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Fifth EC-JRC aromatic compounds inter-laboratory comparison with automatic analysers

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Abstract

This report presents the results of the fifth inter-laboratory comparison for BTEX automatic analysers performed at the JRC Ispra from the 23rd to the 26th of September 2019. Thirteen national reference laboratories and fifteen instruments participated in this exercise. Six concentration levels were tested during the inter-laboratory comparison. Benzene concentrations ranged from 1 to 20 µg/m^3. The exercise was evaluated according to ISO 13528 methodologies for the evaluation of inter-laboratory proficiency assessment and the recommendation of the protocol N37 of the AQUILA network. Participating laboratories were identified as requested by the afore-mentioned protocol.

The robust average value calculated according to ISO13528 was adopted as reference value for the exercise. The report provides information on the technique and instrumentation used by each participant and shows the results of linearity tests, identification of outliers, repeatability, reproducibility, and robustness of the method. Furthermore, parameters to evaluate individual laboratory results: repeatability score, Z-score, bias and E_n scores are also provided.

In general, the results showed in terms of accuracy and precision a behaviour similar to the previous inter-laboratory exercise (EUR-28692-EN). The decrease in concentration avoided problems of sample's overload at the highest concentrations, i.e. toluene. For benzene and toluene, average repeatability and reproducibility values were about 6 % and 13 %, respectively. Ethyl-benzene, m,p-xylene and o-xylene showed higher repeatability values of around 9 %, while their values of reproducibility were about 20 %.

1 Introduction

This aromatic compounds' inter-laboratory comparison exercise is the fifth exercise carried out by the Joint Research Centre aiming to fulfil the QAQC programme for the harmonization of air quality measurements in Europe in accordance with the Directive 2008/50/EC.

The exercise took place in Ispra at the JRC ERLAP bench facility from the 23rd to the 26th September 2019. Participants were required to register and provide a detailed description of their instrumentation. In this exercise, the average robust value was adopted as the reference value of the inter-laboratory comparison. On the other hand, concentrations were also reduced by a factor of two, to fit with a range of concentrations better representing of actual ambient air levels in Europe.

In agreement with the AQUILA N37 protocol, participating laboratories are identified in the report. Measurement results are evaluated according to the repeatability-score, Z-scores and the E_n scores. The report also provides additional information regarding linearity test, blank levels, overall repeatability and reproducibility values and robustness of the method.

2 Inter-laboratory comparison strategy

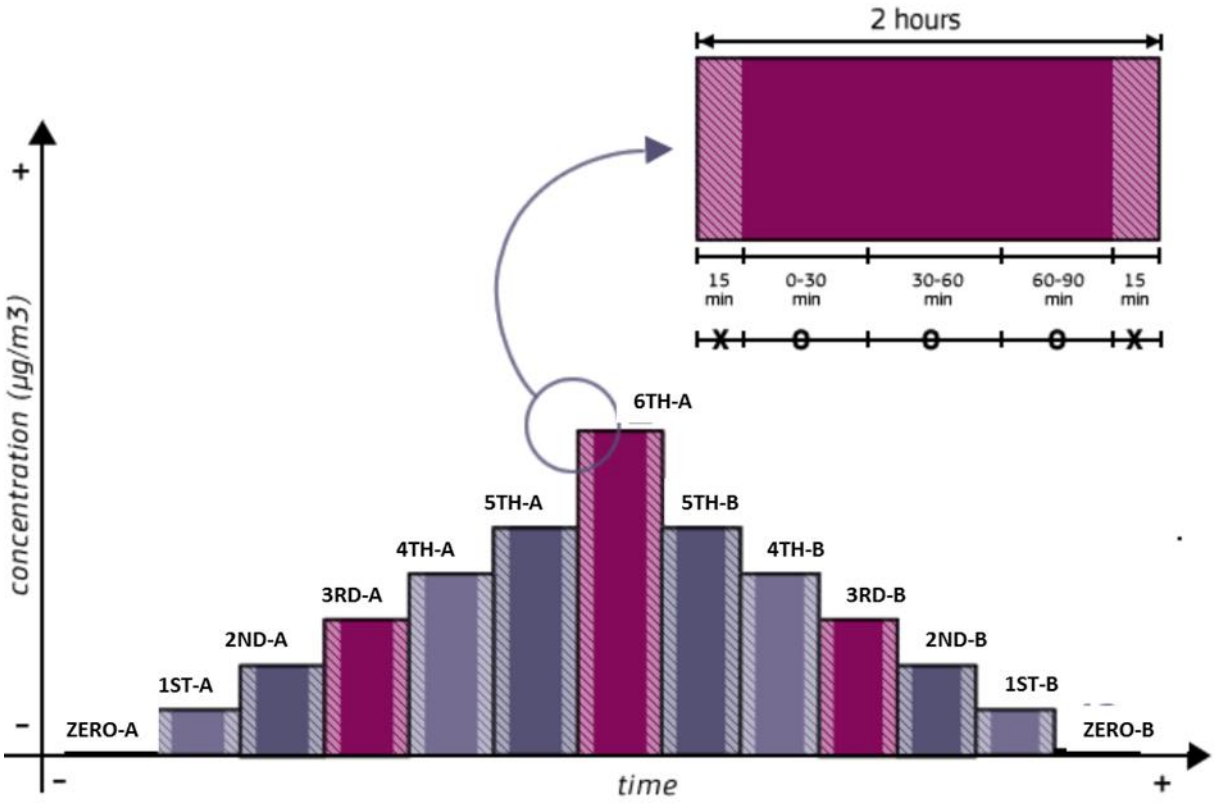
The reporting of results from the participating laboratories was done by uploading the requested information on the JRC web site application at http://interlabo-comparison.jrc.ec.europa.eu. This included the characteristics of the BTEX analyser, description of the calibration method and traceable reference material. 30 min average concentrations and their corresponding associated uncertainties to characterise each 90 min step concentration interval were also requested. The reported information about method, instrumentation and certified reference material from the participants is shown in the Annex 8: Analysers and method description from participating laboratories.

The exercise consisted of a start and end zero-air check and an up and down path of six concentration level steps of two hours each one (see Figure 1). Such a step-time interval allowed the different automatic analysers to perform, according to their modus operandi, from three to six complete measurements, varying from 15 to 30 minutes. The time schedule for the exercise is given in the Annex 1: Work schedule for the inter-laboratory comparison exercise.

In this inter-laboratory comparison, to fit with more realistic sceneries of the current air pollution state in Europe, concentration levels were reduced by half with respect to the previous exercises. As an additional difference from previous inter-laboratory exercises, the reference concentration was derived from the robust average concentration of the exercise. Furthermore, laboratories were requested to calculate the uncertainties associated with the average concentration of each level. On the other hand, ERLAP results were included in the comparison and managed as any other participant.

Concentrations were expressed in µg/m^3 at 20 °C and 1 atm. Conversion factors from ppb (v/v) to µg/m^3 for reporting results were agreed before the inter-laboratory comparison (see Annex 5: Conversion factor for data reporting: Table A 5).

Figure 1.- Time versus concentration steps along the exercise



2.1 Participating laboratories and instrumentation

Fourteen laboratories including JRC participated in the inter-laboratory comparison exercise. Table 1 shows the name of the participating laboratories.

Table 2 identifies the type of instrumentation used by each laboratory. DMRS reported results from two different instruments. Therefore, from the fifteen instruments in comparison, eight had a flame ionization detector (FID), while the others seven used a photo ionization detector (PID). Table 3 shows the reference material or travelling standard used by each laboratory to calibrate their analysers.

Table 1. List of participating laboratories

Acronym	Laboratory	Country	Contact
EKONERG	Energy and Environmental Protection Institute	Croatia	Predrag Hercog, Jean-Luc Picard (AKA)
ISPRA	Istituto Superiore per la Protezione e Ricerca Ambientale - Area Metrologia	Italy	Damiano Centioli, Fabio Cadoni
DLI	Department of Labour Inspection Ministry of Labour, Welfare and Social Insurance Air Quality Section	Cyprus	Christos Kizas, Christos Papadopoulos
GIOS	Chief Inspectorate of Environmental Protection	Poland	Andrzej Pindel, Tomasz Fraczkowski
VMM	Vlaamse Milieumaatschappij	Belgium	Jan Petré, Tine Fierens
EPA	Environmental Protection Agency	Ireland	Kevin Delaney, Joe Reilly
REE	Ricardo Energy and Environment	United Kingdom	James Dernie, Luke Doman
LIKZ	Ambient Air Testing Laboratory Croatian Hydrological and Meteorological Service	Croatia	Lovro Hrust, Mladen Rupcic
AAA	Environmental Protection Agency	Lithuania	Juozas. Molis, Rolandas Kybartas
DCMR	DCMR Milieudienst Rijnmond	The Netherlands	Ed van der Gaag, Han Scaf
APPA	Agenzia Provinciale Per l'Ambiente e la Tutela del Clima (Bolzano)	Italy	Oswald Vigl, Günther Kerschbaumer
SHMU	Slovak Hydrometeorological Institute	Slovakia	Peter Holoman, Maros Jurcovic
IPH	Institute of Public Health of Belgrado	Serbia	Andrej Sostaric, Slaviša Mladenovic'
JRC	Joint Research Centre – ERLAP	European Commission	Andrea Baù, Pascual Pérez Ballesta,

Table 2. Instrumentation used by the participants during the inter-laboratory comparison exercise

Code	Analyser	Cycle time, min	Detector	Column: Length, i.d.*, film thickness Operational conditions	Adsorbent, Sampled volume Desorption conditions
EKONERG	Chromatotec AirmoVOC GC866 (2014)	15	FID	MXT30CE 30 m, 0.28 mm, 1 µm 44°C,2°C/min, 45°C,15°C/min, 165°C(360s)	Carbopack B, 470 ml 80°C for 120 s
ISPRA	ORION BTX 2000 – SRI 8610C (2006)	30	PID	RESTEK #80129 5% RT1200 / 5% Bentone on 100/120 Silcoport, 2 m, 2 mm i.d. T=80°C	Tenax GR 200 °C for 210 s at 20 ml/min
DLI	Chromatotec airmoVOC (BTEX)	15	FID	MX T30 ce , 30 m, 0.28 mm i.d., 1 µm 45-165 °C	Tenax GR, Carbopack B, X & C, 782.35 ml 380 °C for 120 s
GIOS	SYNSPEC Analyser GC 955, Vers. 601 (2018)	15	PID	SY-5: 12 m, 0.32 mm, 1 µm 50°C (3 min), 10°C/min,70°C (7 min)	Tenax GR, 35 ml 180°C for 26 s, 1.5 ml/min
VMM	Chromatotec Airmo BTEX Mcerts-A21022 (2018)	15	FID	MXT30CE: 30 m, 0.28 mm, 1 µm 43-45°C (2°C/min) 45-165°C (15°C/min)	2-phases C6, 450 ml 380°C for 120 s, 3-4 ml/min
EPA	SYNTECH Analyser GC 955, Vers. 600, 2008	15	PID	AT-5, 13 m, 0.32 mm, 1µm 45°C (240 s),14°C/min, 80°C (1 min)	Tenax GR 35/60, 210 ml 180°C for 60 s, 1.5 ml/min
REE	Environment S.A. VOC71M (2005)	15	PID	SPB-624: 13 m, 0.32 mm, 1.8 µm 34°C (115 s),20°C/min,150°C (155 s)	Carbopack-X, 900 ml 350°C for 180 s, 1 ml/min
LIKZ	Chromatotec GC866 FID airmoVOC	15	FID	MXT 30 XE: 30 m, 0.28 mm i.d. 1 µm --	Carbotrap, 425 ml 350°C for 180 s
AAA	AMA Instrument, CG5000 BTX FID, 2017	30	FID	AMAsep1, 30 m, 0.32 mm, 1.5 µm 50°C (180 s),8°C/min,130°C (5')	Carbotrap, 300 ml 230°C for 180 s, 2 ml/min
DCMR	Environment S.A. ENVEA) VOC72M (2017)	15	PID	aplar: 15 m, 0.25 mm, 1 µm 20°C - 170°C	Carbotrap, 220 ml 380°C for 380 s
DCMR2	AMA instruments GmbH GC5000 BTX, 2017	20	FID	AMAsep-1 : 30 m, 0.32 mm, 1.5 µm 30°C-210°C	Tenax, 300 ml 350°C for 9 s
APPA	Syntech Spectras GC955-600 vers. 2 2008	30	PID	AT-5, 13 m, 0.32 mm i.d., 1 µm 50°C-70°C	Tenax GR 35-60 mesh, 175°C for 1.5 s
SHMU	Syntech Spectras GC955 Model 601, 2015	15	PID	Synspec SY-1, 15 m, .32 mm i.d., 1 µm 50°C (3 min),10°C/min,70°C (7 min), 10°C/min,50°C	Tenax GR -175°C
IPH	SYNTECH SPECTRAS Analyser GC 955, 2009	15	PID	AT-624: 15 m, 0.32 mm, 1 µm 50°C (3 min),10°C/min,70°C (7 min), 10°C/min,50°C	Tenax GR, 210 ml -180°C for 60 s, 1.5 ml/min
JRC	GC6890N Agilent ATD-50 Perkin Elmer	30	FID	Dean switch double column DB-1, 50 m 0.32 mm i.d. 1.2 µm Al2O3 KCl 50 m 0.32 mm i.d. 8 µm 40°C (5 min),6°C/min,200°C (15 min)	Air Toxic trap, 600 ml. 300 °C 10 min

* i.d.: internal diameter
** n.a.: not available

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)	Producer	Certified by	Certification date
EKONERG	Press. Cyl. D.D.	1380±75	1319±72	1255±69	2699±146		1326±73	Hungary meteorogy service	Hungary meteorogy service	12/09/2019
ISPRA	Press. Cyl. D.D. Orion OGD2000	9.98 ± 0.20 410±32	9.98 ± 0.20 395±31	9.98 ± 0.28 409±32	10.01± 0.41 392±31	9.99 ± 0.37 391±31	10.00 ± 0.38 395±31	SIAD S.p.A	SIAD	23/05/2019
DLI	Press. Cyl. D.D. (Dilutor Sabio 4010)	681±20	683±20	693±21	665±20	662±20	686±21	VSL	VSL	27/11/2017
GIOS	Press. Cyl. D.D. MCZ CGM200	1142±57	1184±118	1274±127	1200±120	1218±122	1232±123	AirLiquid	AirLiquid	11/08/2017
VMM	Press. Cyl. D.D. (AirQrate)	4.89± --	4.89± --	4.917± --	4.846± --	4.917± --	-	NPL	NPL	17/01/2018
EPA	Press. Cyl.	9.88±0.20	9.614±0.25	10.39±0.26	20.2±0.60		9.34±0.25	NPL	NPL	21/05/2019
REE	Press. Cyl VOC 30 HC.	4.00 ± 0.08	4.00±0.08	4.00±0.08	8.00±0.16		4.03± 0.08	NPL	NPL	08/03/2019
LIKZ	Press. Cyl.	12.18±0.25	11.85±0.30	12.81±0.33	24.90±0.70		12.26±0.31	NPL	NPL	26/6/2018
AAA	Press. Cyl. DD. (Umwelttechnik MCZ)	4830±130	4670± 120	-	-	-	-	NPL	NPL	06/02/2019
DCMR	Press. Cyl.	12.00 ± 0.50	12.00±0.50	12.10±0.50	24.00±0.50		11.80 ±0.50	VSL	VSL	12/09/2017
APPA	Press. Cyl. P.T. (Horiba 360)	189.8 ±3.8	189.7±3.8	190.1 ±59	190.7 ± 4.2			SIAD	ACCREDIA	
SHMU	Press. Cyl.	1.000±0.021, 5.00±0.10, 10± --						NPL	NPL	21/11/2017
IPH	Press. Cyl. D.D. (ASGU 370 P)	2000						MESSER	MESSER	22/06/2019
JRC	Press. Cyl. D.D.	4 200	4 200	4 200	4 200		4 200	NPL AirLiquid	NPL AirLiquid	29/06/2016

Press. Cyl.: Pressurised cylinder; D.D.: Dynamic Dilution; n.a.: not available; P.T.: Permeation Tubes; ppb(m/m): concentration in part per billion with respect to molar fraction ± its expanded uncertainty (k=2)

2.2 Reference values and uncertainties

Based on the experience from previous inter-laboratory comparison exercise, the robust average value calculated according to ISO 13528 has been shown as an appropriate estimator of the reference value (see Annex 3.- Robust Analysis: Estimation of robust average and standard).Therefore, the robust average has been adopted as the reference value of the comparison.

It is noted that in the calculation of the robust average, those laboratories identified by the h statistic with more than 50 % of outliers in their results were, a priori, excluded from the calculation of the robust average. This was the case of REE and SHMU for benzene and IPH for m,p-xylene (see Figure A 7).

In line with ISO 13528, the standard uncertainty assigned to the robust value of the proficiency test, u_{pt}, was estimated as:

$$u_{pt} = \frac{1.25 \cdot s^*}{\sqrt{p}}$$

Eq. 1

Where *s** is the robust standard deviation of the robust analysis, *p* the number of participants and *1.25* is, a conservative non-gaussian behaviour correction factor.

The reference concentrations and corresponding uncertainties are given in Table 4.

Table 4. Reference values and associated uncertainties of the exercise

Level	Benzene	uncertainty (1σ)	Toluene	uncertainty (1σ)	Ethylbenzene	uncertainty (1σ)
	Conc., µg/m³	%	Conc., µg/m³	%	Conc., µg/m³	%
1ST-A	0.43	15.54	2.08	3.08	0.30	21.77
2ND-A	2.56	2.88	10.01	2.92	1.62	5.26
3RD-A	5.22	1.88	19.91	1.09	3.26	3.36
4TH-A	10.79	1.12	40.68	1.08	7.25	1.57
5TH-A	15.62	1.12	59.71	1.15	10.76	1.32
6TH-A	21.66	0.88	81.09	1.33	14.77	1.05
5TH-B	15.46	2.05	59.54	1.93	10.87	1.23
4TH-B	10.37	2.07	39.10	1.63	7.28	1.47
3RD-B	4.90	2.32	18.73	3.10	3.36	2.82
2ND-B	2.74	3.12	10.67	4.02	1.94	4.82
1ST-B	0.62	10.61	2.80	4.58	0.43	20.03

Level	m,p-Xylene	uncertainty (1σ)	o-Xylene	uncertainty (1σ)
	Conc., µg/m³	%	Conc., µg/ m³	%
1ST-A	0.34	19.25	0.39	16.44
2ND-A	2.02	5.15	1.84	3.94
3RD-A	3.65	2.45	3.46	2.28
4TH-A	7.82	1.38	7.78	1.28
5TH-A	11.54	1.03	11.75	1.09
6TH-A	15.88	0.96	15.87	0.94
5TH-B	11.68	1.39	11.62	1.52
4TH-B	7.80	1.47	7.68	1.70
3RD-B	3.61	2.75	3.49	2.76
2ND-B	1.94	4.07	2.08	3.56
1ST-B	0.42	15.60	0.56	12.62

2.3 Statistical considerations

2.3.1 Reported concentration and uncertainty

Laboratories were requested to provide for each level at least three concentration values and the corresponding average concentration and uncertainty. Average values and associated uncertainties were used as input values for the statistical evaluation of the exercise.

2.3.2 Linearity test

Linearity of the analysers was tested according to EN14662-3 by comparing at each concentration level, the average value, $\overline{C}$, with its respective reference value, C_{ref}, for which the residual, R_c, is calculated according to the following expression:

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

Eq. 2

where a and b are the correlation coefficients of the linear regression ($\overline{C}$ vs C_{ref}). As a criterion of linearity, residuals higher than 10 % were highlighted in red, while values lower than 5 % were acceptable.

2.3.3 Repeatability, reproducibility and robustness of the method

The repeatability and reproducibility derived from the inter-laboratory comparison exercise results were calculated after the elimination of outliers identified by converging Mandel's h and k statistic (see Annex 7.- h and k statistic results of the inter-laboratory comparison).

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, $S_{\bar{c}_i}$.

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:

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

Eq. 3

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

As a result, the uncertainty of the inter-laboratory average value, $\overline{C}$, 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, in this case being the variance associated with the uncertainty of the method [ISO 5725 Part 1, Part 2, 1994]:

$$u = \sqrt{s_L^2 + s_r^2} = s_R$$

Eq. 4

being

$$s_r^2 = \frac{1}{p}\sum_i^p s_i^2$$

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

Eq. 5, Eq. 6

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: 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, the ratio between reproducibility and repeatability standard deviations, i.e. gamma value, $\gamma = s_R/s_r$, can be adopted as indicator of robustness of the method, being robust ratios those lower than 2 [P. Pérez Ballesta et al., 2001].

