of p interlaboratory measurements is derived from a convergence process of the following equation:

$$\overline{C_i}^* = \frac{\sum C_i^*}{p}$$

$$s^* = 1.134 \cdot \sqrt{\frac{\sum (C_i - \overline{C_i}^*)^2}{(p-1)}}$$

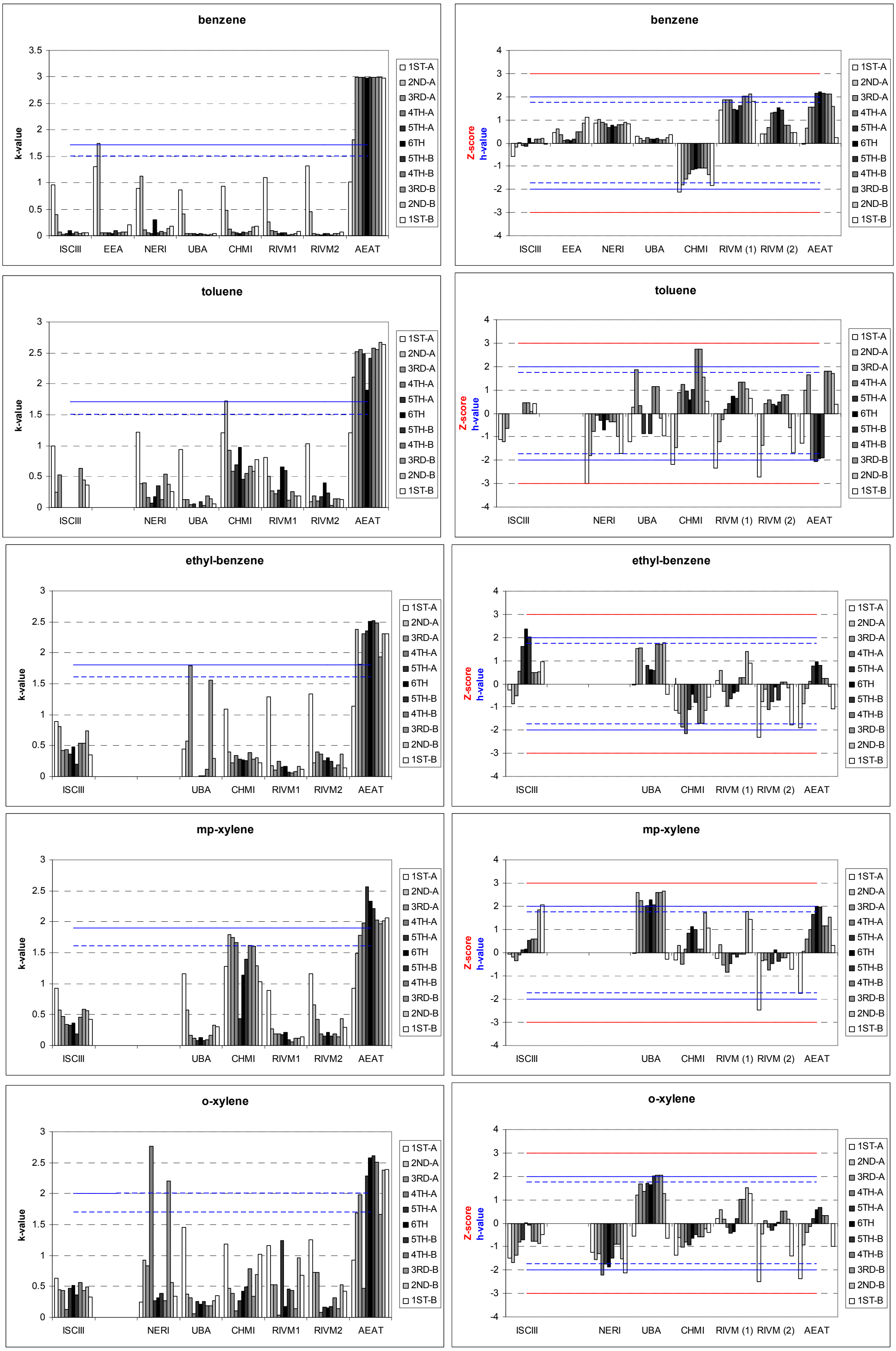
Where recurrent values are calculated from these equations:

$$C_i^* = \begin{cases} \overline{C_i}^* - 1.5 \cdot s^* & \text{if} \quad C_i < \overline{C_i}^* - 1.5 \cdot s^* \\ \overline{C_i}^* + 1.5 \cdot s^* & \text{if} \quad C_i > \overline{C_i}^* + 1.5 \cdot s^* \\ C_i & \text{otherwise} \end{cases}$$