2.3.4 Repeatability score

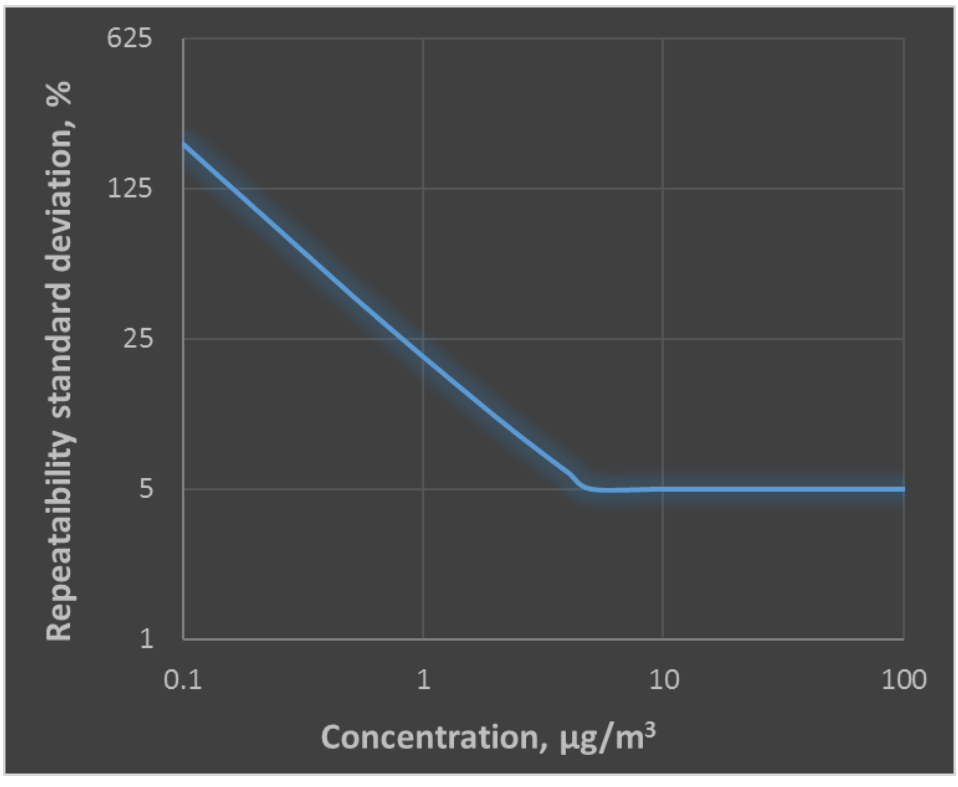
Following the AQUILA N37 recommendations, the standard deviation for the proficiency assessment, σ_{N37}, is calculated as a function of the concentration level in µg/m^3, *C*, by the following equation:

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

Eq. 7

To evaluate the performance criterion as established by EN 14662-3 for benzene automatic analysers, a repeatability scores has been derived from the k-statistic. Therefore, from a minimum value of repeatability standard deviation of 5 %, at concentrations over the limit value (i.e. 0.25 µg/m^3), until 0.2 µg/m^3 for values lower than 0.1 x LV by considering a linear decrease of the absolute value of the standard deviation in between was considered (see Figure 2). Therefore, 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 follows the k statistic indicators, as a thumb approach, values lower than $\sqrt{2}$ are considered as acceptable, while values between $\sqrt{2}$ and $\sqrt{3}$ are questionable and higher than $\sqrt{3}$, i.e. outside the 99 % confidence level interval, are considered as poor performers.

Figure 2. Repeatability standard deviation: Performance criteria (EN 14662-3)



2.3.5 Z-scores and minimum standard deviation of the proficiency assessment

In agreement with ISO 13528, the ratio between the between-laboratory standard deviation of the inter-laboratory comparison, s_L, and that derived from the prescribed standard deviation for the proficiency assessment, s_{LN37}, should be lower than 2 to represent a realistic choice. Therefore, as the inter-laboratory standard deviation from the prescribed conditions of proficiency assessment is calculated according to the following expression:

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

Eq. 8

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

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

Eq. 9

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. Otherwise, the corresponding expected reproducibility standard deviations cannot be achieved in practice.

Furthermore, for single laboratories, in the framework of the AQUILA N37 requirements, it is possible to identify outliers by means of a Z-scores statistic derived from the minimum standard deviation of the proficiency assessment, $\hat{\sigma}_m$. This statistic would provide a criterion for identification of outliers independent of the comparison exercise performance:

$$Z = \frac{C_{lab} - C_{ref}}{\hat{\sigma}_m}$$

Eq. 10

As indicators for this statistic, the h values for the 95 % and 99 % confidence level interval can be adopted.

It is noted that the Z-scores and the repeatability scores previously described provide a statistic for comparison independent of the results of the comparison exercise, as these scores are delimited by the standard deviation of the proficiency assessment defined in AQUILA N37.

2.3.6 E_n scores

As laboratories were requested to report uncertainty values for each concentration level, the evaluation of the laboratory performance was based on the E_n scores as recommended by ISO 13528 (2005). This number is calculated according to the following equation:

$$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

Eq. 11

where U_{lab} and U_{ref} are the expanded uncertainties for the laboratory and reference value, respectively. E_n scores evaluate the compatibility between bias and expanded uncertainty for each result. The critical value for E_n scores is 1. E_n scores higher than 1 identify results that are incompatible with the reference value after allowing for the stated uncertainties. The overall evaluation of the laboratory results should consider both bias and E_n scores because a low E_n scores could be due to a large stated uncertainty.

3 RESULTS AND DISCUSSION

3.1 Data reporting

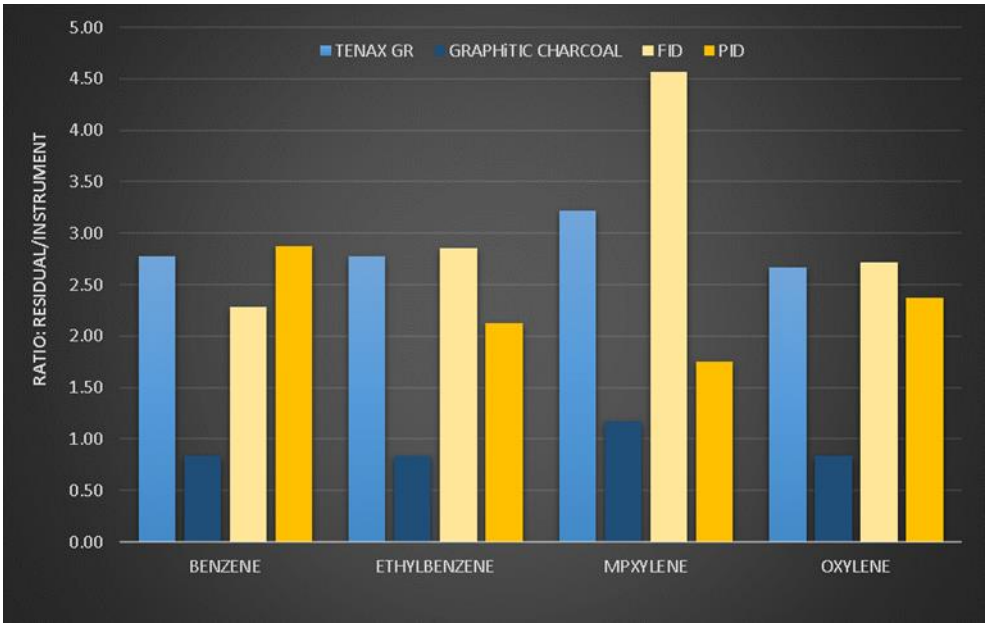
Laboratories were requested to report for each concentration level and compound, three concentration values and the corresponding average value and associated uncertainty representing the whole concentration step. Laboratories were also requested to describe the instrument used in the exercise, the analytical method, the use of certified reference material for calibration and the calculation of the reported uncertainties.

Although this was not a common trend, some laboratories limited the number of reported compounds: REE and SHMU reported only benzene, while AAA reported only benzene and toluene.

3.2 Linearity test

Table 5 to Table 7 show the results of the linearity test for the correlation between reported and reference values. Residuals were calculated by Eq.3. In these tables, the percentage of residuals was indicated for those values higher than 5 %. Values were highlighted in red when these were higher than 10 %. Linearity problems were frequently identified at the lowest concentration levels, eventually with higher incidence on the heaviest compounds (i.e. m,p-xylene) and those instruments using Tenax GR. No clear conclusion could however be drawn for the use of FID or PID detector (see Figure 3).

Figure 3.- number of non-linear cases per adsorbent or detector



Ratio: Residuals > 5 % / number of instruments with the evaluated factor

Outliers laboratories are excluded from the analysis

Table 5. Linearity tests for benzene and toluene

benzene	EKONERG	ISPRA	EPA	GIOS	REE	VMM	LIKZ	SHMU	DLI	IPH_S	AAA	DCMR	DCMR2	APPA BZ	ERLAP
1st -A	10	6	29	-8	21	OK	8	-7	7	-14	8	72	-6	14	-27
2nd -A	OK	OK	OK	OK	-11	7	OK	OK	6	-10	-6	OK	8	OK	OK
3rd -A	OK	OK	-8	OK	OK	OK	OK	OK	OK	OK	OK	-12	OK	-5	6
4th -A	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
5th -A	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
6th	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
5th -B	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
4th -B	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
3rd -B	OK	OK	OK	OK	OK	OK	OK	OK	OK	7	OK	-11	OK	OK	OK
2nd -B	OK	7	OK	OK	OK	OK	OK	OK	OK	OK	OK	-6	OK	OK	OK
1st -B	8	26	19	-8	21	-6	OK	13	OK	OK	OK	59	-8	17	-15
toluene	EKONERG	ISPRA	EPA	GIOS	REE	VMM	LIKZ	SHMU	DLI	IPH_S	AAA	DCMR	DCMR2	APPA BZ	ERLAP
1st -A	OK	50	48	-18		OK	-5		5	-24	OK	-21	-22	OK	-13
2nd -A	OK	OK	OK	5		OK	OK		5	-10	-7	8	9	OK	OK
3rd -A	OK	-5	-6	OK		OK	OK		OK	OK	OK	OK	OK	OK	8
4th -A	OK	OK	OK	OK		OK	OK		OK	OK	OK	OK	OK	OK	OK
5th -A	OK	OK	OK	OK		OK	OK		OK	OK	OK	OK	-5	OK	OK
6th	OK	OK	OK	OK		OK	OK		OK	OK	OK	OK	OK	OK	OK
5th -B	OK	OK	OK	OK		OK	OK		OK	OK	OK	OK	OK	OK	OK
4th -B	OK	OK	OK	OK		OK	OK		OK	OK	OK	OK	OK	OK	OK
3rd -B	OK	OK	OK	OK		OK	OK		OK	OK	OK	OK	OK	OK	OK
2nd -B	OK	OK	OK	OK		OK	OK		OK	7	OK	OK	OK	OK	-5
1st -B	OK	50	48	-18		OK	-5		5	-24	OK	-21	-22	OK	-13

(*) Residual values in percentage

Table 6. Linearity test for ethyl-benzene and m,p-xylene

ethyl-benzene	EKONERG	ISPRA	EPA	GIOS	REE	VMM	LIKZ	SHMU	DLI	IPH_S	AAA	DCMR	DCMR2	APPA BZ	ERLAP
1st -A	-32	50	30	-44		8	-8		-13	OK		101	-20	-8	-36
2nd -A	5	-19	OK	6		OK	OK		OK	-21		17	12	OK	OK
3rd -A	OK	OK	OK	OK		-6	OK		OK	-7		-10	OK	OK	OK
4th -A	OK	OK	OK	OK		OK	OK		OK	OK		-7	OK	OK	OK
5th -A	OK	OK	OK	OK		OK	OK		OK	OK		OK	-5	OK	OK
6th	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
5th -B	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
4th -B	OK	OK	OK	OK		OK	OK		OK	OK		-8	OK	OK	OK
3rd -B	OK	OK	OK	OK		-7	OK		OK	OK		-12	OK	OK	OK
2nd -B	OK	OK	OK	OK		OK	OK		-6	OK		OK	OK	OK	OK
1st -B	-29	19	17	-25		8	-9		-19	34		74	-17	OK	-26
m,p-xylene	EKONERG	ISPRA	EPA	GIOS	REE	VMM	LIKZ	SHMU	DLI	IPH_S	AAA	DCMR	DCMR2	APPA BZ	ERLAP
1st -A	-47	22	21	-19		31	-7		OK	10		63	-18	-10	-38
2nd -A	OK	OK	OK	OK		OK	-8		OK	-13		OK	8	-8	16
3rd -A	6	-5	OK	OK		-10	OK		5	OK		-10	5	OK	9
4th -A	OK	-8	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
5th -A	OK	OK	OK	OK		OK	OK		OK	OK		OK	-6	OK	OK
6th	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
5th -B	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
4th -B	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
3rd -B	6	OK	OK	OK		-9	OK		5	OK		-9	OK	OK	OK
2nd -B	6	6	OK	5		OK	OK		-7	OK		-12	OK	7	-5
1st -B	-41	71	-7	-21		23	OK		-19	22		38	-21	OK	-38

(*) Residual values in percentage

Table 7. Linearity test for o-xylene

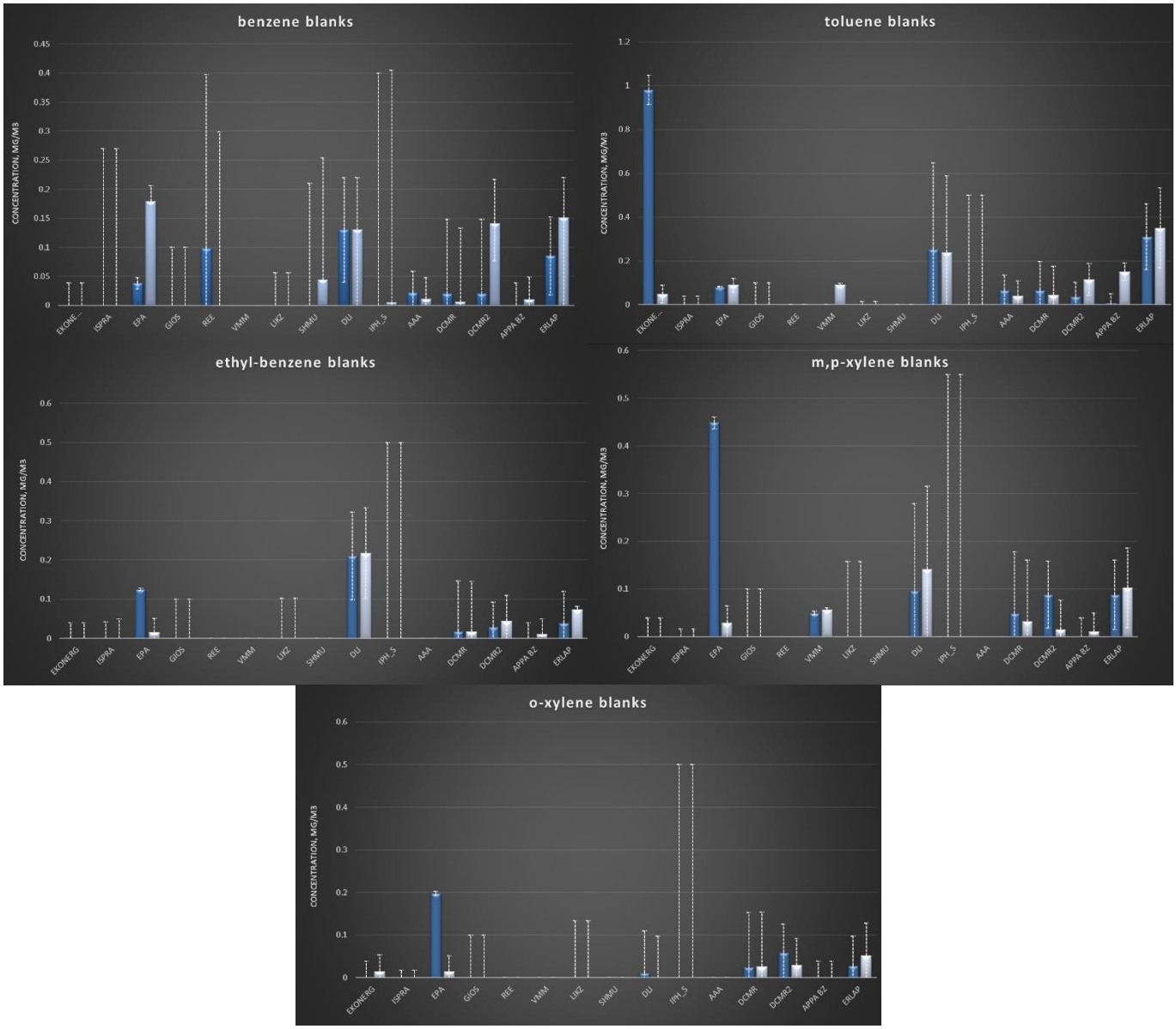
o-xylene	EKONERG	ISPRA	EPA	GIOS	REE	VMM	LIKZ	SHMU	DLI	IPH_S	AAA	DCMR	DCMR2	APPA BZ	ERLAP
1st -A	-19	27	-18	-28		-10	-17		-20	-22		80	-23	23	-22
2nd -A	OK	-12	10	OK		OK	-6		7	-30		6	10	OK	8
3rd -A	OK	OK	OK	OK		OK	OK		OK	OK		-8	OK	OK	OK
4th -A	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
5th -A	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
6th	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
5th -B	OK	OK	OK	OK		OK	OK		OK	OK		OK	OK	OK	OK
4th -B	OK	OK	OK	OK		OK	OK		OK	6		OK	OK	OK	OK
3rd -B	OK	OK	5	OK		OK	OK		OK	10		-9	OK	OK	OK
2nd -B	OK	17	OK	OK		OK	OK		OK	-11		-11	OK	OK	OK
1st -B	-9	OK	-17	-12		OK	-10		-20	21		49	-18	33	-13

(*) Residual values in percentage

3.3 Blank levels

Figure 4 shows the concentrations reported by the participants during the zero air concentration steps (Zero-A and Zero-B). The inter-laboratory median of the measured blank values ranged from 4.3 % to 16.5 % of the reference concentrations at the 1st level of concentration, being approximately the same percentage of their corresponding uncertainties.

Figure 4. Reported blank levels



3.4 Outliers, repeatability, reproducibility and robustness of the method

As indicated in the previous section, repeatability and reproducibility standard deviation were calculated on the converged results of elimination of outliers based on the k and h statistics (see Annex 7.- h and k statistic results of the inter-laboratory comparison). The values of repeatability, reproducibility standard deviation are represented in Figure 5, while Figure 6 shows the corresponding robustness derived for each concentration level and compound. It is noted that the repeatability values are representing the average of the uncertainties reported by the participating laboratories at each level, while the reproducibility is associated with the uncertainty of the method for this exercise shows how the values of repeatability and reproducibility increase with the decrease in the concentration. In less extension, such an increase is also observed for the gamma values (Figure 6).