The initial values are calculated as:

$$\overline{C_i}^* = \text{median of } C_\text{i} \text{ (i} = 1, 2, \ldots\text{p)}$$
$$s^* = 1.483 \cdot \text{median of } \left| C_i - \overline{C_i}^* \right| \text{(i} = 1, 2, \ldots\text{p)}$$

k and h values of the intercomparison exercise



h and k values: —— 99 % c.l. outlier identification - - - 95 % c.l. straggler identification Z-score: —— limit for an action signal

As the uncertainty of the reference method is negligible with respect to the standard deviation of the exercise, Z'-score and Z-score provide similar results. In the graphs below results for the identification of outliers by means of k-statistic for repeatability and h-statistic or Z-score for inter-laboratory reproducibility are represented.

Analysers and method description from participating laboratories

Participating Laboratory	NERI, Denmark
Person(s) responsible	Hans Nielsen and Henrik Skov
Contact e-mails:	HNI@dmu.dk and HSK@dmu.dk
Telephone contact:	

Characteristic of your BTEX analyser

Trademark	AIRMOTECH
Model:	BTX 1000
Version:	S/N 2840802
Year of manufacture:	2004

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:			X		
Other gases used:					X

Operating system:	Airmo VISTA software: V 5.5

Cycle time, min:	15		
Adsorbent material:	Carbotrab B		
Sampling control			
Sampling temperature, °C	ambient		
Sample volume, ml	App. 800 ml		
Number of adsorbent tubes	3		
Desorption temperature, `	350		
Desorption time, sec	180		
Desorption flow, ml/min	2		
Cryo-trap detail	Carbopack B		
Trapping temperature, °C	40		
Desorption temperature, °C	350	Desorption time, sec	120
Desorption flow, ml/min	2	split flow, ml/min	
Stripper column			
Analytical column	DB624		
phase:			
length, m:	12 meters		
diameter (ID) mm:	0.2 mm		
thickness (µm):	1.12		
analytical conditions:	40 to 140 dg.C		

Traceability of your calibration Standard

Certified reference material (CRM):	
Certified by	

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	10	1
Toluene	20	2
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene	20	2

Other methods

Dilution of CRM	
Static Injection	
Permeation	

Additional comments

Participating Laboratory	Federal Environment Agency
Person(s) responsible	Mr. Stephan Rutschewski
Contact e-mails:	Stephan.rutschewski@uba.de
Telephone contact:	+49-(0)6103-704-181

Characteristic of your BTEX analyser

Trademark	Syntech Spectras
Model:	GC 955
Version:	600
Year of manufacture:	2005

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:		X			
Other gases used:					

Operating system:	Windows 98

Cycle time, min:	14 min 52 sec		
Adsorbent material:	precon with Tenax GR 60-80 mesh, 8 cm		
Sampling control	Pump, MFC		
Sampling temperature, °C	27		
Sample volume, ml	30		
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	54		
Desorption flow, ml/min	1,5		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	capilary column AT624; ID 0,32 mm; film 1,8 µm; 2 m		
Analytical column	capilary column AT624; ID 0,32 mm; film 1,8 µm; 13 m		
phase:	94 % dimethylpolysiloxane, 6 % cyanopropylphenyl		
length, m:	13		
diameter (ID) mm:	0,32		
thickness (µm):	1,8		
analytical conditions:	Initial 0 min - 3 min 60 °C; 3 min. - 6 min to 80°C; 6 min - 11 min 80 °C; 11 min - 14 min to 60 °C		

Traceability of your calibration Standard

Certified reference material (CRM):	
Certified by	Federal Environment Agency

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene		
Toluene		
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		