Figure 5. Repeatability and reproducibility of the inter-laboratory exercise

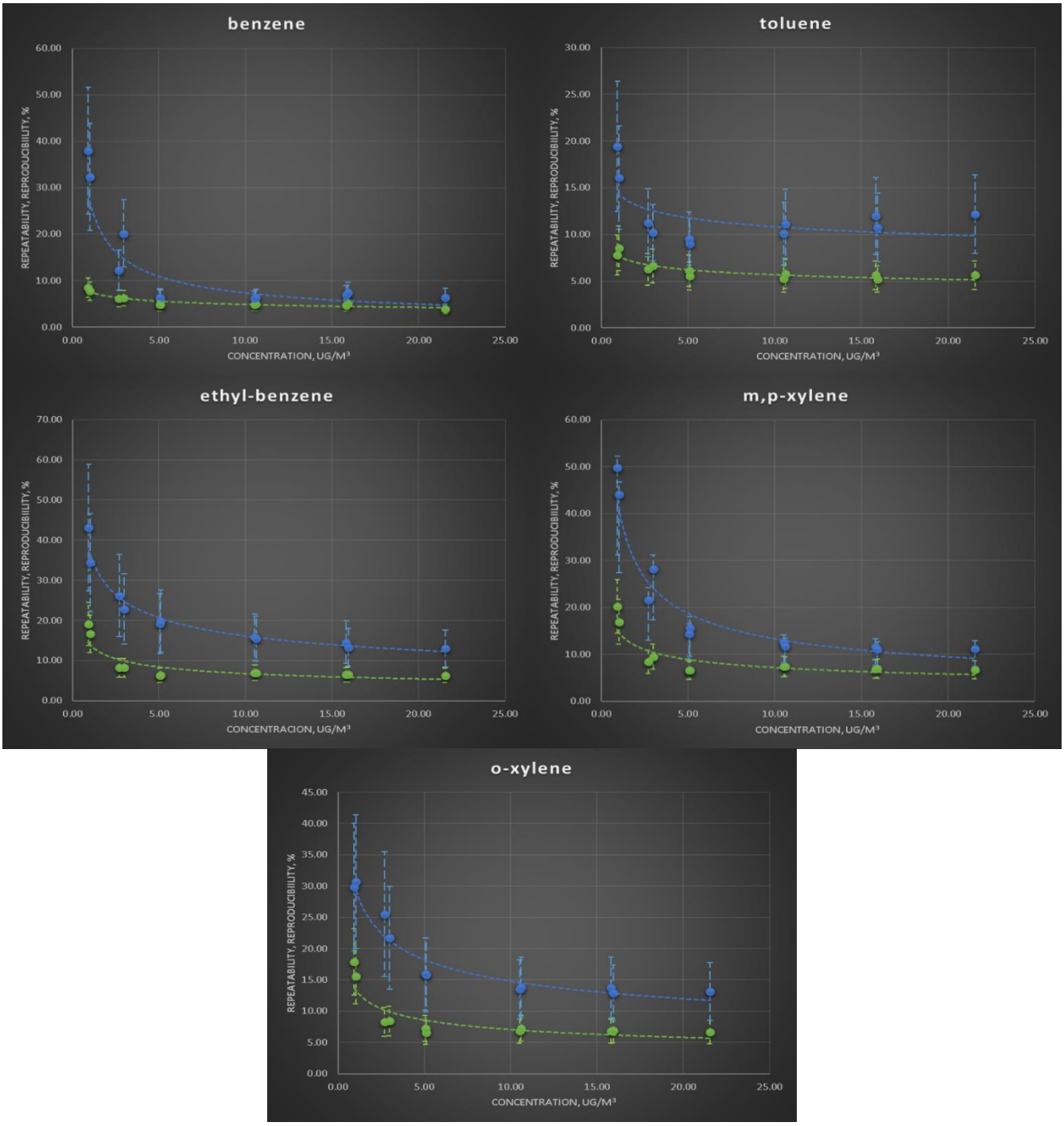
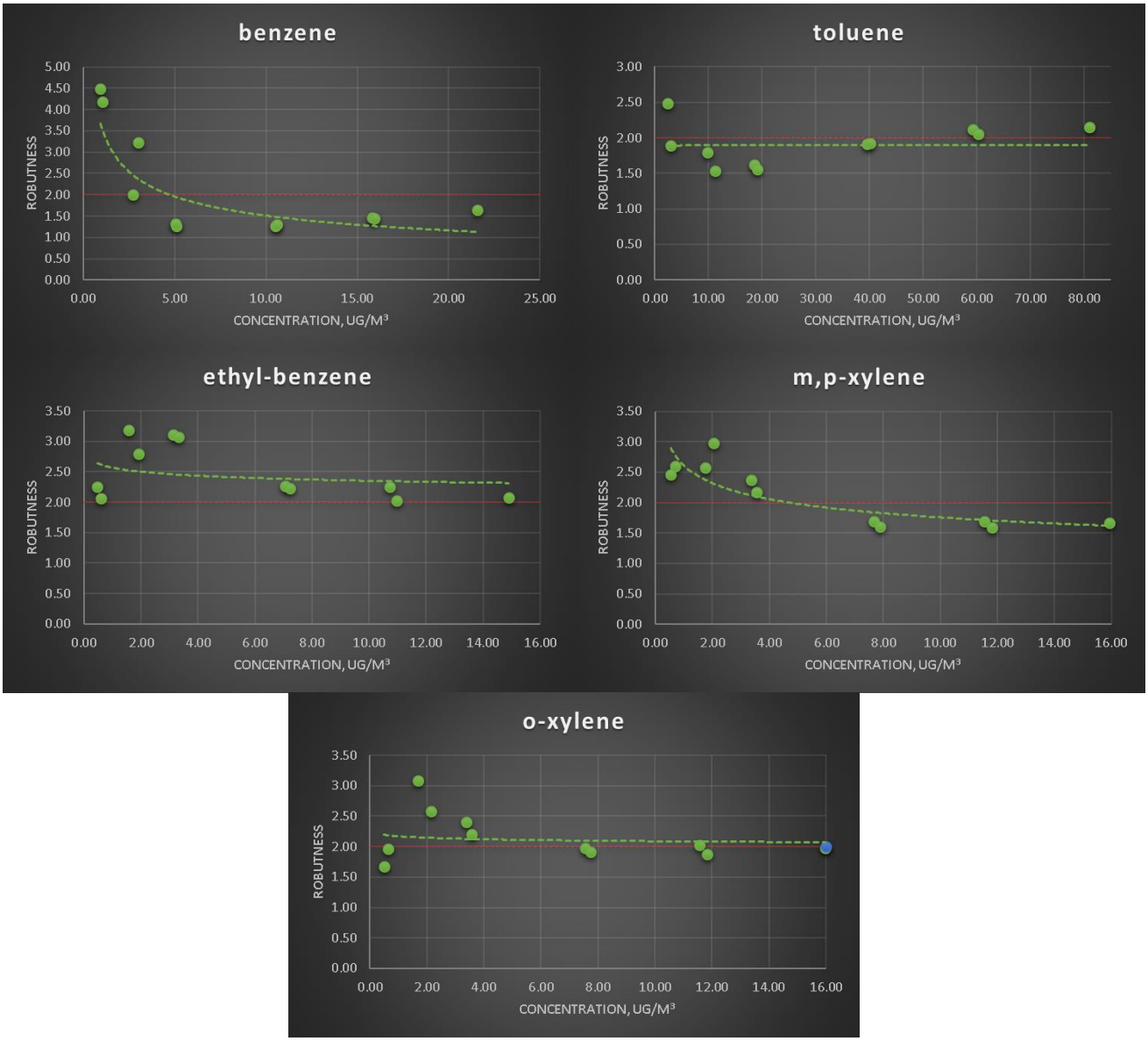


Figure 6. Robustness of the inter-laboratory exercise



Compared to the previous inter-laboratory exercise (EUR 28692 EN), a slight increase in the reproducibility and repeatability values is noted. This is probably due to the decrease by half of the concentration level tested during the exercise. Nevertheless, such variations did not affect the robustness of the method (gamma value), which did not differ significantly from the previous inter-laboratory comparison (see Table 8).

Table 8. Average repeatability, reproducibility and γ values of the inter-laboratory exercise

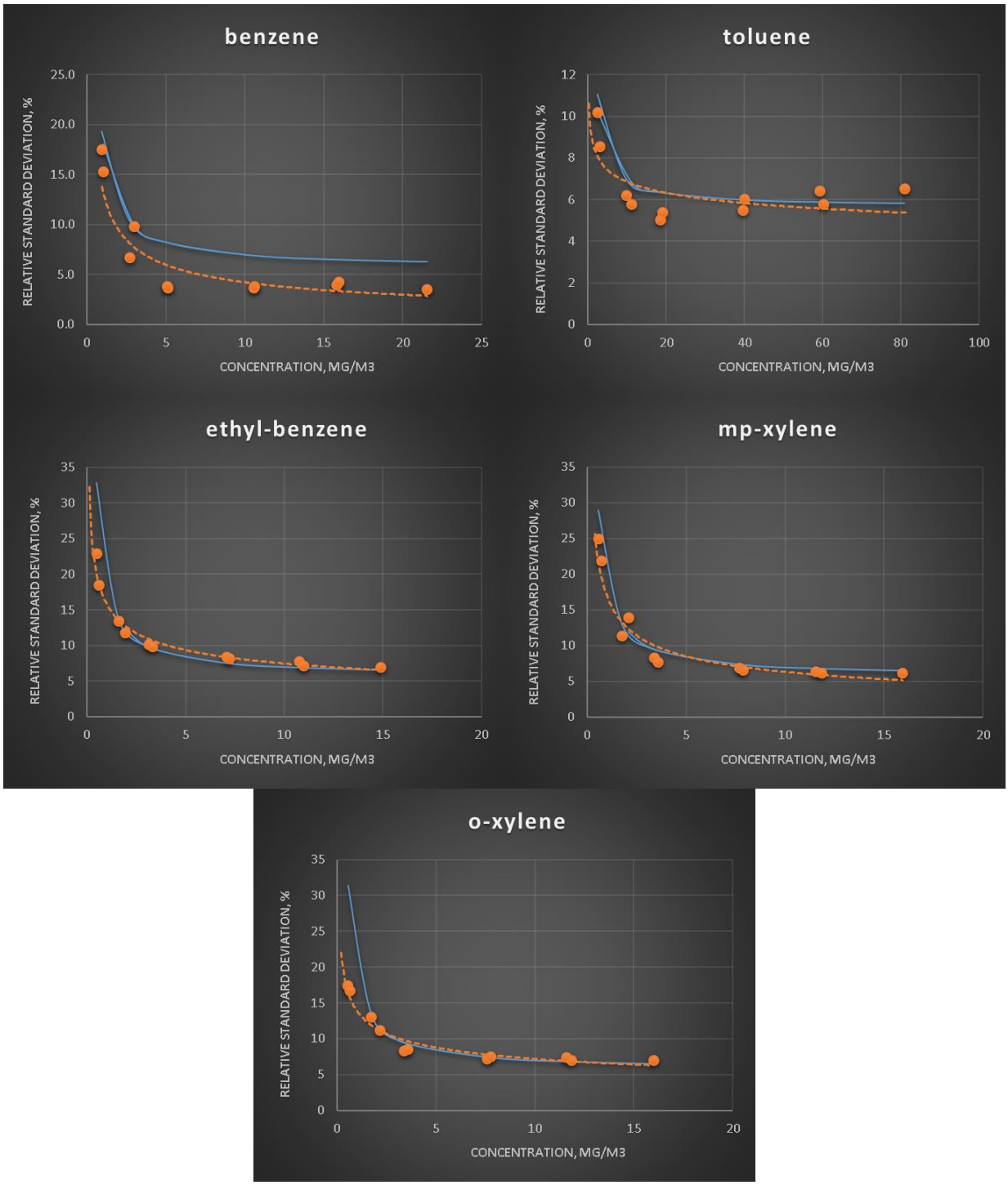
	Repeatability, %	Reproducibility, %	Robustness (γ)
Benzene	5.62	13.51	2.15
Toluene	6.23	11.96	1.91
Ethyl-benzene	8.91	21.62	2.48
m,p-Xylene	9.38	21.04	2.13
o-Xylene	8.94	18.80	2.15

Outliers excluded in the analysis.
Repeatability, reproducibility and robustness values of previous inter-laboratory exercises are provided in Annex 4.

3.5 Standard deviation of the proficiency assessment N37

The minimum relative standard deviation compatible with the reproducibility of the exercise, σ_m, and the relative standard deviation for proficiency assessment σ_{N37} are represented in Figure 7. Repeatability and reproducibility values for the method were those calculated after excluding outliers by the converging k and h statistics, as described in section 3.4. As shown in the Figure 7, the minimum relative standard deviations of the proficiency test fulfil the N37 criteria for all compounds and concentrations.

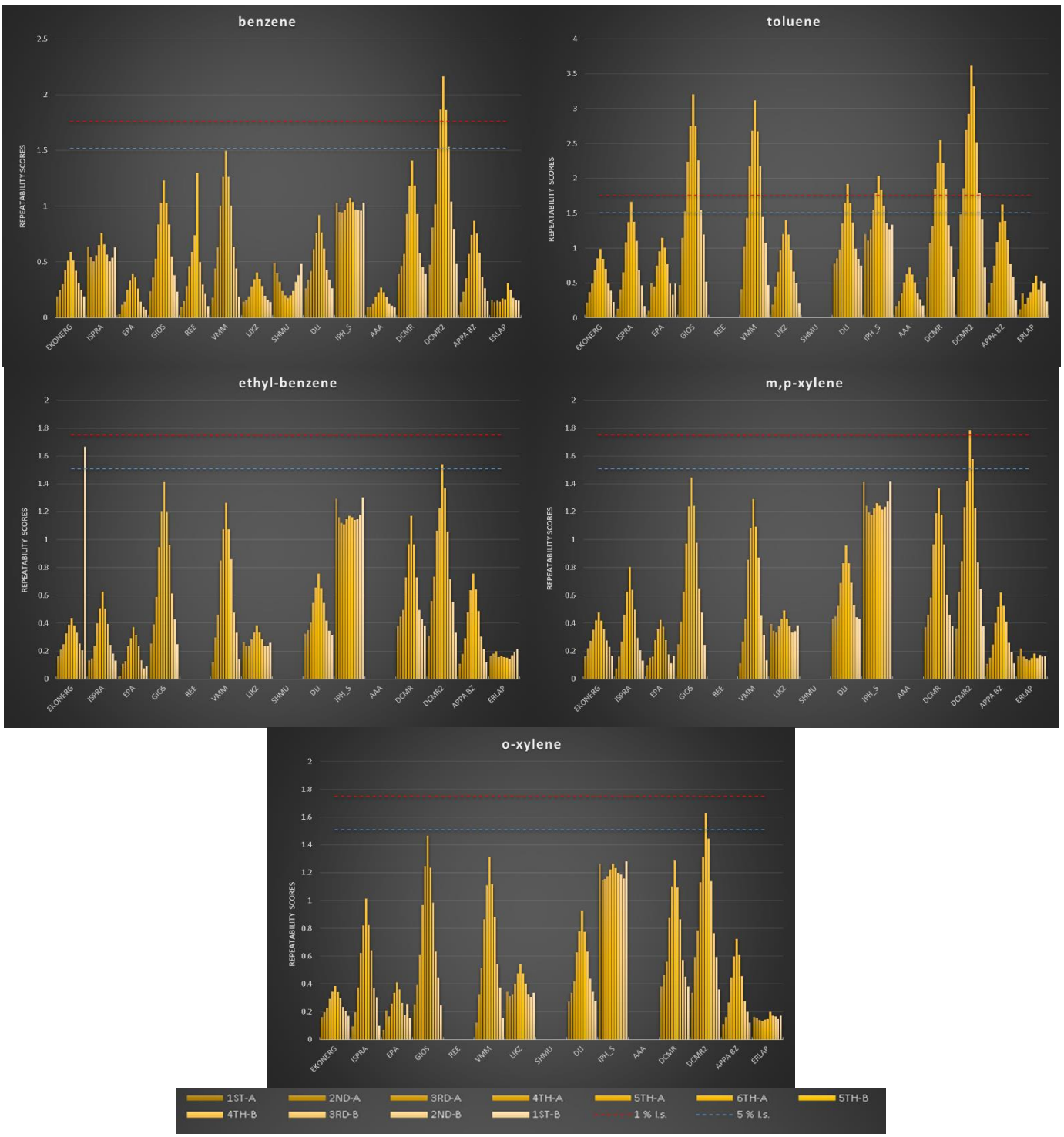
Figure 7. Minimum standard deviation compatible with reproducibility of the tests and standard deviation for proficiency assessment N37



3.6 Repeatability-score, Z-scores and E_n scores

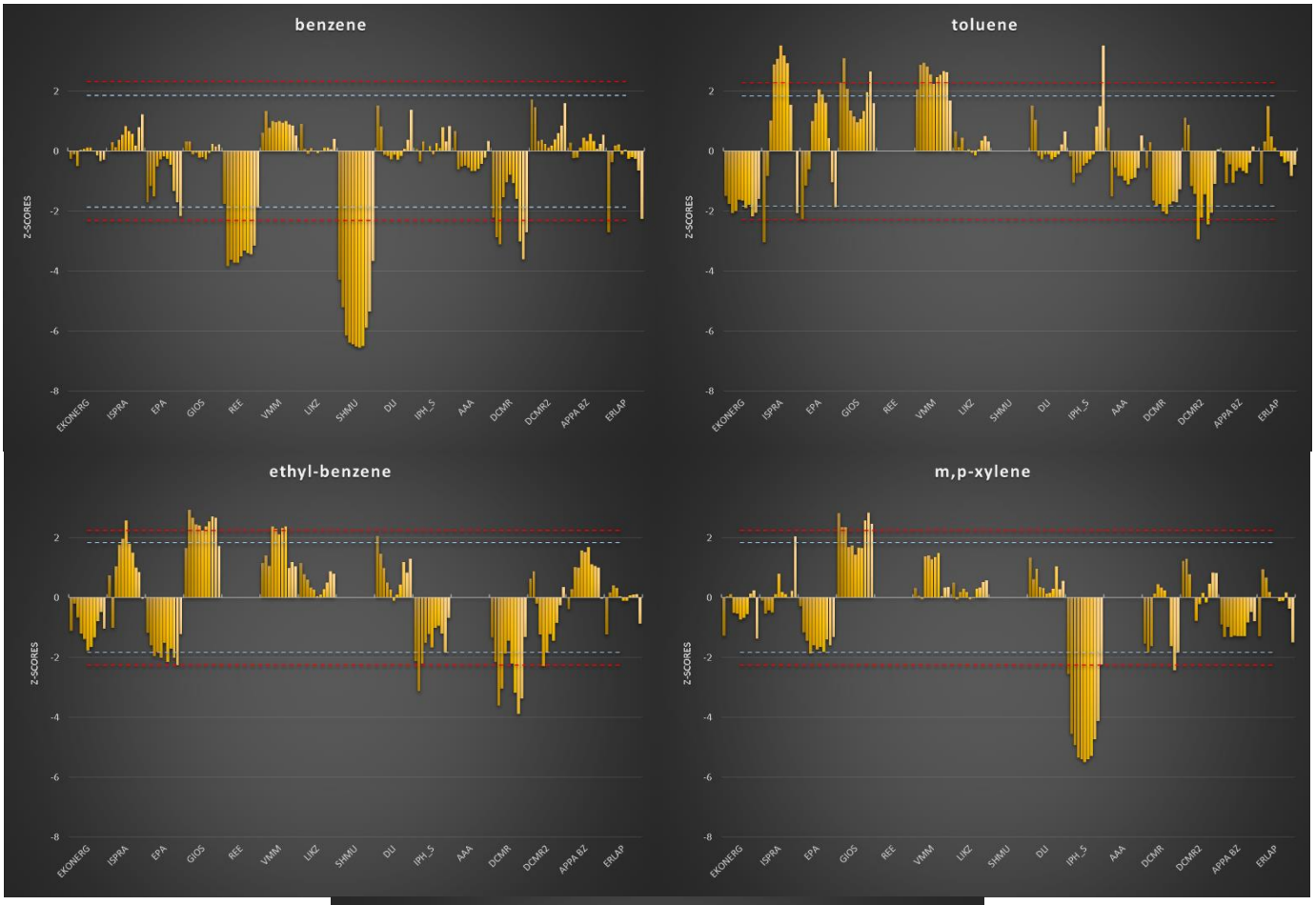
The individual evaluation of the laboratory test performance was carried out by means of the previously defined repeatability scores, Z-scores and E_n scores. Results of the corresponding statistics are shown in Figure 8, Figure 9 and Figure 10.