Other methods

Dilution of CRM	
Static Injection	Static volumetric method, according ISO 6144
Permeation	

Additional comments

Participating Laboratory	INSTITUTO DE SALUD CARLOS III
Person(s) responsible	Dra. Dña. Rosalía Fernández Patier Dña. Pilar Morillo Gómez
Contact e-mails:	rferndez@isciii.es pmorillo@isciii.es
Telephone contact:	+34 91 822 35 05 or +34 91 822 3518

Characteristic of your BTEX analyser

Trademark	SYNTECH SPECTRAS
Model:	GC 955
Version:	600
Year of manufacture:	2004

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:	---	YES	---	---	---
Other gases used:	---	---	---	---	YES

Operating system:	MICROSOFT WINDOWS 98 SECOND EDITION
Cycle time, min:	15 min
Adsorbent material:	TENAX GR 35-60 mesh (Length 8 cm)
Sampling control	Piston - pump
Sampling temperature, °C	Ambient temperature
Sample volume, ml	100 mL
Number of adsorbent tubes	1
Desorption temperature, `	
Desorption time, sec	
Desorption flow, ml/min	
Cryo-trap detail	TENAX GR 35-60 mesh (Length 8 cm)

Trapping temperature, °C			
Desorption temperature, °C	180 °C	Desorption time, sec	40 s
Desorption flow, ml/min	1,5 mL/min	split flow, ml/min	

Stripper column	Capillary column AT624: 94% dimethylpolysiloxane- 6% cyanopropylphenyl ID 0,32 mm; Film 1,8 □m; Length 2 m
Analytical column	Capillary column AT624
phase:	94% dimethylpolysiloxane - 6% cyanopropylphenyl
length, m:	13 m
diameter (ID) mm:	0,32 mm
thickness (µm):	1,8 –m
analytical conditions:	0 min-3 min at 50 °C; 3 min-6 min ramp at 20/3 °C/min; 6 min-11 min at 70 °C; 11 min-14 min ramp at 20/3 °C/min; 14 min-15 min at 50 °C

Traceability of your calibration Standard

Certified reference material (CRM):	Nederlands Meetinstituut (NMI)
Certified by	Nederlands Meetinstituut (NMI)

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	500×10^{-9} mol/mol	± 15×10^{-9} mol/mol
Toluene	487×10^{-9} mol/mol	± 15×10^{-9} mol/mol
Ethyl-benzene	254×10^{-9} mol/mol	± 7×10^{-9} mol/mol
m-Xylene	128×10^{-9} mol/mol	± 4×10^{-9} mol/mol
p-Xylene	124×10^{-9} mol/mol	± 4×10^{-9} mol/mol
o-Xylene	243×10^{-9} mol/mol	± 7×10^{-9} mol/mol

Other methods

Dilution of CRM	CALIBRATOR API MODEL 700. RANGE 0 nmol/mol - 13,9 nmol/mol
Static Injection	
Permeation	

Additional comments

Participating Laboratory	Czech Hydrometeorological Institute - Calibration Laboratory of Immission
Person(s) responsible	Ing. Miroslav Vokoun
Contact e-mails:	vokoun@chmi.cz
Telephone contact:	+420 24403 3458, +420 24403 3442

Characteristic of your BTEX analyser

Trademark	SYNTECH SPECTRAS
Model:	GC 855, s/n 543
Version:	600
Year of manufacture:	2001

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:		5.0 ~3bar			
Other gases used:					~3bar

Operating system:	Windows 3.11

Cycle time, min:	15		
Adsorbent material:	Tenax GR		
Sampling control	piston		
Sampling temperature, °C	25 ÷ 35		
Sample volume, ml	100ml		
Number of adsorbent tubes	1		
Desorption temperature, °C	180°C		
Desorption time, sec	40		
Desorption flow, ml/min	1.8		
Cryo-trap detail	no		
Trapping temperature, °C	no trap		
Desorption temperature, °C	no trap	Desorption time, sec	
Desorption flow, ml/min	no trap	split flow, ml/min	
Stripper column	capillary column AT624; 2m; ID 0,32 mm; film 1,8 µm		
Analytical column	capillary column AT624; 13m; ID 0,32 mm; film 1,8 µm		
phase:			
length, m:	13		
diameter (ID) mm:	0.32		
thickness (µm):	1.8		
analytical conditions:	PID detector with 10,6 eV lamp		