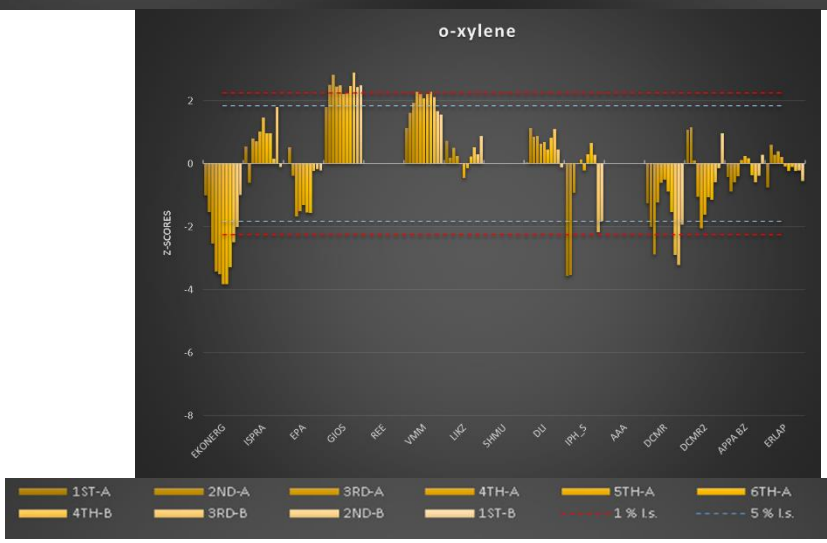
Figure 8. Repeatability-scores (N37) for the inter-laboratory comparison exercise



-------- 99 % confidence level interval: outlier identification -------- 95 % confidence level interval: straggler identification

Figure 9.- Z-scores (σ_m) for the inter-laboratory comparison exercise





-------- 99 % confidence level interval: outlier identification --------- 95 % confidence level interval: straggler identification

*Under N37 AQUILA proficiency test criteria with $S_L = 2\ S_{LN37}$ ($\sigma_m \lesssim \sigma_{N37}$)

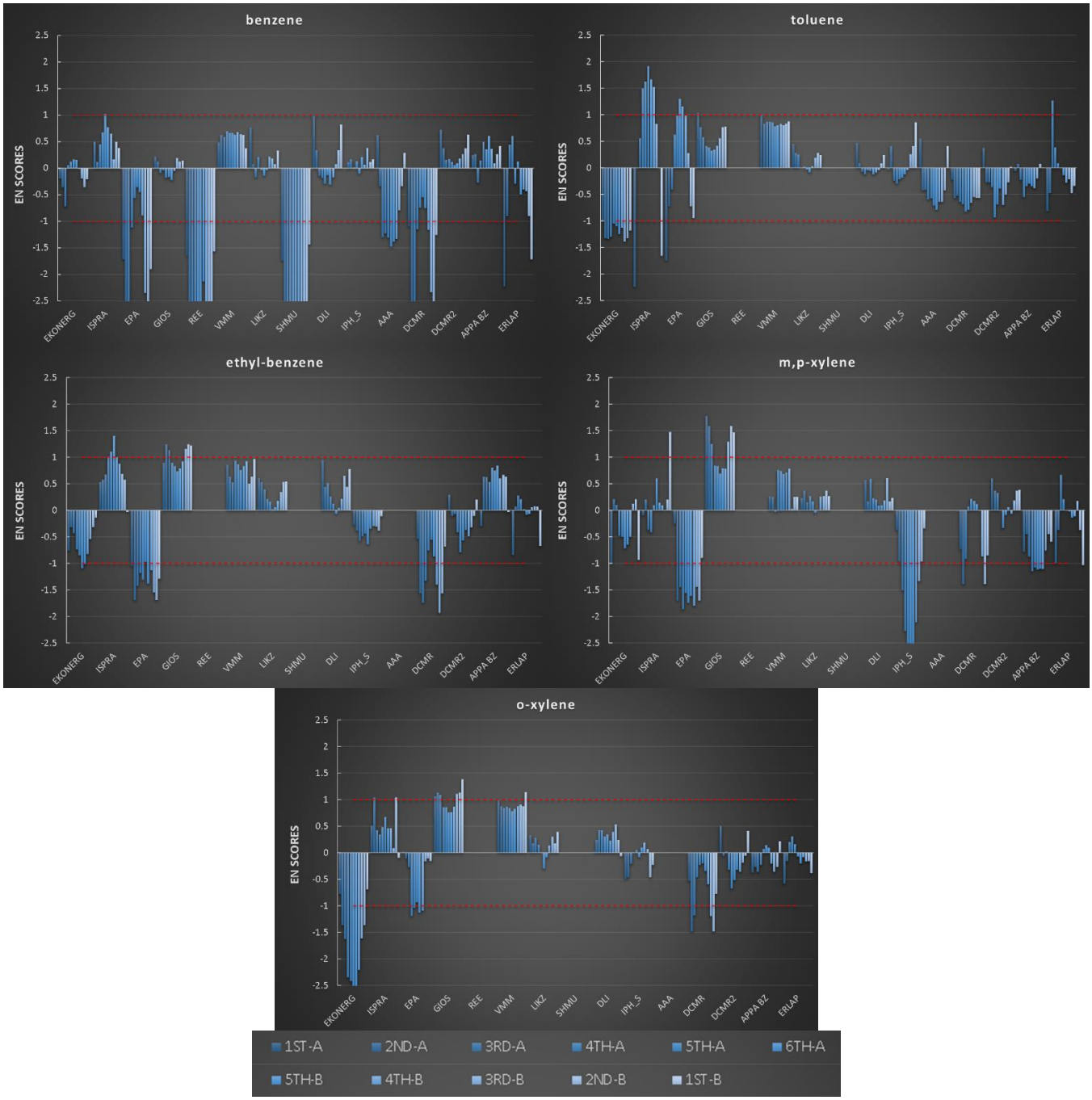


Figure 10.- E_n scores for the inter-laboratory comparison exercise

The results of the inter-laboratory comparison are given in Table 9 to Table 13, providing for each laboratory and concentration level, the reported concentrations and expanded uncertainties, biases, repeatability scores N37, Z-scores (σ_m) and E_n scores. E_n scores equal or higher than 1 are highlighted in red, repeatability scores and Z-scores over the limit at 95 % confidence level interval are highlighted in blu, while those at 99 % confidence level interval are highlighted in red. The results of the laboratory comparison are shown in terms of deviation (%) in the Annex 6: Scattering of Laboratory Results. Figure A 1.

Repeatability scores and E_n scores can be considered as complementary tests in the evaluation of the results. As a relatively high reported uncertainty could compensate a high bias and, consequently, pass the E_n scores test, the repeatability scores test can, in such cases, identify this problem. In this regard, Z-scores (σ_m) is not affected by the reported uncertainty of the laboratory, because the σ_m is used to relativize the scores. Therefore, Z-scores (σ_m) could also be used to identify possible cases where high biases have been compensated by a high reported uncertainty value and, consequently, misidentified by the E_n scores statistic.

Therefore, under this criterion the below tables provide a clear overview of the instrument performance of each participant. The interpretation and actions to be addressed because of the results are responsibility of each laboratory and are outside the scope of this report.

Table 9.- E_n score, bias and reported expanded uncertainty of the participants: benzene

Compound	EKONERG							ISPRA							EPA						
benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.89	18.2	-5.2	OK	-0.2	-0.26	0.19	0.94	57.8	0.5	OK	0.0	0.02	0.64	0.62	4.2	-34.0	Check	-1.7	-1.71	0.03
2nd-A	2.66	9.7	-4.3	OK	-0.4	-0.10	0.25	2.83	17.8	10.4	OK	0.5	0.31	0.54	2.24	4.6	-22.1	Check	-2.7	-1.17	0.12
3rd-A	4.79	8.1	-6.1	OK	-0.7	-0.49	0.30	5.18	12.6	1.5	OK	0.1	0.12	0.51	4.14	4.4	-18.8	Check	-3.7	-1.52	0.14
4th-A	10.57	6.8	0.4	OK	0.1	0.04	0.42	10.98	8.7	4.3	OK	0.4	0.37	0.56	9.89	4.4	-6.1	Check	-1.1	-0.52	0.25
5th-A	15.97	6.5	0.9	OK	0.1	0.08	0.51	16.79	7.9	6.1	OK	0.7	0.54	0.65	15.31	4.4	-3.2	OK	-0.6	-0.28	0.33
6th-A	21.81	6.3	1.2	OK	0.2	0.11	0.59	23.53	7.5	9.2	Check	1.0	0.83	0.76	21.09	4.3	-2.1	OK	-0.4	-0.19	0.39
5th-B	16.13	6.5	1.2	OK	0.2	0.11	0.51	17.10	7.8	7.3	OK	0.8	0.66	0.66	15.47	4.7	-2.9	OK	-0.4	-0.26	0.36
4th-B	10.60	6.8	-0.1	OK	0.0	-0.01	0.42	11.30	8.6	6.5	OK	0.6	0.57	0.57	10.06	4.4	-5.2	OK	-0.9	-0.46	0.26
3rd-B	4.97	8.0	-1.9	OK	-0.2	-0.15	0.31	5.18	12.6	2.3	OK	0.2	0.19	0.51	4.24	4.4	-16.3	Check	-2.4	-1.33	0.15
2nd-B	2.86	9.7	-4.3	OK	-0.4	-0.33	0.25	3.30	17.8	10.4	OK	0.5	0.80	0.54	2.32	4.6	-22.1	Check	-2.7	-1.71	0.10
1st-B	0.98	17.0	-5.3	OK	-0.2	-0.30	0.19	1.26	43.5	21.6	OK	0.4	1.23	0.63	0.64	9.4	-38.1	Check	-1.9	-2.16	0.07
Compound	GIOS							REE							VMM						
benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	1.00	20.1	6.2	OK	0.2	0.31	0.23	0.61	13.2	-35.2	Check	-1.7	-1.77	0.09	1.05	14.5	12.1	OK	0.5	0.61	0.18
2nd-A	2.83	13.6	1.8	OK	0.1	0.32	0.36	1.19	13.1	-40.8	Check	-3.8	-3.83	0.15	3.23	14.5	11.1	OK	0.6	1.34	0.44
3rd-A	5.03	13.6	-1.4	OK	-0.1	-0.11	0.53	2.82	13.1	-44.7	Check	-5.5	-3.62	0.29	5.59	14.6	9.7	OK	0.6	0.79	0.63
4th-A	10.47	13.6	-0.6	OK	0.0	-0.05	0.83	6.00	13.1	-43.0	Check	-5.2	-3.72	0.46	11.75	14.6	11.6	OK	0.7	1.01	1.00
5th-A	15.41	13.6	-2.6	OK	-0.2	-0.23	1.03	9.14	13.1	-42.2	Check	-5.0	-3.72	0.59	17.56	14.6	11.0	OK	0.7	0.97	1.26
6th-A	21.05	13.6	-2.3	OK	-0.2	-0.21	1.23	13.18	13.1	-38.8	Check	-4.3	-3.52	0.74	23.91	14.6	11.0	OK	0.7	0.99	1.50
5th-B	15.43	13.6	-3.1	OK	-0.2	-0.28	1.03	10.09	26.2	-36.7	Check	-2.1	-3.31	1.30	17.60	14.6	10.5	OK	0.6	0.95	1.26
4th-B	10.53	13.6	-0.8	OK	-0.1	-0.07	0.84	6.51	13.1	-38.7	Check	-4.3	-3.41	0.50	11.82	14.6	11.4	OK	0.7	1.01	1.01
3rd-B	5.21	13.6	2.9	OK	0.2	0.23	0.55	2.93	13.1	-42.0	Check	-4.4	-3.44	0.30	5.61	14.6	10.9	OK	0.6	0.89	0.63
2nd-B	3.04	13.6	1.8	OK	0.1	0.14	0.38	1.77	13.1	-40.8	Check	-3.8	-3.15	0.21	3.31	14.5	11.1	OK	0.6	0.85	0.44
1st-B	1.07	18.7	3.9	OK	0.1	0.22	0.23	0.69	13.0	-33.1	Check	-1.6	-1.88	0.10	1.13	14.6	9.2	OK	0.4	0.52	0.19
Compound	LIKZ							SHMU							DLI						
benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	1.11	11.0	18.0	OK	0.8	0.90	0.14	0.14	308.8	-85.5	Check	-1.7	-4.29	0.49	1.22	18.5	30.4	OK	1.0	1.52	0.27
2nd-A	2.73	5.8	0.6	OK	0.1	0.07	0.15	0.65	45.5	-69.4	Check	-4.4	-5.20	0.40	3.02	11.9	4.9	OK	0.3	0.81	0.34
3rd-A	5.04	4.9	-1.1	OK	-0.2	-0.09	0.19	1.22	34.1	-76.1	Check	-8.5	-6.15	0.32	5.02	10.8	-1.6	OK	-0.1	-0.13	0.42
4th-A	10.65	4.5	1.2	OK	0.2	0.10	0.28	2.76	14.9	-73.8	Check	-14.1	-6.39	0.24	10.33	10.2	-1.9	OK	-0.2	-0.17	0.61
5th-A	15.78	4.5	-0.3	OK	0.0	-0.02	0.35	4.25	9.6	-73.1	Check	-16.0	-6.45	0.20	15.34	10.1	-3.0	OK	-0.3	-0.27	0.76
6th-A	21.36	4.4	-0.9	OK	-0.1	-0.08	0.41	6.03	6.8	-72.0	Check	-16.3	-6.52	0.18	21.24	10.1	-1.4	OK	-0.1	-0.13	0.92
5th-B	15.89	4.5	-0.2	OK	0.0	-0.02	0.35	4.37	9.3	-72.6	Check	-14.0	-6.54	0.20	15.40	10.1	-3.3	OK	-0.3	-0.30	0.76
4th-B	10.75	4.5	1.3	OK	0.2	0.11	0.28	2.82	14.6	-73.5	Check	-13.2	-6.49	0.24	10.41	10.1	-1.9	OK	-0.2	-0.17	0.62
3rd-B	5.13	4.9	1.4	OK	0.2	0.11	0.20	1.42	29.2	-72.0	Check	-7.2	-5.88	0.32	5.11	10.8	0.9	OK	0.1	0.07	0.43
2nd-B	3.00	5.8	0.6	OK	0.1	0.05	0.16	0.91	45.5	-69.4	Check	-4.4	-5.35	0.38	3.13	11.9	4.9	OK	0.3	0.37	0.34
1st-B	1.11	11.0	7.3	OK	0.3	0.42	0.14	0.37	113.9	-64.4	Check	-1.4	-3.66	0.48	1.28	17.9	24.2	OK	0.8	1.37	0.27
Compound	IPH_S							AAA							DCMR						
benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.95	92.1	1.5	OK	0.0	0.08	1.03	1.06	7.5	13.3	OK	0.6	0.67	0.09	0.52	63.6	-44.3	Check	-1.1	-2.22	0.39
2nd-A	2.57	33.7	4.1	OK	0.1	-0.35	0.95	2.46	4.0	-2.8	OK	-0.3	-0.61	0.10	1.57	31.3	-46.7	Check	-2.6	-2.87	0.47
3rd-A	5.30	23.1	4.0	OK	0.2	0.32	0.95	4.77	3.5	-6.4	Check	-1.3	-0.52	0.13	3.14	23.4	-38.4	Check	-2.6	-3.11	0.57
4th-A	10.55	15.6	0.2	OK	0.0	0.02	0.96	9.94	3.2	-5.6	Check	-1.2	-0.49	0.19	8.65	18.3	-17.8	Check	-1.2	-1.54	0.93
5th-A	16.10	13.0	1.8	OK	0.1	0.16	1.03	14.83	3.1	-6.3	Check	-1.3	-0.55	0.23	13.97	17.2	-11.7	OK	-0.7	-1.03	1.18
6th-A	21.28	11.8	-1.3	OK	-0.1	-0.11	1.07	19.98	3.1	-7.3	Check	-1.5	-0.66	0.27	19.67	16.7	-8.7	OK	-0.6	-0.79	1.41
5th-B	16.38	12.9	2.8	OK	0.2	0.25	1.04	14.75	3.1	-7.4	Check	-1.4	-0.67	0.23	14.03	17.2	-11.9	OK	-0.8	-1.08	1.18
4th-B	10.73	15.5	1.1	OK	0.1	0.09	0.97	9.90	3.2	-6.7	Check	-1.3	-0.59	0.18	8.70	18.3	-18.0	Check	-1.2	-1.59	0.93
3rd-B	5.55	22.4	9.7	OK	0.4	0.79	0.96	4.79	3.5	-5.3	OK	-0.8	-0.43	0.13	3.19	23.3	-36.9	Check	-2.3	-3.02	0.58
2nd-B	3.11	33.7	4.1	OK	0.1	0.32	0.96	2.90	4.0	-2.8	OK	-0.3	-0.22	0.11	1.59	31.3	-46.7	Check	-2.6	-3.60	0.46
1st-B	1.19	75.4	14.8	OK	0.2	0.84	1.03	1.09	7.3	6.0	OK	0.3	0.34	0.09	0.54	62.0	-47.5	Check	-1.3	-2.70	0.39
Compound	DCMR2							APPA BZ							ERLAP						
benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	1.26	32.1	34.2	OK	0.7	1.72	0.47	0.99	12.1	5.7	OK	0.2	0.29	0.14	0.43	31.1	-53.9	Check	-2.2	-2.71	0.16
2nd-A	3.28	26.2	11.1	OK	0.4	1.47	0.81	2.61	9.4	3.2	OK	0.3	-0.24	0.23	2.56	6.2	-8.3	OK	-0.9	-0.37	0.14
3rd-A	5.31	24.8	4.1	OK	0.2	0.33	1.02	4.96	9.2	-2.7	OK	-0.3	-0.22	0.35	5.22	3.8	2.3	OK	0.4	0.19	0.15
4th-A	10.97	23.7	4.2	OK	0.2	0.37	1.52	10.67	9.1	1.3	OK	0.1	0.12	0.57	10.79	2.2	2.5	OK	0.6	0.22	0.14
5th-A	16.25	23.3	2.7	OK	0.1	0.24	1.87	16.62	9.1	5.1	OK	0.5	0.45	0.74	15.62	2.2	-1.3	OK	-0.3	-0.11	0.17
6th-A	21.81	23.1	1.2	OK	0.1	0.11	2.16	22.33	9.1	3.6	OK	0.4	0.33	0.87	21.66	1.8	0.5	OK	0.1	0.05	0.16
5th-B	16.27	23.3	2.1	OK	0.1	0.19	1.86	16.96	9.1	6.5	OK	0.6	0.58	0.76	15.46	4.1	-3.0	OK	-0.5	-0.27	0.31
4th-B	11.08	23.6	4.4	OK	0.2	0.39	1.53	11.01	9.1	3.8	OK	0.4	0.33	0.58	10.37	4.1	-2.3	OK	-0.4	-0.20	0.25
3rd-B	5.43	24.8	7.3	OK	0.3	0.59	1.04	5.11	9.2	1.0	OK	0.1	0.08	0.36	4.90	4.6	-3.2	OK	-0.4	-0.26	0.18
2nd-B	3.32	26.2	11.1	OK	0.4	0.86	0.79	3.08	9.4	3.2	OK	0.3	0.25	0.27	2.74	6.2	-8.3	OK	-0.9	-0.64	0.16
1st-B	1.32	31.6	28.1	OK	0.6	1.59	0.48	1.13	11.3	9.5	OK	0.4	0.54	0.15	0.62	21.2	-39.7	Check	-1.7	-2.25	0.15

En scores ≥ 1 are highlighted in red. Z-scores and Repeatability scores ≥ of the 95 % confident level interval are highlighted in blue and those ≥ of the 99 % confident level interval in red

Table 10.- E_n scores, bias and reported expanded uncertainty of the participants: toluene

Compound	EKONERG							ISPRA							EPA						
toluene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	1.98	11.3	-16.7	OK	-1.0	-1.49	0.22	1.57	8.8	-33.9	Check	-2.2	-3.03	0.13	1.77	5.7	-25.5	Check	-1.7	-2.27	0.10
2nd-A	8.70	6.9	-11.9	Check	-1.3	-1.75	0.37	9.28	7.3	0.0	OK	0.0	-0.83	0.41	9.09	5.4	-6.0	OK	-0.7	-1.14	0.50
3rd-A	16.45	6.5	-10.9	Check	-1.3	-2.07	0.49	19.44	7.3	5.4	OK	0.6	1.02	0.65	17.86	5.5	-3.2	OK	-0.4	-0.61	0.46
4th-A	35.07	6.1	-11.4	Check	-1.3	-2.01	0.69	46.09	7.3	16.4	Check	1.5	2.89	1.08	41.83	5.5	5.7	OK	0.6	1.00	0.75
5th-A	53.06	6.0	-10.5	Check	-1.0	-1.64	0.85	70.97	7.3	19.7	Check	1.6	3.07	1.38	65.38	5.5	10.3	OK	1.0	1.60	0.96
6th-A	72.29	6.0	-10.8	Check	-1.1	-1.65	0.99	99.89	7.3	23.3	Check	1.9	3.56	1.67	91.87	5.4	13.4	Check	1.3	2.05	1.15
5th-B	53.36	6.0	-11.4	Check	-1.3	-1.91	0.85	71.67	7.3	19.0	Check	1.7	3.18	1.38	67.04	5.7	11.3	Check	1.2	1.89	1.00
4th-B	35.72	6.1	-10.8	Check	-1.1	-1.79	0.70	47.14	7.3	17.7	Check	1.5	2.93	1.10	43.92	5.4	9.7	OK	1.0	1.61	0.77
3rd-B	16.84	6.5	-11.8	Check	-1.4	-2.19	0.49	20.67	7.3	8.3	OK	0.8	1.54	0.68	19.53	5.5	2.3	OK	0.3	0.43	0.49
2nd-B	9.88	6.9	-11.9	Check	-1.3	-2.05	0.39	11.21	7.3	0.0	OK	0.0	0.00	0.47	10.53	5.4	-6.0	OK	-0.7	-1.04	0.33
1st-B	2.42	10.3	-17.8	Check	-1.2	-1.60	0.23	2.27	8.0	-23.0	Check	-1.7	-2.06	0.17	2.33	23.1	-20.9	OK	-0.9	-1.88	0.49
Compound	GIOS							REE							VMM						
toluene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	2.98	16.2	25.4	Check	1.0	2.27	0.47								2.92	14.6	23.0	Check	1.0	2.05	0.42
2nd-A	11.76	16.2	15.3	OK	0.8	3.09	1.15								11.63	14.6	15.2	OK	0.8	2.87	1.03
3rd-A	20.46	16.2	10.9	OK	0.6	2.07	1.53								21.32	14.6	15.5	OK	0.9	2.95	1.43
4th-A	42.64	16.2	7.7	OK	0.4	1.36	2.24								45.90	14.6	15.9	OK	0.9	2.81	2.17
5th-A	63.66	16.2	7.4	OK	0.4	1.15	2.75								68.99	14.6	16.4	OK	0.9	2.55	2.68
6th-A	86.09	16.2	6.3	OK	0.3	0.96	3.20								92.91	14.6	14.7	OK	0.8	2.25	3.12
5th-B	64.08	16.2	6.4	OK	0.3	1.07	2.75								69.07	14.6	14.7	OK	0.8	2.46	2.68
4th-B	43.28	16.2	8.1	OK	0.4	1.34	2.26								46.20	14.6	15.4	OK	0.8	2.54	2.18
3rd-B	21.11	16.2	10.6	OK	0.6	1.97	1.55								21.83	14.6	14.4	OK	0.8	2.67	1.45
2nd-B	12.92	16.2	15.3	OK	0.8	2.65	1.19								12.91	14.6	15.2	OK	0.8	2.63	1.08
1st-B	3.47	16.2	17.8	OK	0.8	1.60	0.52								3.50	14.6	18.8	OK	0.9	1.69	0.47
Compound	LIKZ							SHMU							DLI						
toluene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	2.54	7.6	7.3	OK	0.4	0.65	0.19								2.78	28.7	17.1	OK	0.5	1.53	0.78
2nd-A	9.89	7.6	2.9	OK	0.3	0.13	0.45								10.46	13.0	1.3	OK	0.1	1.04	0.85
3rd-A	18.90	7.6	2.4	OK	0.2	0.45	0.66								18.29	11.6	-0.9	OK	-0.1	-0.17	0.98
4th-A	39.60	7.6	0.0	OK	0.0	0.00	0.97								38.97	10.7	-1.6	OK	-0.1	-0.27	1.35
5th-A	59.49	7.6	0.3	OK	0.0	0.05	1.20								58.88	10.5	-0.7	OK	-0.1	-0.11	1.65
6th-A	80.73	7.6	-0.4	OK	0.0	-0.05	1.40								80.41	10.4	-0.8	OK	-0.1	-0.12	1.92
5th-B	59.74	7.6	-0.8	OK	-0.1	-0.14	1.20								59.27	10.5	-1.6	OK	-0.1	-0.27	1.65
4th-B	40.19	7.6	0.4	OK	0.0	0.06	0.98								39.54	10.7	-1.2	OK	-0.1	-0.20	1.37
3rd-B	19.45	7.6	1.9	OK	0.2	0.35	0.67								18.97	11.6	-0.6	OK	0.0	-0.11	1.00
2nd-B	11.53	7.6	2.9	OK	0.3	0.50	0.50								11.35	13.0	1.3	OK	0.1	0.22	0.84
1st-B	3.05	7.6	3.6	OK	0.2	0.32	0.21								3.16	25.7	7.3	OK	0.2	0.65	0.75
Compound	IPH_S							AAA							DCMR						
toluene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	2.33	53.0	-2.0	OK	0.0	-0.18	1.20	2.58	6.8	8.7	OK	0.5	0.77	0.17	2.22	26.8	-6.4	OK	-0.2	-0.57	0.58
2nd-A	9.14	18.3	8.6	OK	0.4	-1.05	1.11	8.85	4.4	-3.3	OK	-0.4	-1.51	0.24	9.99	17.9	-9.9	OK	-0.6	0.30	1.08
3rd-A	17.74	15.6	-3.9	OK	-0.2	-0.73	1.27	17.91	4.2	-3.0	OK	-0.4	-0.56	0.35	16.86	16.9	-8.7	OK	-0.5	-1.65	1.31
4th-A	37.97	12.6	-4.1	OK	-0.3	-0.72	1.55	37.73	4.2	-4.7	OK	-0.6	-0.83	0.51	35.52	16.1	-10.3	OK	-0.6	-1.81	1.85
5th-A	57.47	11.7	-3.1	OK	-0.2	-0.48	1.79	56.12	4.2	-5.3	OK	-0.6	-0.83	0.63	52.61	15.9	-11.3	OK	-0.7	-1.75	2.23
6th-A	78.89	11.3	-2.6	OK	-0.2	-0.40	2.04	75.80	4.2	-6.4	OK	-0.7	-0.99	0.73	70.39	15.7	-13.1	OK	-0.8	-2.01	2.54
5th-B	59.22	11.7	-1.7	OK	-0.1	-0.28	1.84	56.24	4.2	-6.6	OK	-0.8	-1.11	0.62	52.71	15.9	-12.5	OK	-0.8	-2.09	2.22
4th-B	39.79	12.5	-0.6	OK	0.0	-0.10	1.61	37.81	4.2	-5.6	OK	-0.6	-0.92	0.51	35.74	16.1	-10.7	OK	-0.7	-1.78	1.85
3rd-B	19.92	15.1	4.4	OK	0.3	0.82	1.36	18.17	4.2	-4.8	OK	-0.6	-0.89	0.35	17.36	16.8	-9.0	OK	-0.5	-1.68	1.33
2nd-B	12.17	18.3	8.6	OK	0.4	1.49	1.27	10.84	4.4	-3.3	OK	-0.4	-0.57	0.27	10.10	17.9	-9.9	OK	-0.6	-1.71	1.03
1st-B	4.24	34.3	43.9	OK	0.9	3.94	1.34	3.12	6.1	5.8	OK	0.4	0.52	0.17	2.53	25.4	-14.1	OK	-0.6	-1.27	0.59
Compound	DCMR2							APPA BZ							ERLAP						
toluene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	2.67	27.1	12.5	OK	0.4	1.11	0.70	2.35	9.6	-0.9	OK	-0.1	-0.08	0.22	2.08	6.2	-12.2	OK	-0.8	-1.09	0.12
2nd-A	10.35	23.7	-6.4	OK	-0.3	0.87	1.48	9.13	9.1	0.8	OK	0.1	-1.07	0.50	10.01	8.0	-4.8	OK	-0.5	0.32	0.35
3rd-A	17.32	23.3	-6.1	OK	-0.3	-1.16	1.85	18.02	9.1	-2.4	OK	-0.2	-0.45	0.75	19.91	2.2	7.9	Check	1.3	1.50	0.20
4th-A	36.37	22.9	-8.1	OK	-0.4	-1.43	2.70	37.22	9.1	-6.0	OK	-0.5	-1.05	1.09	40.68	2.2	2.8	OK	0.4	0.49	0.29
5th-A	48.09	22.8	-18.9	OK	-0.9	-2.94	2.93	56.79	9.1	-4.2	OK	-0.3	-0.66	1.37	59.71	2.3	0.7	OK	0.1	0.11	0.37
6th-A	69.26	22.7	-14.5	OK	-0.7	-2.22	3.61	78.09	9.1	-3.6	OK	-0.3	-0.55	1.62	81.09	2.7	0.1	OK	0.0	0.01	0.50
5th-B	55.05	22.8	-8.6	OK	-0.4	-1.44	3.32	57.83	9.1	-4.0	OK	-0.3	-0.67	1.39	59.54	3.9	-1.2	OK	-0.1	-0.19	0.61
4th-B	34.15	22.9	-14.7	OK	-0.7	-2.43	2.52	38.24	9.1	-4.5	OK	-0.4	-0.74	1.12	39.10	3.3	-2.3	OK	-0.3	-0.39	0.41
3rd-B	16.98	23.3	-11.0	OK	-0.5	-2.05	1.79	18.68	9.1	-2.1	OK	-0.2	-0.39	0.77	18.73	6.2	-1.9	OK	-0.2	-0.35	0.53
2nd-B	10.49	23.7	-6.4	OK	-0.3	-1.10	1.42	11.30	9.1	0.8	OK	0.1	0.15	0.59	10.67	8.0	-4.8	OK	-0.5	-0.83	0.49
1st-B	2.96	26.6	0.6	OK	0.0	0.05	0.72	2.95	9.4	0.2	OK	0.0	0.01	0.26	2.80	9.2	-5.1	OK	-0.3	-0.46	0.24

En scores ≥ 1 are highlighted in red. Z-scores and Repeatability scores ≥ of the 95 % confident level interval are highlighted in blue and those ≥ of the 99 % confident level interval in red

Table 11.- E_n scores, bias and reported expanded uncertainty of the participants: ethyl-benzene

Compound	EKONERG							ISPRA							EPA						
ethyl-benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.32	40.0	-32.2	OK	-0.8	-1.11	0.16	0.57	18.5	21.4	OK	0.5	0.74	0.13	0.31	5.2	-34.5	Check	-1.0	-1.19	0.02
2nd-A	1.53	11.1	-6.1	OK	-0.3	-0.20	0.21	1.34	8.4	10.9	OK	0.6	-1.03	0.15	1.21	5.4	-28.7	Check	-1.7	-1.58	0.11
3rd-A	2.90	9.6	-7.2	OK	-0.4	-0.66	0.25	3.48	7.6	11.3	OK	0.7	1.04	0.24	2.46	5.7	-21.2	Check	-1.4	-1.96	0.13
4th-A	6.35	7.5	-10.1	OK	-0.7	-1.20	0.33	8.12	7.1	14.8	Check	1.0	1.77	0.40	5.99	5.7	-15.2	Check	-1.2	-1.82	0.23
5th-A	9.58	7.0	-10.7	OK	-0.8	-1.39	0.39	12.37	7.1	15.2	Check	1.1	1.96	0.51	9.05	5.6	-15.7	Check	-1.3	-2.02	0.29
6th-A	13.05	6.6	-12.4	Check	-1.1	-1.77	0.44	17.58	7.1	18.1	Check	1.4	2.58	0.63	13.30	5.5	-10.7	OK	-1.0	-1.52	0.37
5th-B	9.66	6.9	-11.8	Check	-1.0	-1.65	0.39	12.37	7.1	12.9	Check	1.0	1.80	0.50	9.27	6.0	-15.4	Check	-1.4	-2.15	0.32
4th-B	6.44	7.5	-10.9	OK	-0.8	-1.32	0.33	8.12	7.1	12.3	OK	0.9	1.50	0.39	6.21	5.6	-14.0	Check	-1.1	-1.71	0.24
3rd-B	3.05	9.4	-8.3	OK	-0.5	-0.79	0.25	3.67	7.5	10.5	OK	0.7	1.00	0.24	2.62	5.8	-21.0	Check	-1.5	-2.01	0.13
2nd-B	1.80	11.1	-6.1	OK	-0.3	-0.48	0.21	2.13	8.4	10.9	OK	0.6	0.86	0.18	1.37	5.4	-28.7	Check	-1.7	-2.25	0.08
1st-B	0.40	333.3	-31.3	OK	-0.1	-1.04	1.67	0.58	18.3	-0.9	OK	0.0	-0.03	0.13	0.37	20.1	-37.1	Check	-1.3	-1.23	0.09
Compound	GIOS							REE							VMM						
ethyl-benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.70	28.7	47.9	OK	0.9	1.65	0.25								0.63	14.6	33.1	OK	0.9	1.14	0.12
2nd-A	2.26	16.2	34.1	Check	1.2	2.92	0.39								1.91	14.6	15.1	OK	0.6	1.41	0.30
3rd-A	4.02	16.2	28.8	Check	1.1	2.66	0.59								3.48	14.6	11.5	OK	0.5	1.06	0.46
4th-A	8.52	16.2	20.6	OK	0.9	2.45	0.95								8.47	14.6	19.8	OK	0.9	2.36	0.85
5th-A	12.74	16.2	18.7	OK	0.8	2.41	1.20								12.65	14.6	17.9	OK	0.9	2.30	1.08
6th-A	17.22	16.2	15.7	OK	0.7	2.24	1.41								17.10	14.6	14.8	OK	0.8	2.12	1.26
5th-B	12.81	16.2	16.9	OK	0.8	2.36	1.20								12.77	14.6	16.6	OK	0.8	2.31	1.08
4th-B	8.73	16.2	20.8	OK	0.9	2.53	0.96								8.63	14.6	19.4	OK	0.9	2.36	0.86
3rd-B	4.26	16.2	28.3	Check	1.2	2.70	0.61								3.67	14.6	10.3	OK	0.5	0.99	0.48
2nd-B	2.57	16.2	34.1	Check	1.2	2.67	0.43								2.21	14.6	15.1	OK	0.6	1.19	0.33
1st-B	0.89	22.4	52.2	Check	1.2	1.73	0.25								0.77	14.6	31.2	OK	1.0	1.03	0.14
Compound	LIKZ							SHMU							DLI						
ethyl-benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.63	33.0	33.5	OK	0.6	1.16	0.26								0.75	33.7	59.6	OK	0.9	2.06	0.32
2nd-A	1.76	10.8	11.1	OK	0.5	0.77	0.24								1.92	15.9	10.7	OK	0.4	1.47	0.35
3rd-A	3.33	7.9	6.5	OK	0.4	0.60	0.24								3.45	12.9	10.5	OK	0.5	0.97	0.40
4th-A	7.26	5.7	2.8	OK	0.2	0.33	0.28								7.37	10.8	4.3	OK	0.3	0.51	0.55
5th-A	10.95	5.3	2.0	OK	0.2	0.26	0.33								10.95	10.3	2.0	OK	0.1	0.26	0.65
6th-A	14.92	5.1	0.2	OK	0.0	0.03	0.39								14.77	10.1	-0.8	OK	-0.1	-0.12	0.75
5th-B	11.04	5.3	0.7	OK	0.1	0.10	0.33								11.03	10.3	0.6	OK	0.0	0.09	0.65
4th-B	7.39	5.6	2.3	OK	0.2	0.28	0.28								7.48	10.7	3.5	OK	0.2	0.43	0.55
3rd-B	3.50	7.7	5.2	OK	0.3	0.50	0.24								3.74	12.6	12.4	OK	0.7	1.19	0.42
2nd-B	2.13	10.8	11.1	OK	0.5	0.87	0.24								2.12	15.9	10.7	OK	0.4	0.84	0.35
1st-B	0.73	28.7	24.0	OK	0.5	0.80	0.26								0.82	31.2	39.2	OK	0.8	1.30	0.32
Compound	IPH_S							AAA							DCMR						
ethyl-benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.18	565.6	-61.9	OK	-0.3	-2.13	1.29								0.29	102.4	-38.3	OK	-0.5	-1.32	0.38
2nd-A	0.85	78.1	-23.4	OK	-0.4	-3.12	1.16								1.08	38.5	-43.0	Check	-1.6	-2.15	0.45
3rd-A	2.38	52.1	-23.9	OK	-0.6	-2.21	1.12								1.90	28.7	-39.1	Check	-1.7	-3.61	0.49
4th-A	6.17	26.2	-12.7	OK	-0.5	-1.51	1.11								5.27	20.2	-25.4	Check	-1.3	-3.03	0.73
5th-A	9.73	20.3	-9.4	OK	-0.4	-1.21	1.15								9.18	18.1	-14.5	OK	-0.8	-1.86	0.97
6th-A	13.15	17.6	-11.7	OK	-0.6	-1.67	1.17								13.38	17.3	-10.2	OK	-0.6	-1.45	1.17
5th-B	10.16	19.8	-7.3	OK	-0.3	-1.02	1.16								9.23	18.1	-15.8	OK	-0.9	-2.20	0.96
4th-B	6.67	25.1	-7.7	OK	-0.3	-0.93	1.14								5.33	20.1	-26.2	Check	-1.4	-3.19	0.73
3rd-B	2.91	44.4	-12.5	OK	-0.3	-1.19	1.14								1.97	28.2	-40.6	Check	-1.9	-3.88	0.49
2nd-B	1.47	78.1	-23.4	OK	-0.4	-1.83	1.18								1.09	38.5	-43.0	Check	-1.6	-3.37	0.43
1st-B	4.24	225.9	-20.9	OK	-0.1	-0.69	1.30								0.35	86.7	-39.7	OK	-0.7	-1.31	0.38
Compound	DCMR2							APPA BZ							ERLAP						
ethyl-benzene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.56	44.0	18.5	OK	0.3	0.64	0.31	0.42	20.5	-11.0	OK	-0.3	-0.38	0.11	0.30	43.5	-36.1	OK	-0.8	-1.25	0.17
2nd-A	1.78	29.0	-3.3	OK	-0.1	0.87	0.56	1.64	9.7	12.7	OK	0.6	0.27	0.18	1.62	9.6	1.3	OK	0.1	0.17	0.18
3rd-A	3.06	26.5	-2.1	OK	-0.1	-0.20	0.73	3.47	9.3	11.1	OK	0.6	1.02	0.29	3.26	6.7	4.4	OK	0.3	0.40	0.20
4th-A	6.34	24.5	-10.4	OK	-0.4	-1.23	1.06	7.66	9.1	8.4	OK	0.5	1.00	0.48	7.25	3.1	2.6	OK	0.2	0.31	0.16
5th-A	8.82	23.9	-17.8	OK	-0.8	-2.30	1.23	12.04	9.1	12.2	OK	0.8	1.57	0.64	10.76	2.6	0.2	OK	0.0	0.03	0.17
6th-A	12.98	23.5	-12.8	OK	-0.6	-1.83	1.54	16.47	9.1	10.6	OK	0.8	1.51	0.76	14.77	2.1	-0.8	OK	-0.1	-0.11	0.16
5th-B	10.00	23.7	-8.8	OK	-0.4	-1.22	1.37	12.28	9.1	12.1	OK	0.8	1.69	0.64	10.87	2.5	-0.8	OK	-0.1	-0.11	0.15
4th-B	6.37	24.4	-11.9	OK	-0.5	-1.45	1.06	7.89	9.1	9.2	OK	0.6	1.12	0.49	7.28	2.9	0.7	OK	0.1	0.08	0.15
3rd-B	3.03	26.6	-8.9	OK	-0.3	-0.85	0.71	3.69	9.3	11.1	OK	0.7	1.06	0.31	3.36	5.6	1.1	OK	0.1	0.10	0.17
2nd-B	1.85	29.0	-3.3	OK	-0.1	-0.26	0.55	2.16	9.7	12.7	OK	0.6	1.00	0.22	1.94	9.6	1.3	OK	0.1	0.10	0.19
1st-B	0.65	41.1	10.5	OK	0.2	0.35	0.33	0.58	16.2	-0.9	OK	0.0	-0.03	0.12	0.43	40.1	-26.2	OK	-0.7	-0.87	0.22

En scores ≥ 1 are highlighted in red. Z-scores and Repeatability scores ≥ of the 95 % confident level interval are highlighted in blue and those ≥ of the 99 % confident level interval in red

Table 12.- E_n scores, bias and reported expanded uncertainty of the participants: m,p-xylene