Traceability of your calibration Standard

Certified reference material (CRM):	PRM NPL 30HCs species in N2
Certified by	D41 9240, 13.3.2008

Compound	Concentration, ppb (nmol/mol)	Expanded Uncertainty, ±ppb(nmol/mol)
Benzene	10.1	0.2
Toluene	10.0	0.2
Ethyl-benzene	10.4	0.2
m-Xylene	10.3	0.2
p-Xylene	10.3	0.2
o-Xylene	10.2	0.2

Other methods

Dilution of CRM	for linearity MCZ calibrator BTEX CMK5 - 0611-111 + TL M650613, 0 ÷ 7 ppb
Static Injection	
Permeation	

Additional comments

Canister Silcosteel 6 l #2106 traceable to PRM BTEX D41 9240 before and after IE BTEX Ispra

Participating Laboratory	Calibration Laboratory , Executive Environment Agency
Person(s) responsible	Nikolay Panayotov
Contact e-mails:	npanayotov@avb.bg
Telephone contact:	

Characteristic of your BTEX analyser

Trademark	Syntech Spectras
Model:	Syntech Spectras GC 855
Version:	600
Year of manufacture:	2004

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:		x			
Other gases used:					

Operating system:	Windows 98.

Cycle time, min:	15		
Adsorbent material:	Tenax GR 35-60 mesh 8 cm		
Sampling control			
Sampling temperature, °C	20		
Sample volume, ml			
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	30		
Desorption flow, ml/min	0.5		
Cryo-trap detail	Peltier-cooling system		
Trapping temperature, °C	50-70		
Desorption temperature, °C	180	Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	Capillary column AT5, IDO 32 mm; film 1 micrometer; 2 m		
Analytical column	Cappilary column AT5, IDO 32, film 1micrometer		
phase:	95% dimethylpolysiloxane 5% diphenylpolysiloxane		
length, m:	13		
diameter (ID) mm:	IDO 32		
thickness (µm):	1		
analytical conditions:			

Traceability of your calibration Standard

Certified reference material (CRM):	Linde Gas
Certified by	NPL

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	10,20,40,60,80,150ppb	± 3%
Toluene		
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		

Other methods

Dilution of CRM	Dillution 150 ppb Benzene/ HORIBA ASGU-360
Static Injection	
Permeation	Permeation rate benzene, 68.12 ng/min,HORIBA ASGU-360, dilution flow 1l/min ,5 10 15 20 nmol/mol

Additional comments

Participating Laboratory	AEA Technology plc
Person(s) responsible	Steve Telling / Peter Dumitrean
Contact e-mails:	steve.telling@aeat.co.uk
Telephone contact:	+44 870 190 6583

Characteristic of your BTEX analyser

Trademark	Environement
Model:	VOC71M
Version:	
Year of manufacture:	2004

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:		Y			
Other gases used:					

Operating system:	Windows

Cycle time, min:	15 or 30 minutes		
Adsorbent material:	Mix of Carbotrap and Carbopack X		
Sampling control	Internal pump with critical oriface		
Sampling temperature, °C	Ambient		
Sample volume, ml	1050 / 2100		
Number of adsorbent tubes	2		
Desorption temperature, `	350		
Desorption time, sec	180		
Desorption flow, ml/min	1		
Cryo-trap detail	CarboPack X		
Trapping temperature, °C	32		
Desorption temperature, °C	350	Desorption time, sec	3
Desorption flow, ml/min	1	split flow, ml/min	
Stripper column			
Analytical column	Supelco SPB 624		
phase:	Proprietary, bonded		
length, m:	13		
diameter (ID) mm:	0.32		
thickness (µm):	1.8		
analytical conditions:	34 C for 115 sec, ramp of 20 C/min for 260 sec, 150 C for 155 sec		

Traceability of your calibration Standard

Certified reference material (CRM):	
Certified by	NPL

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	3.76	0.08
Toluene	3.78	0.08
Ethyl-benzene	3.81	0.08
m-Xylene	3.78	0.08
p-Xylene	3.8	0.08
o-Xylene	3.8	0.08