Compound	EKONERG							ISPRA							EPA						
m,p-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.34	38.5	-38.4	OK	-1.0	-1.27	0.16	0.53	11.3	-3.2	OK	-0.1	-0.11	0.08	0.50	15.6	-8.8	OK	-0.3	-0.29	0.10
2nd-A	1.75	10.7	3.5	OK	0.2	0.03	0.22	1.59	9.6	3.3	OK	0.2	-0.53	0.16	1.40	7.0	-23.5	Check	-1.7	-1.17	0.15
3rd-A	3.42	9.0	1.5	OK	0.1	0.12	0.27	3.19	9.5	-5.4	OK	-0.4	-0.42	0.27	2.75	6.6	-18.4	Check	-1.4	-1.44	0.16
4th-A	7.24	7.3	-5.5	OK	-0.5	-0.53	0.35	7.26	9.5	-5.3	OK	-0.4	-0.51	0.46	6.15	6.8	-19.8	Check	-1.9	-1.88	0.28
5th-A	10.93	6.8	-5.4	OK	-0.5	-0.54	0.42	11.69	9.5	1.2	OK	0.1	0.12	0.63	9.71	6.5	-15.9	Check	-1.6	-1.60	0.36
6th-A	14.76	6.5	-7.3	OK	-0.7	-0.74	0.47	17.17	9.5	7.9	OK	0.6	0.80	0.80	13.20	6.5	-17.1	Check	-1.7	-1.73	0.42
5th-B	11.03	6.8	-6.7	OK	-0.7	-0.69	0.42	12.04	9.5	1.9	OK	0.1	0.19	0.64	9.93	6.7	-16.0	Check	-1.6	-1.65	0.37
4th-B	7.44	7.3	-5.5	OK	-0.5	-0.55	0.36	7.97	9.5	1.2	OK	0.1	0.12	0.50	6.45	6.5	-18.1	Check	-1.8	-1.82	0.28
3rd-B	3.60	8.8	1.6	OK	0.1	0.14	0.28	3.54	9.5	0.0	OK	0.0	0.00	0.29	2.97	6.9	-16.2	Check	-1.4	-1.40	0.18
2nd-B	2.13	10.7	3.5	OK	0.2	0.24	0.23	2.12	9.6	3.3	OK	0.2	0.22	0.21	1.57	7.0	-23.5	Check	-1.7	-1.59	0.11
1st-B	0.45	30.4	-35.4	OK	-0.9	-1.37	0.17	1.06	10.0	52.9	Check	1.5	2.04	0.13	0.46	29.8	-34.1	OK	-0.9	-1.32	0.17
Compound	GIOS							REE							VMM						
m,p-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	1.01	19.7	84.9	Check	1.8	2.82	0.25								0.60	14.7	9.4	OK	0.3	0.31	0.11
2nd-A	2.43	16.2	41.7	Check	1.6	2.35	0.41								1.76	14.6	5.0	OK	0.3	0.06	0.27
3rd-A	4.38	16.2	30.1	Check	1.3	2.36	0.63								3.35	14.6	-0.7	OK	0.0	-0.05	0.43
4th-A	9.03	16.2	17.7	OK	0.8	1.68	0.97								8.78	14.6	14.5	OK	0.8	1.37	0.85
5th-A	13.56	16.2	17.4	OK	0.8	1.74	1.24								13.16	14.6	14.0	OK	0.7	1.40	1.08
6th-A	18.16	16.2	14.1	OK	0.7	1.43	1.45								17.93	14.6	12.6	OK	0.7	1.29	1.29
5th-B	13.74	16.2	16.2	OK	0.8	1.67	1.24								13.37	14.6	13.1	OK	0.7	1.35	1.09
4th-B	9.16	16.2	16.3	OK	0.8	1.64	0.98								9.04	14.6	14.7	OK	0.8	1.48	0.87
3rd-B	4.60	16.2	29.9	Check	1.3	2.58	0.65								3.56	14.6	0.5	OK	0.0	0.04	0.45
2nd-B	2.91	16.2	41.7	Check	1.6	2.83	0.48								2.16	14.6	5.0	OK	0.3	0.34	0.32
1st-B	1.13	17.7	63.6	Check	1.5	2.46	0.24								0.75	14.6	9.0	OK	0.2	0.35	0.13
Compound	LIKZ							SHMU							DLI						
m,p-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.63	50.1	15.0	OK	0.2	0.50	0.40								0.77	45.1	40.0	OK	0.6	1.33	0.43
2nd-A	1.72	15.4	7.7	OK	0.4	-0.07	0.35								1.92	20.4	4.2	OK	0.2	0.60	0.45
3rd-A	3.45	10.9	2.4	OK	0.1	0.19	0.33								3.79	15.6	12.4	OK	0.6	0.97	0.52
4th-A	7.91	7.2	3.1	OK	0.3	0.29	0.38								7.95	13.0	3.7	OK	0.2	0.35	0.69
5th-A	11.76	6.5	1.8	OK	0.2	0.19	0.43								11.91	12.4	3.1	OK	0.2	0.31	0.83
6th-A	15.83	6.3	-0.5	OK	-0.1	-0.05	0.49								16.11	12.1	1.2	OK	0.1	0.12	0.96
5th-B	11.83	6.5	0.0	OK	0.0	0.00	0.43								11.99	12.4	1.4	OK	0.1	0.15	0.83
4th-B	8.10	7.1	2.9	OK	0.3	0.29	0.38								8.10	13.0	2.9	OK	0.2	0.29	0.69
3rd-B	3.68	10.4	3.9	OK	0.3	0.34	0.33								3.97	15.4	12.1	OK	0.6	1.04	0.53
2nd-B	2.21	15.4	7.7	OK	0.4	0.53	0.34								2.14	20.4	4.2	OK	0.2	0.29	0.44
1st-B	0.80	39.7	14.9	OK	0.3	0.58	0.39								0.79	45.1	14.2	OK	0.2	0.55	0.43
Compound	IPH_S							AAA							DCMR						
m,p-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.13	893.7	-77.0	OK	-0.4	-2.56	1.41								0.30	101.0	-46.2	OK	-0.7	-1.53	0.37
2nd-A	0.42	156.6	-60.8	OK	-1.0	-4.56	1.24								1.21	34.5	-35.7	Check	-1.4	-1.83	0.46
3rd-A	1.25	107.7	-62.8	Check	-1.5	-4.92	1.19								2.67	24.8	-20.8	OK	-0.9	-1.63	0.59
4th-A	3.35	52.9	-56.4	Check	-2.3	-5.35	1.18								7.78	18.6	1.4	OK	0.1	0.14	0.96
5th-A	5.34	40.6	-53.8	Check	-2.6	-5.40	1.22								12.06	17.5	4.4	OK	0.2	0.44	1.19
6th-A	7.32	35.0	-54.0	Check	-3.0	-5.49	1.26								16.45	16.9	3.3	OK	0.2	0.34	1.37
5th-B	5.62	39.6	-52.5	Check	-2.6	-5.41	1.24								12.10	17.5	2.3	OK	0.1	0.24	1.18
4th-B	3.73	49.5	-52.6	Check	-2.1	-5.30	1.22								7.87	18.6	-0.1	OK	0.0	-0.01	0.96
3rd-B	1.60	89.0	-55.0	Check	-1.3	-4.74	1.24								2.88	24.1	-18.8	OK	-0.9	-1.62	0.60
2nd-B	0.81	156.6	-60.8	OK	-1.0	-4.13	1.27								1.32	34.5	-35.7	Check	-1.4	-2.42	0.46
1st-B	0.29	399.3	-58.1	OK	-0.3	-2.25	1.41								0.37	84.2	-46.8	OK	-0.8	-1.81	0.38
Compound	DCMR2							APPA BZ							ERLAP						
m,p-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.75	38.7	36.7	OK	0.6	1.22	0.36	0.40	21.5	-27.1	OK	-0.8	-0.90	0.11	0.34	38.5	-38.8	Check	-1.0	-1.29	0.16
2nd-A	2.12	27.7	12.3	OK	0.4	1.29	0.63	1.36	9.9	-7.1	OK	-0.4	-1.32	0.15	2.02	8.1	-5.5	OK	-0.4	0.95	0.22
3rd-A	3.70	25.8	10.0	OK	0.3	0.78	0.85	2.95	9.4	-12.4	OK	-0.9	-0.97	0.25	3.65	4.9	8.4	OK	0.7	0.66	0.16
4th-A	7.69	24.1	0.3	OK	0.0	0.03	1.23	6.61	9.1	-13.8	Check	-1.1	-1.31	0.40	7.82	2.8	2.0	OK	0.2	0.19	0.14
5th-A	10.66	23.7	-7.7	OK	-0.3	-0.77	1.42	10.09	9.1	-12.6	Check	-1.1	-1.27	0.52	11.54	2.1	-0.1	OK	0.0	-0.01	0.13
6th-A	15.57	23.3	-2.2	OK	-0.1	-0.22	1.78	13.90	9.1	-12.7	Check	-1.1	-1.29	0.62	15.88	1.9	-0.2	OK	0.0	-0.02	0.15
5th-B	12.00	23.6	1.5	OK	0.1	0.15	1.58	10.34	9.1	-12.5	Check	-1.1	-1.29	0.52	11.68	2.8	-1.2	OK	-0.1	-0.12	0.18
4th-B	7.75	24.1	-1.6	OK	-0.1	-0.16	1.23	6.86	9.1	-12.9	Check	-1.1	-1.30	0.41	7.80	2.9	-1.0	OK	-0.1	-0.10	0.15
3rd-B	3.73	25.8	5.4	OK	0.2	0.47	0.84	3.20	9.4	-9.7	OK	-0.8	-0.83	0.26	3.61	5.5	2.0	OK	0.2	0.17	0.17
2nd-B	2.31	27.7	12.3	OK	0.4	0.84	0.65	1.91	9.9	-7.1	OK	-0.4	-0.48	0.19	1.94	8.1	-5.5	OK	-0.4	-0.38	0.16
1st-B	0.84	37.0	21.1	OK	0.4	0.82	0.38	0.55	16.7	-20.5	OK	-0.6	-0.79	0.11	0.42	31.2	-38.7	Check	-1.0	-1.50	0.16

En scores ≥ 1 are highlighted in red. Z-scores and Repeatability scores ≥ of the 95 % confident level interval are highlighted in blue and those ≥ of the 99 % confident level interval in red

Table 13.- E_n scores, bias and reported expanded uncertainty of the participants: o-xylene

Compound	EKONERG							ISPRA							EPA						
o-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.36	36.4	-28.3	OK	-0.8	-1.01	0.16	0.57	13.3	15.1	OK	0.5	0.54	0.10	0.50	10.8	0.4	OK	0.0	0.01	0.07
2nd-A	1.32	12.6	-24.2	Check	-1.4	-1.54	0.20	1.54	11.8	21.6	Check	1.0	-0.61	0.19	1.82	12.3	-2.1	OK	-0.1	0.52	0.21
3rd-A	2.60	10.0	-22.9	Check	-1.6	-2.53	0.23	3.62	11.7	7.3	OK	0.4	0.80	0.37	3.25	5.8	-3.6	OK	-0.3	-0.40	0.17
4th-A	5.65	7.8	-25.3	Check	-2.3	-3.42	0.29	7.95	11.7	5.2	OK	0.3	0.71	0.62	6.62	5.9	-12.5	Check	-1.2	-1.69	0.26
5th-A	8.57	7.1	-25.9	Check	-2.4	-3.51	0.34	12.45	11.7	7.6	OK	0.5	1.03	0.82	10.28	5.8	-11.2	Check	-1.0	-1.52	0.34
6th-A	11.67	6.7	-27.0	Check	-2.8	-3.83	0.39	17.64	11.7	10.4	OK	0.7	1.47	1.01	14.51	5.8	-9.2	OK	-0.9	-1.31	0.41
5th-B	8.66	7.1	-26.8	Check	-2.8	-3.83	0.34	12.62	11.7	6.7	OK	0.5	0.96	0.82	10.54	6.1	-10.9	Check	-1.1	-1.56	0.36
4th-B	5.83	7.7	-24.7	Check	-2.2	-3.29	0.30	8.30	11.7	7.2	OK	0.5	0.96	0.64	6.83	5.8	-11.8	Check	-1.1	-1.57	0.26
3rd-B	2.77	9.8	-22.4	Check	-1.6	-2.49	0.23	3.62	11.7	1.3	OK	0.1	0.15	0.37	3.49	5.8	-2.2	OK	-0.2	-0.24	0.18
2nd-B	1.62	12.6	-24.2	Check	-1.4	-2.02	0.20	2.60	11.8	21.6	Check	1.0	1.80	0.31	2.10	12.3	-2.1	OK	-0.1	-0.18	0.26
1st-B	0.50	27.8	-21.5	OK	-0.7	-1.00	0.17	0.62	13.0	-2.5	OK	-0.1	-0.12	0.10	0.60	20.9	-4.8	OK	-0.2	-0.22	0.16
Compound	GIOS							REE							VMM						
o-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.75	26.7	50.6	Check	1.1	1.81	0.25								0.66	14.6	31.7	OK	1.0	1.13	0.12
2nd-A	2.29	16.2	29.1	Check	1.1	2.49	0.39								2.08	14.6	20.1	OK	0.9	1.61	0.32
3rd-A	4.23	16.2	25.6	Check	1.1	2.82	0.61								3.96	14.7	17.5	OK	0.8	1.92	0.51
4th-A	8.92	16.2	18.1	OK	0.9	2.45	0.97								8.83	14.6	16.8	OK	0.9	2.27	0.86
5th-A	13.69	16.2	18.3	OK	0.9	2.48	1.25								13.46	14.6	16.3	OK	0.8	2.21	1.11
6th-A	18.46	16.2	15.5	OK	0.8	2.20	1.47								18.32	14.6	14.6	OK	0.8	2.07	1.31
5th-B	13.66	16.2	15.5	OK	0.8	2.22	1.23								13.65	14.6	15.4	OK	0.8	2.21	1.12
4th-B	9.17	16.2	18.5	OK	0.9	2.46	0.98								9.07	14.6	17.1	OK	0.9	2.28	0.88
3rd-B	4.50	16.2	26.0	Check	1.1	2.89	0.63								4.25	14.7	19.0	OK	0.9	2.11	0.54
2nd-B	2.76	16.2	29.1	Check	1.1	2.43	0.45								2.57	14.6	20.1	OK	0.9	1.67	0.38
1st-B	0.97	20.6	53.2	Check	1.4	2.48	0.25								0.85	14.7	33.5	Check	1.1	1.56	0.15
Compound	LIKZ							SHMU							DLI						
o-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.60	45.5	20.1	OK	0.3	0.72	0.34								0.50	42.9	1.0	OK	0.0	0.04	0.27
2nd-A	1.74	13.9	3.6	OK	0.2	0.19	0.31								1.96	15.2	5.3	OK	0.2	1.12	0.34
3rd-A	3.52	10.3	4.5	OK	0.3	0.49	0.32								3.63	13.1	7.7	OK	0.4	0.85	0.42
4th-A	7.69	7.7	1.8	OK	0.1	0.24	0.40								8.05	11.7	6.5	OK	0.4	0.88	0.63
5th-A	11.58	7.3	0.1	OK	0.0	0.01	0.47								12.12	11.4	4.7	OK	0.3	0.64	0.78
6th-A	15.46	7.1	-3.2	OK	-0.3	-0.46	0.54								16.76	11.3	4.9	OK	0.3	0.69	0.93
5th-B	11.71	7.3	-1.0	OK	-0.1	-0.15	0.47								12.20	11.4	3.1	OK	0.2	0.45	0.78
4th-B	7.87	7.7	1.6	OK	0.1	0.22	0.40								8.22	11.7	6.2	OK	0.4	0.82	0.63
3rd-B	3.74	10.0	4.7	OK	0.3	0.52	0.32								3.92	12.9	9.8	OK	0.5	1.09	0.44
2nd-B	2.22	13.9	3.6	OK	0.2	0.30	0.31								2.25	15.2	5.3	OK	0.2	0.44	0.34
1st-B	0.75	36.4	18.8	OK	0.4	0.88	0.34								0.62	36.7	-2.7	OK	-0.1	-0.13	0.28
Compound	IPH_S							AAA							DCMR						
o-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.00		-100.0	OK	-0.5	-3.57	1.26								0.32	93.5	-35.1	OK	-0.5	-1.25	0.38
2nd-A	0.84	73.3	-26.2	OK	-0.5	-3.54	1.14								1.21	34.5	-38.5	Check	-1.5	-2.01	0.46
3rd-A	3.09	42.4	-8.5	OK	-0.2	-0.93	1.16								2.49	25.5	-26.2	Check	-1.2	-2.89	0.56
4th-A	7.56	23.2	0.0	OK	0.0	0.00	1.17								6.87	19.1	-9.1	OK	-0.5	-1.24	0.87
5th-A	11.69	18.6	1.0	OK	0.0	0.13	1.22								11.05	17.7	-4.5	OK	-0.2	-0.61	1.10
6th-A	15.73	16.4	-1.6	OK	-0.1	-0.22	1.26								15.40	17.0	-3.7	OK	-0.2	-0.52	1.29
5th-B	12.07	18.3	2.1	OK	0.1	0.30	1.23								11.09	17.7	-6.2	OK	-0.3	-0.89	1.09
4th-B	8.12	22.3	4.9	OK	0.2	0.65	1.20								6.85	19.1	-11.5	OK	-0.6	-1.53	0.87
3rd-B	3.66	37.4	2.5	OK	0.1	0.28	1.19								2.64	24.9	-26.1	Check	-1.2	-2.90	0.57
2nd-B	1.58	73.3	-26.2	OK	-0.5	-2.19	1.16								1.32	34.5	-38.5	Check	-1.5	-3.21	0.45
1st-B	0.38	270.3	-39.3	OK	-0.2	-1.84	1.28								0.37	84.0	-41.7	OK	-0.8	-1.95	0.38
Compound	DCMR2							APPA BZ							ERLAP						
o-xylene	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores	Concentration, µg/m3	U, %	bias, %	State	En	Z-scores (sigma m)	Repeatability scores
1st-A	0.65	41.1	29.9	OK	0.5	1.07	0.34	0.44	0.1	-11.6	OK	-0.4	-0.42	0.11	0.39	32.9	-21.2	OK	-0.6	-0.76	0.16
2nd-A	1.97	28.3	-1.8	OK	-0.1	1.15	0.60	1.48	0.2	-4.7	OK	-0.3	-0.88	0.16	1.84	7.1	-2.6	OK	-0.2	0.60	0.15
3rd-A	3.40	26.1	0.8	OK	0.0	0.09	0.78	3.19	0.3	-5.3	OK	-0.4	-0.59	0.27	3.46	4.6	2.6	OK	0.2	0.28	0.14
4th-A	6.97	24.3	-7.8	OK	-0.3	-1.06	1.13	7.33	0.7	-3.0	OK	-0.2	-0.41	0.45	7.78	2.6	2.9	OK	0.3	0.40	0.13
5th-A	9.82	23.8	-15.1	OK	-0.7	-2.05	1.32	11.67	1.1	0.8	OK	0.1	0.12	0.60	11.75	2.2	1.5	OK	0.2	0.20	0.14
6th-A	14.14	23.4	-11.5	OK	-0.5	-1.63	1.62	16.26	1.5	1.7	OK	0.1	0.25	0.72	15.87	1.9	-0.7	OK	-0.1	-0.10	0.15
5th-B	10.94	23.7	-7.5	OK	-0.3	-1.08	1.44	11.96	1.1	1.1	OK	0.1	0.16	0.61	11.62	3.0	-1.7	OK	-0.2	-0.25	0.20
4th-B	7.07	24.3	-8.7	OK	-0.4	-1.16	1.14	7.53	0.7	-2.7	OK	-0.2	-0.37	0.45	7.68	3.4	-0.9	OK	-0.1	-0.11	0.17
3rd-B	3.38	26.1	-5.3	OK	-0.2	-0.58	0.77	3.38	0.3	-5.3	OK	-0.4	-0.59	0.27	3.49	5.5	-2.1	OK	-0.2	-0.24	0.17
2nd-B	2.10	28.3	-1.8	OK	-0.1	-0.15	0.59	2.04	0.2	-4.7	OK	-0.3	-0.39	0.20	2.08	7.1	-2.6	OK	-0.2	-0.22	0.15
1st-B	0.76	38.2	20.7	OK	0.4	0.96	0.36	0.67	0.1	5.8	OK	0.2	0.27	0.12	0.56	25.2	-12.0	OK	-0.4	-0.56	0.17

En scores ≥ 1 are highlighted in red. Z-scores and Repeatability scores ≥ of the 95 % confident level interval are highlighted in blue and those ≥ of the 99 % confident level interval in red

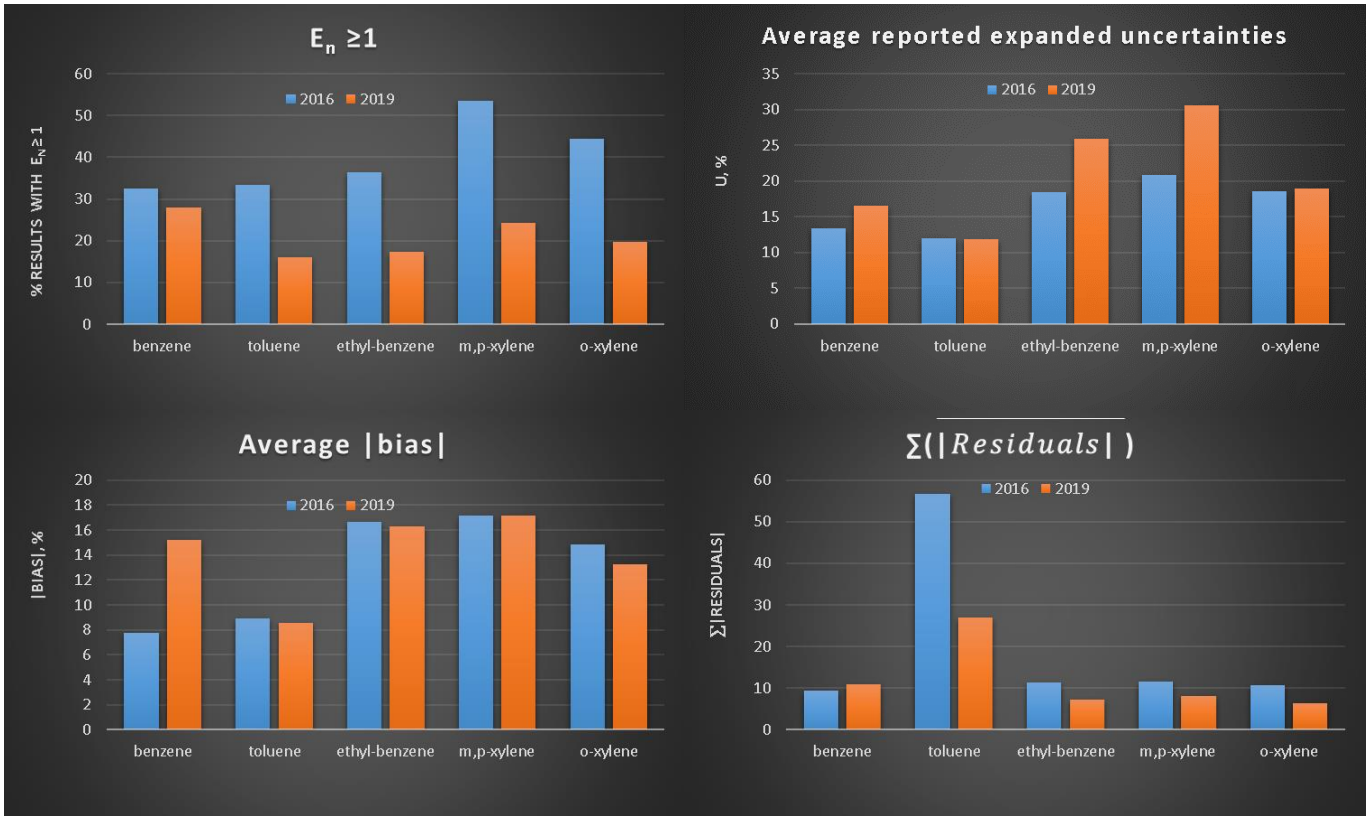
In this exercise, 7 of the 13 laboratories were also participating in the last inter-laboratory comparison (EUR 28692 EN, 2017). With respect to the last comparison, there is a general improvement of the E_n scores, more evident for the heaviest aromatic compounds (see Figure 11).

In the case of benzene, the improvement in the E_n scores may not reflect a general improvement in the quality of the measurement, as the 20 % decrease in the number of results with E_n scores ≥ 1 could be due to the average increase of 20 % in the value of the reported uncertainties. In contrast, in this exercise the average absolute bias for benzene is double that obtained in the previous inter-laboratory comparison.

The results for toluene showed a real improvement in the results reflected in a reduction by a half of the E_n scores cases ≥1. Note that the average reported uncertainties as the average absolute bias remained similar in both exercises. Such an improvement is explained by the reduction of the concentration level to a half in order to fit with a more realistic scenario, avoiding at the same time, a possible sampling overload for toluene.

The increase of circa 40 % in the average reported uncertainty value for the xylenes (excluding o-xylene that did not change) cannot explain the reduction to a half of the number of E_n scores cases ≥1, which reported similar average absolute bias in both comparison, reducing to a half the sum of average absolute residuals. Consequently, a proper improvement in analytical method for these compounds is evident.

Figure 11.- Comparison of proficiency test exercises 2016 and 2019



$$\sum \overline{|Residuals|} = \sum_{i}^{Levels} \left(\overline{|bias|}_i \cdot C_{ref_i}/100 \right)$$

4 Conclusions

The reproducibility values of the comparison exercise fulfilled the criteria established by the N37 AQUILA report agreed for proficiency assessment.

In comparison to the previous inter-laboratory exercise (EUR 28692 EN), a slight increase of the reproducibility and the repeatability values were observed. Such an increase was explained by the decrease in the levels of concentration used for comparison. No significant variations in the robustness of the method were, however, observed. Therefore, the average benzene repeatability and reproducibility standard deviation of the exercise were of about 6 % and 14 %, respectively. While ethyl-benzene, m,p-xylene and o-xylene showed higher repeatability and reproducibility standard deviations of around 9 % and 20 %, respectively. The repeatability/reproducibility ratio was describing a robust method for all the considered compounds (with $\gamma \lesssim 2$).

When statistic scores are compared to those from the previous inter-laboratory exercise, an improvement in the proficiency tests results of the heavier aromatic compounds, i.e. from toluene to o-xylene, was observed.

It is noted that those laboratories using Tenax GR, as a trapping adsorbent, showed a poorer performance in the linearity tests when compared to other adsorbent of higher capacity.

The combined use of the bias, uncertainty and E_n scores brings a better understanding of the individual laboratory performance within the exercise. On the other hand, Z-scores (σ_m) and the repeatability scores provide independent criteria for comparison based on AQUILA N37 protocol and out of the context of the exercise.

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Annexes:

Annex 1.- Work schedule for the inter-laboratory comparison exercise

Sept. 23rd: Arrival of participants and installation of equipment: 14:00 to 17:30

Sept. 24th: Calibration and Synchronization: 9:00 – 13:30 / Measurements starting: 14:30

Sept. 25th: End of measurements: 15:30 / Calibration 15:30 – 17:30

Sept.26th: Dismantling of equipment and departure of participants.

Annex 2.- Indicators of Mandel's statistic

Table A 1.- k and h values

Number of Laboratories	k values at of s.l. *				h values at s.l. *	
	3 replicants		5 replicants			
p	1%	5 %	1%	5 %	1%	5 %
3	1.64	1.53	1.53	1.4	1.15	1.15
4	1.77	1.59	1.6	1.44	1.49	1.42
5	1.85	1.62	1.65	1.46	1.72	1.57
6	1.9	1.64	1.68	1.48	1.87	1.66
7	1.94	1.66	1.7	1.49	1.98	1.71
8	1.97	1.67	1.71	1.5	2.06	1.75
9	1.99	1.68	1.73	1.5	2.13	1.78
10	2	1.68	1.74	1.5	2.18	1.8
11	2.01	1.69	1.74	1.51	2.22	1.82
12	2.02	1.69	1.75	1.51	2.25	1.83
13	2.03	1.69	1.76	1.51	2.27	1.84
14	2.04	1.7	1.76	1.52	2.3	1.85
15	2.05	1.7	1.76	1.52	2.32	1.86
16	2.05	1.7	1.77	1.52	2.33	1.86
17	2.06	1.7	1.77	1.52	2.35	1.87
18	2.06	1.71	1.77	1.52	2.36	1.88
19	2.07	1.71	1.78	1.52	2.37	1.88
20	2.07	1.71	1.78	1.52	2.39	1.89
21	2.07	1.71	1.78	1.52	2.39	1.89
22	2.08	1.71	1.78	1.52	2.4	1.89
23	2.08	1.71	1.78	1.53	2.41	1.9
24	2.08	1.71	1.79	1.53	2.42	1.9
25	2.08	1.71	1.79	1.53	2.42	1.9
26	2.09	1.71	1.79	1.53	2.43	1.9
27	2.09	171	1.79	1.53	2.44	1.91

* s.l. : significance level

Annex 3.- Robust Analysis: Estimation of robust average and standard deviation

The robust estimation of an average value, $\bar{C}_i^*$, and standard deviation, s*, of p inter-laboratory measurements is derived from a convergence process of the following equation:

$$\bar{C}_i^* = \frac{\sum C_i^*}{p}$$

Eq.A-1

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

Eq. A-2

Where recurrent values are calculated from these equations:

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

Eq. A-3

The initial values are calculated as:

$$\bar{C}_i^* = \text{ median of } C_i \ (i = 1, 2, \ldots p)$$
$$s^* = 1.483 \cdot \text{ median of } |C_i - \bar{C}_i^*| \ (i = 1, 2, \ldots p)$$

Eq. A-4

Annex 4.- Repeatability, reproducibility and robustness: Previous comparison exercises:

Table A 2.- Average repeatability, reproducibility and gamma values for the 2nd inter-laboratory exercise

	Repeatability, %	Reproducibility, %	Robustness (γ)
Benzene	1.4	17.8	17.2
Toluene	1.8	10.0	7.1
Ethyl-benzene	2.2	9.7	6.1
m,p-Xylene	4.2	8.0	2.1
o-Xylene	3.1	16.5	6.7

(EUR 23792EN 2009)

Table A 3.- Average repeatability, reproducibility and gamma values for the 3rd inter-laboratory exercise

	Repeatability, %	Reproducibility, %	Robustness (γ)
Benzene	4.7	7.9	1.7
Toluene	4.2	15.1	3.6
Ethyl-benzene	9.4	20.0	2.2
m,p-Xylene	9.3	26.6	2.8
o-Xylene	9.7	17.7	1.8

(EUR 27012EN 2014)

Table A 4.- Average repeatability, reproducibility and gamma values for the 4th inter-laboratory exercise

	Repeatability, %	Reproducibility, %	Robustness (γ)
Benzene	4.26	8.38	2.05
Toluene	3.97	9.15	2.36
Ethyl-benzene	6.44	12.22	1.99
m,p-Xylene	7.46	14.31	2.06
o-Xylene	6.02	14.19	2.34

(EUR 28692 EN 2017).

Annex 5.- Conversion factors for data reporting

Table A 5.- . µg/m^3 to ppb (v/v) conversion factors

	Conversion factor µg/m3 / ppb (v/v)
Benzene	3.25
Toluene	3.83
Ethyl-benzene	4.41
Xylenes	4.41

ppb(m/m) to ppb(v/v) factors were not taken into account.

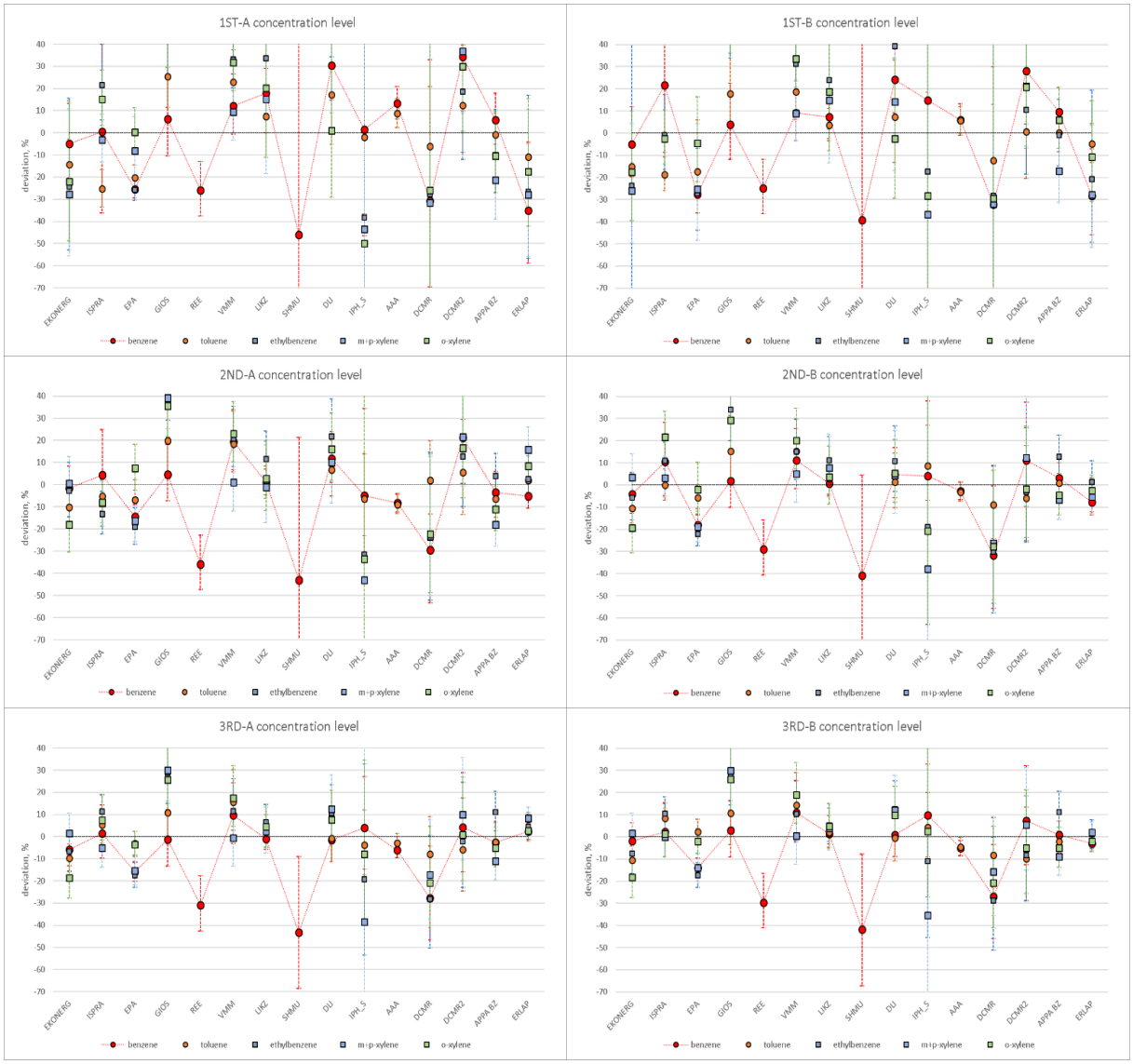
Annex 6.- Scattering of Laboratory Results

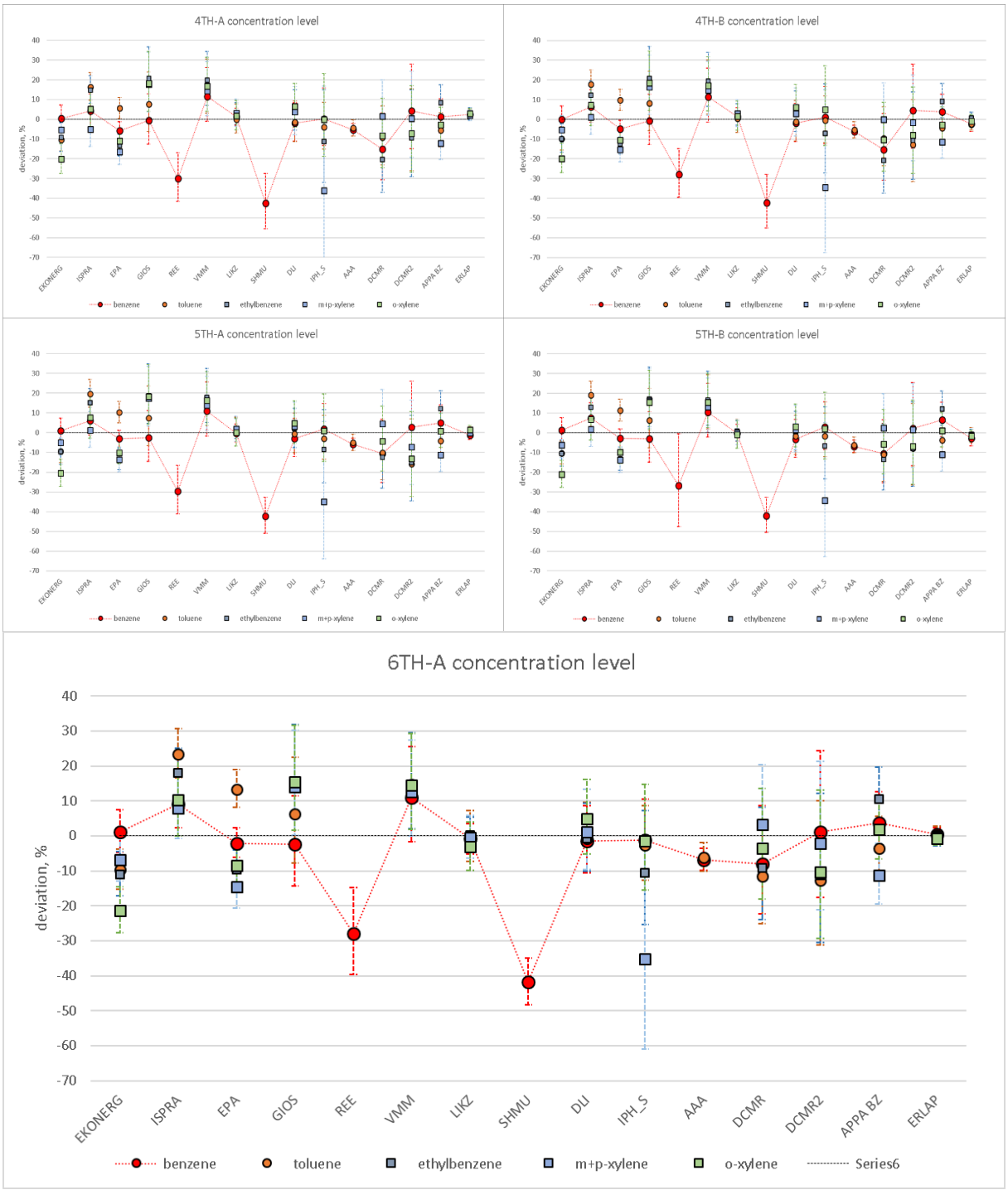
The scattering of results is represented in terms of biases with respect to the reference value or deviations of the reference value with respect to the reported laboratory value when this value is lower than the reference's one:

$$bias(\%) = deviation(\%), \qquad if\ laboratory\ value\ >\ reference\ value$$

$$bias\ (\%)\ = \frac{deviation\ (\%)}{100 + deviation\ (\%)} \cdot 100, \qquad if\ laboratory\ value\ <\ reference\ value$$

Figure A 1.- Results of the inter-laboratory comparison: Deviation (%)