Other methods

Dilution of CRM	
Static Injection	
Permeation	

Additional comments

Participating Laboratory	RIVM
Person(s) responsible	Camelia van Zwol, Hans Verboom
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Telephone contact:	+31 30 2748640

Characteristic of your BTEX analyser

Trademark	Synspec
Model:	GC 955 type 600, serial number 2007
Version:	Software version 4.4.8
Year of manufacture:	2007

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:		x			
Other gases used:					

Operating system:	Windows

Cycle time, min:	15		
Adsorbent material:	Tenax GR 35-60 mesh, 8 cm		
Sampling control	piston pump		
Sampling temperature, °C	room temperature		
Sample volume, ml	175		
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	30		
Desorption flow, ml/min	1.5		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	same as analytical column, only 2m long		
Analytical column	Capillary column AT5		
phase:	95%dimethylpolysiloxane, 5%diphenylpolisiloxane		
length, m:	13		
diameter (ID) mm:	0.32		
thickness (µm):	1		
analytical conditions:	50°C, in 2 min. from 50°C to 70°C, 7 min. on 70 °C, in 2 min. back to 50°C, 1 mi		

Traceability of your calibration Standard

Certified reference material (CRM):	Lindegas_Benelux
Certified by	RIVM, using a PRM from The Netherlands Methrology Institute

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	100	5%
Toluene	100	5%
Ethyl-benzene	100	5%
m-Xylene	100	5%
p-Xylene	100	5%
o-Xylene	100	5%

Other methods

Dilution of CRM	90-100 times dilution using calibrator Sonimix 6000C RIVM
Static Injection	
Permeation	

Additional comments

Participating Laboratory	RIVM
Person(s) responsible	Camelia van Zwol, Hans Verboom
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Telephone contact:	+31 30 2748640

Characteristic of your BTEX analyser

Trademark	Synspec
Model:	GC 955 type 600, serial number 2012
Version:	Software version 4.4.8
Year of manufacture:	2007

	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:		x			
Other gases used:					

Operating system:	Windows

Cycle time, min:	15		
Adsorbent material:	Tenax GR 35-60 mesh, 8 cm		
Sampling control	piston pump		
Sampling temperature, °C	room temperature		
Sample volume, ml	175		
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	30		
Desorption flow, ml/min	1.5		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, sec	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	same as analytical column, only 2m long		
Analytical column	Capillary column AT5		
phase:	95%dimethylpolysiloxane, 5%diphenylpolisiloxane		
length, m:	13		
diameter (ID) mm:	0.32		
thickness (µm):	1		
analytical conditions:	50°C, in 2 min. from 50°C to 70°C, 7 min. on 70 °C, in 2 min. back to 50°C, 1 mi		

Traceability of your calibration Standard

Certified reference material (CRM):	Lindegas_Benelux
Certified by	RIVM, using a PRM from The Netherlands Methrology Institute

Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	100	5%
Toluene	100	5%
Ethyl-benzene	100	5%
m-Xylene	100	5%
p-Xylene	100	5%
o-Xylene	100	5%

Other methods

Dilution of CRM	90-100 times dilution using calibrator Sonimix 6000C RIVM
Static Injection	
Permeation	

Additional comments

European Commission

EUR 23792 EN – Joint Research Centre – Institute for Environment and Sustainability
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Author(s): P. Pérez Ballesta, R. Connolly, N. Cao, F. Lagler, M. Kapus
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Abstract

This report presents the results of the second intercomparison for BTEX automatic analysers carried out by the JRC on the 17-19 June 2008. Seven national reference laboratories participated in this exercise. Six concentrations levels were tested during the intercomparison, ranging from circa 3 to 50 μg/m^3, for benzene. With respect to the first intercomparison carried out in 2005, the reference value was assigned by ERLAP and the exercise was evaluated according to ISO 13528 methodologies for the evaluation of interlaboratory proficiency assessment and the recommendation of the protocol N37 of the AQUILA network. Participating laboratories are identified as requested by the AQUILA for further actions.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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