|--------| Expanded uncertainty

Annex 7.- h and k statistic results of the inter-laboratory comparison

Figure A 2.- Benzene: initial and converged h and k statistics

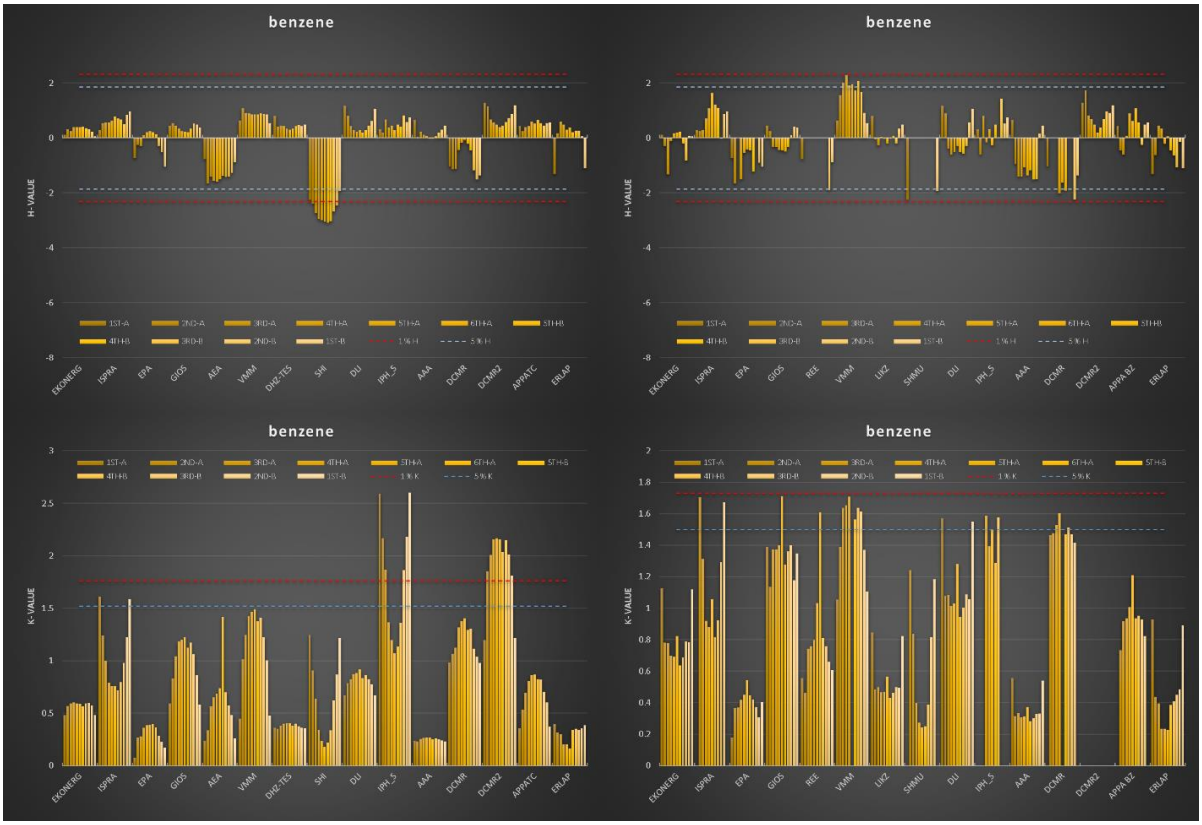


Figure A 3.- Toluene: initial and converged h and k statistics

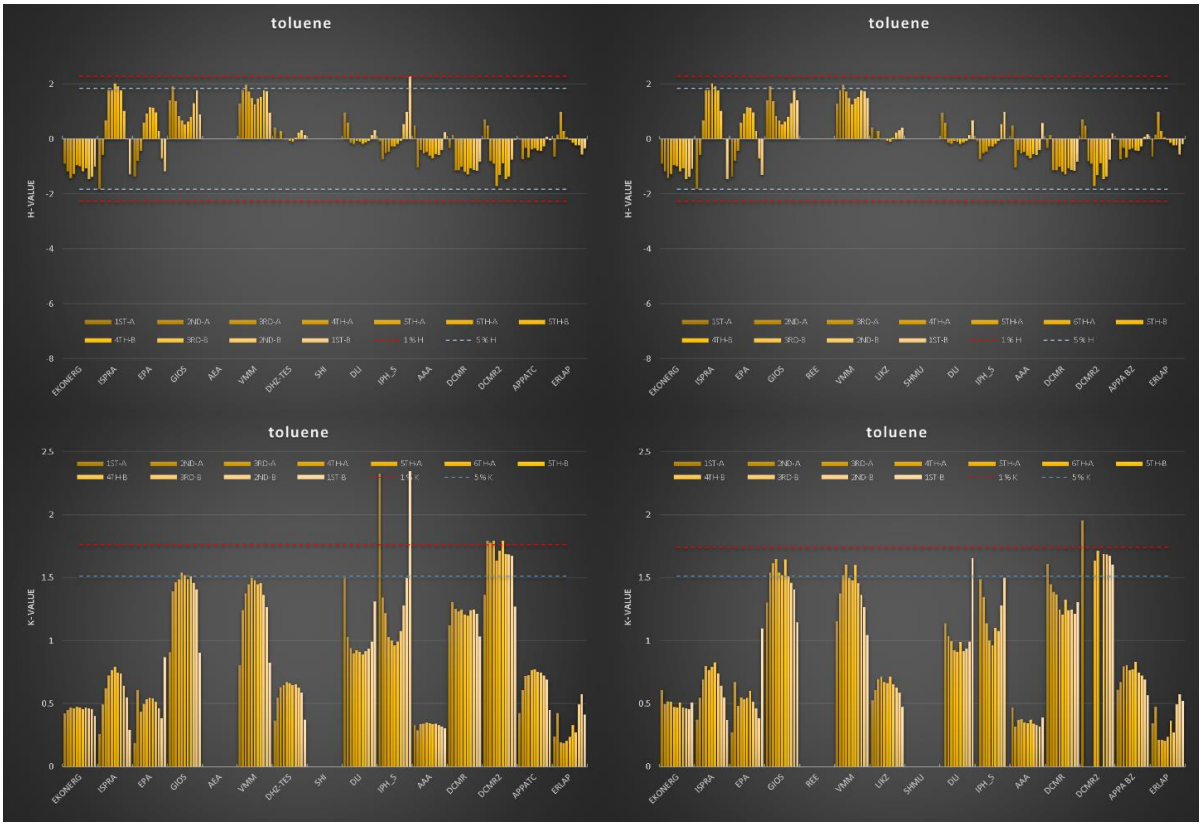


Figure A 4.-Ethyl-benzene: initial and converged h and k statistics

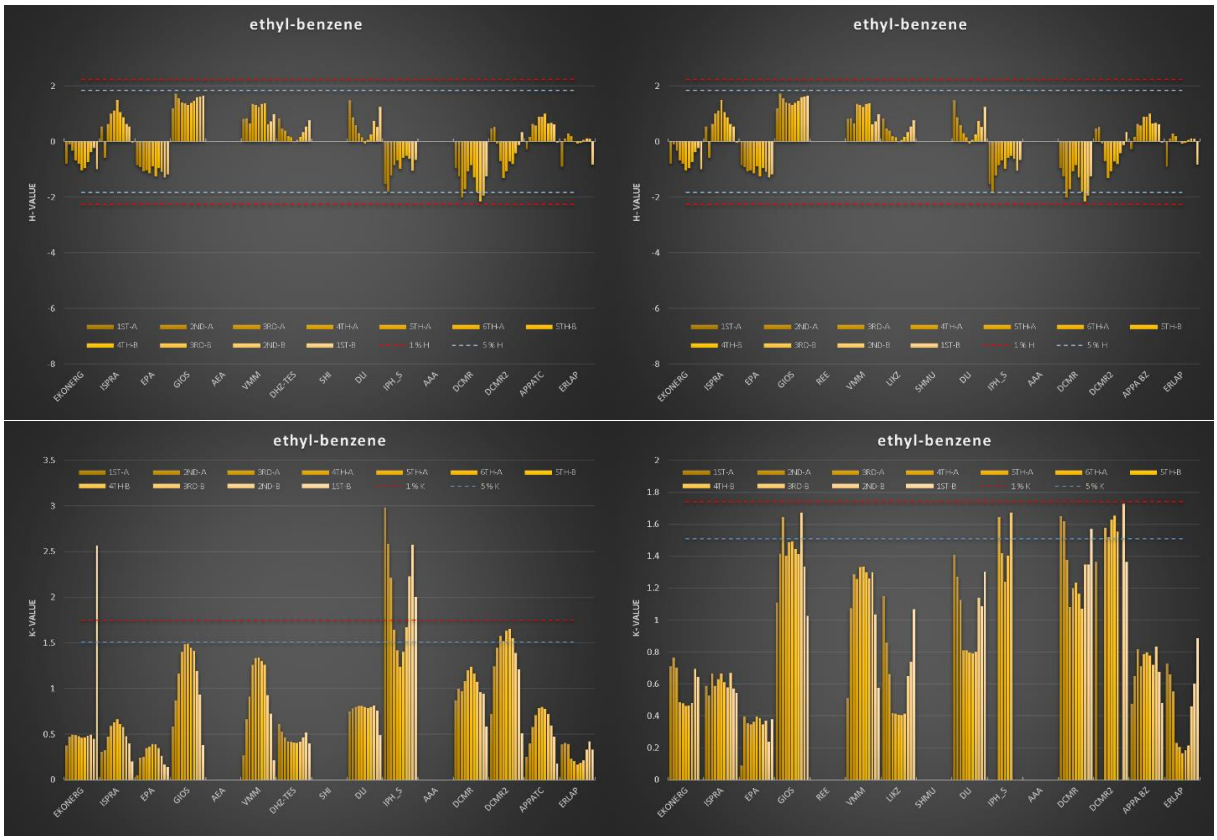


Figure A 5.- m,p-Xylene: initial and converged h and k statistics

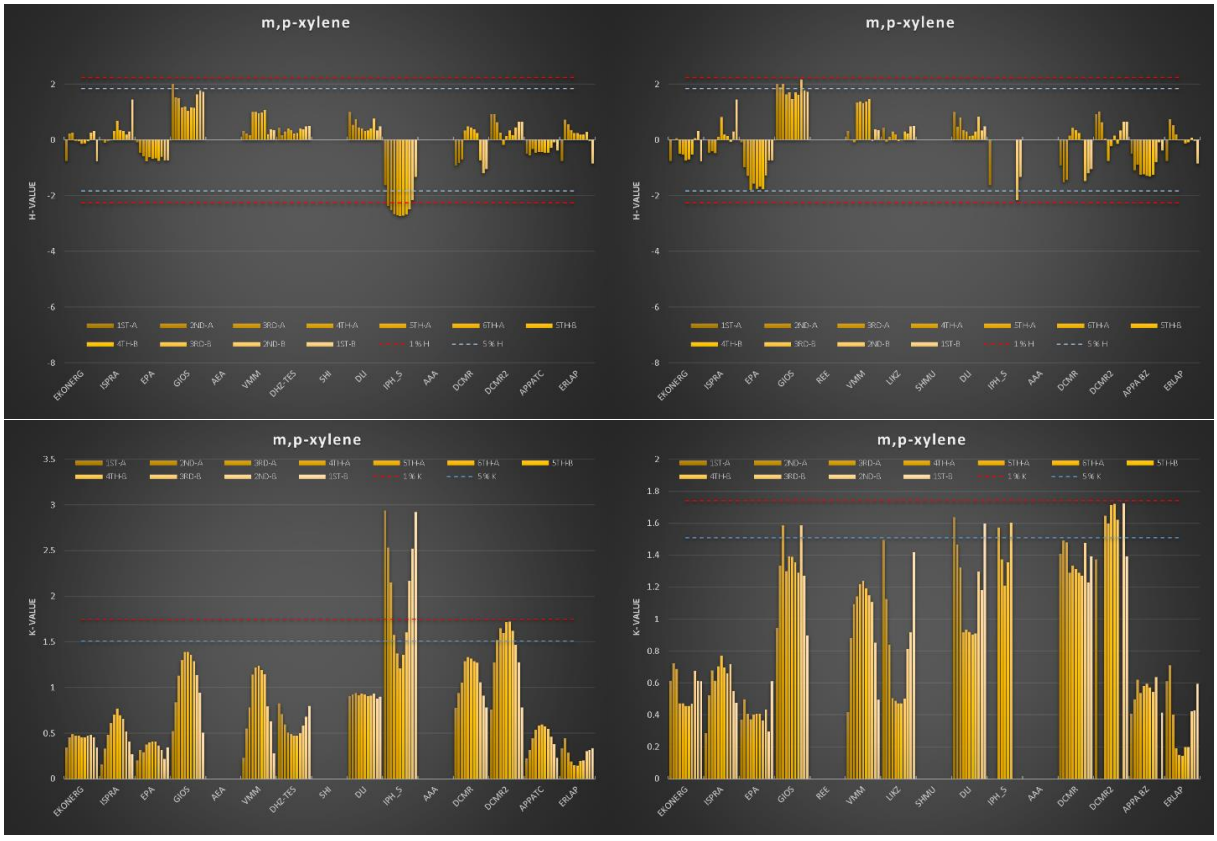


Figure A 6.- o-Xylene: initial and converged h and k statistics

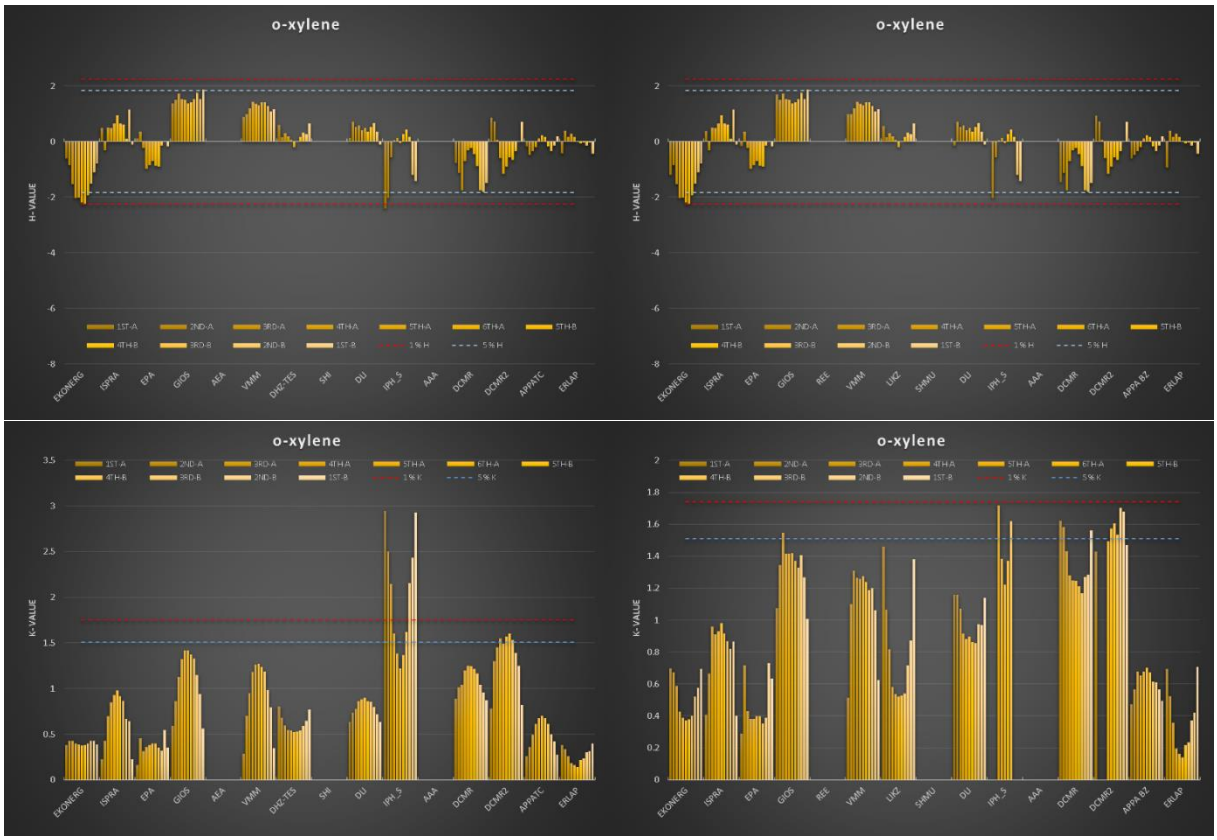
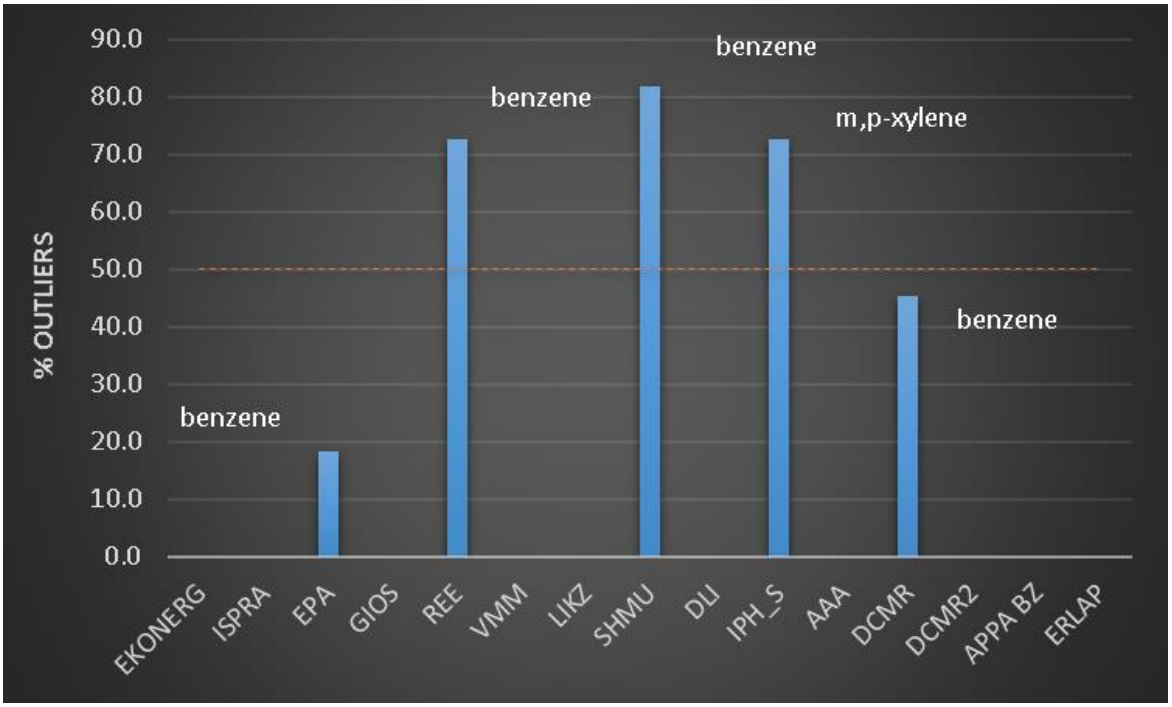


Figure A 7.- Percentage of outliers identified by laboratory and compound



Annex 8.- Analysers and method description from participating laboratories

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EKONERG

ISPRA

DLI

GIOS

VMM

EPA

REE

LIKZ

AAA

DCMR

APPA

SHMU

IPH_S

JRC-ERLAP

EKONERG

Participating Laboratory	EKONERG
Acronym	
Person(s) responsible	Predrag Hercog (AKA Jean-Luc Picard)
Contact e-mails:	predrag.hercog@ekonerg.hr
Telephone contact:	

Characteristic of your BTEX analyser

Trademark	
Model:	
Version:	Chromatotec airmoVOC
Year of manufacture:	GC 866

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

Operating system:	Vistachrom
Cycle time, min:	15
Adsorbent material:	Carbopack B
Sampling control	
Sampling temperature, °C	
Sample volume, ml	
Number of adsorbent tube	
Desorption temperature,	
Desorption time, sec	
Desorption flow, ml/min	
Cryo-trap detail	
Trapping temperature, °C	Ambient temperature
Desorption temperature, °C	Desorption time, s
Desorption flow, ml/min	split flow, ml/min
Stripper column	
Analytical column	
phase:	
length, m:	
diameter (ID) mm:	
thickness (µm):	
analytical conditions:	

Traceability of your calibration Standard

Certified reference material (CR	CRM	
Certified by	Hungarian meteorology service	
Certified number:	128/2017	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ppb (mol/mol)
Benzene	1380	75
Toluene	1319	72
Ethyl-benzene	1255	69
m+p-Xylene	2699	146
o-Xylene	1326	73

Other methods

Dilution of CRM	yes (dynymic dilution wth MFCs)
Static Injection	
Permeation	

EKONERG d.o.o. ✦ Odjel za mjerenja i analitiku
Umjerni laboratorij, Koranska 5, HR-10000 Zagreb
Tel: +385 (0)1 6000-111; **Faks**: +385 (0)1 6171-560

EKONERG

2471
CAL

POTVRDA O UMJERAVANJU
CALIBRATION CERTIFICATE

Br./No. 158/2019

Radni nalog *Work order*	**I-02-3024/19**
Kupac *Customer*	**Ekonerg d.o.o. Umjerni laboratorij**
Adresa kupca *Customer address*	Koranska 5, HR-10000 Zagreb
Naziv analizatora *Calibrated analyzer*	Analizator benzena
Proizvođač *Manufacturer*	CHROMATOTEC
Tip *Type*	airTOXIC GC 866
Serijski broj *Serial number*	23140414
Veličina *Quantity*	Koncentracija C_6H_6 / µg/m³
Mjerno područje *Measurement range*	0 – 50 µg/m³ (0 – 15 nmol/mol)
Mjesto umjeravanja *Location of calibration*	Umjerni laboratorij, Zagreb, Koranska 5
Datum primitka *Date of receipt*	9.9.2019.
Datum umjeravanja *Date of calibration*	12.9.2019.
Umjeravanje proveo *Calibration provided by*	Predrag Hercog
Broj stranica *Number of pages*	4
Datum izdanja *Date of issue*	16.9.2019.

Voditelj Umjernog laboratorija
Head of Calibration Laboratory

Zlatko Grgić, dipl.ing.univ.spec.

Direktor Odjela za mjerenja i analitiku
Director of MA Department

Bojan Abramović, dipl.ing.

1. POSTUPAK UMJERAVANJA / *CALIBRATION PROCEDURE*

EKONERG

Umjeravanje je provedeno izravnom metodom umjeravanja u nekoliko točaka opisanom u protokolu eLAB *imisijskih analizatora*, izdanje 6, 2017-04-12, točka 3.5.5. Provjera funkcionalnosti provedena je sukladno istom
Dodataka, odstupanja i izuzetaka od metode nema.
Calibration was performed by direct calibration procedure at several points as described in the protocol eLAB-PU-101, Calibration of imission analyzer, issue 6, 2017-04-12, clause 3.5.5. Functional tests are provided according to the same protocol, clause 3.4.
There are no additions to, deviations, nor exclusions from the method.

2. UMJERNA OPREMA / *CALIBRATION EQUIPMENT*

Oprema ili materijal *Equipment or material*	Oznaka *Label*	Namjena *Purpose*	Proizvođač *Manufacturer*
Certificirani referentni plin *Certified reference gas*	RPI-C6H6/1.5	Izvor referentnog plina. *Source of the reference gas.*	Messer
Sustav za dobivanje nultog zraka *Zero gas generator*	UM-GNZ1	Izvor nultog plina. *Source of the zero gas.*	Horiba
Referentni kalibrator *Reference dilution unit*	UM-KAL2	Jedinica za miješanje plinova. *Gas dilution unit.*	Horiba
Termohigrometar *Thermo-hygrometer*	UM-THM1	Mjerenje temperature i vlažnosti. *Measurement of temperature and humidity.*	Rense
Tlakomjer *Pressure gauge*	UM-TLK1	Mjerenje tlaka. *Measurement of pressure.*	Wika

3. MJERNA SLJEDIVOST / *MEASUREMENT TRACEABILITY*

Oprema ili materijal *Equipment or material*	Umjerni laboratorij *Calibration laboratory*	Broj i datum certifikata *Number and date of the certificate*
Certificirani referentni plin *Certified reference gas*	Hungarian Meteorological Service	Calibration Certificate No.155/2019, 19.6.2019.
Referentni kalibrator *Reference dilution unit*	Český metrologický institut	Certificate of Calibration 6013-KL-M0074-19, 30.1.2019. Certificate of Calibration 6013-KL-M0075-19, 30.1.2019.

4. UVJETI OKOLIŠA / *AMBIENT CONDITIONS*

Temperatura zraka / *Air Temperature*:	23 ± 2 °C
Relativna vlažnost zraka / *Relative Humidity of Air*:	44 ± 5 %
Tlak / *Pressure*:	1008 ± 5 hPa

5. BAZNA OSJETLJIVOST / *BASE SENSITIVITY*

	PRIJE UGAĐANJA / *BEFORE ADJUSTMENT*	**NAKON UGAĐANJA** / *AFTER ADJUSTMENT*
B.S.	**2517,00**	**4716,55**

6. UGAĐANJE/ *ADJUSTMENT*

Ugađanje analizatora provedeno je pri c(C_6H_6)= **40,0** µg/m³ (**12,3** nmol/mol).
Adjustment of the analyzer is provided at c(C_6H_6)= **40,0** µg/m³ (**12,3** nmol/mol).

7. REZULTATI UMJERAVANJA/ *CALIBRATION RESULTS*

EKONERG

c,ref / µg/m³	c,an / µg/m³	Δc,an / µg/m³	U,ref / µg/m³	
0,0	0,0	0,0	0,0	0,2
5,0	4,9	-0,1	0,1	0,1
30,0	30,5	0,5	1,8	1,8
40,0	40,6	0,6	2,4	2,4
48,1	49,8	1,7	2,8	2,9

c_{ref} – koncentracija referentnog plina / *reference gas concentration*
c_{an} – koncentracija plina koju pokazuje analizator / *gas concentration indicated by analyzer*
Δc – odstupanje analizatora / *deviation of the analyzer*
U_{ref} – proširena mjerna nesigurnost umjeravanja referentnog plina / *expanded measurement uncertainty of reference gas*
U_{an} – proširena mjerna nesigurnost analizatora / *expanded measurement uncertainty of analyzer*
*__nmol/mol__ uz usvojenu pretpostavku idealnog plina odgovara **ppbv**
*nmol/mol *with the assumption of ideal gas corresponds to* ppbv
faktor pretvorbe/*conversion factor*: 1 ppb = 1 nmol/mol = 3,24 µg/m³

Rezultati se odnose samo na umjereni analizator.
The results are related only to calibrated analyzer.

8. PROVJERA KARAKTERISTIKA / *PERFORMANCE CHARACTERISTICS TESTS*

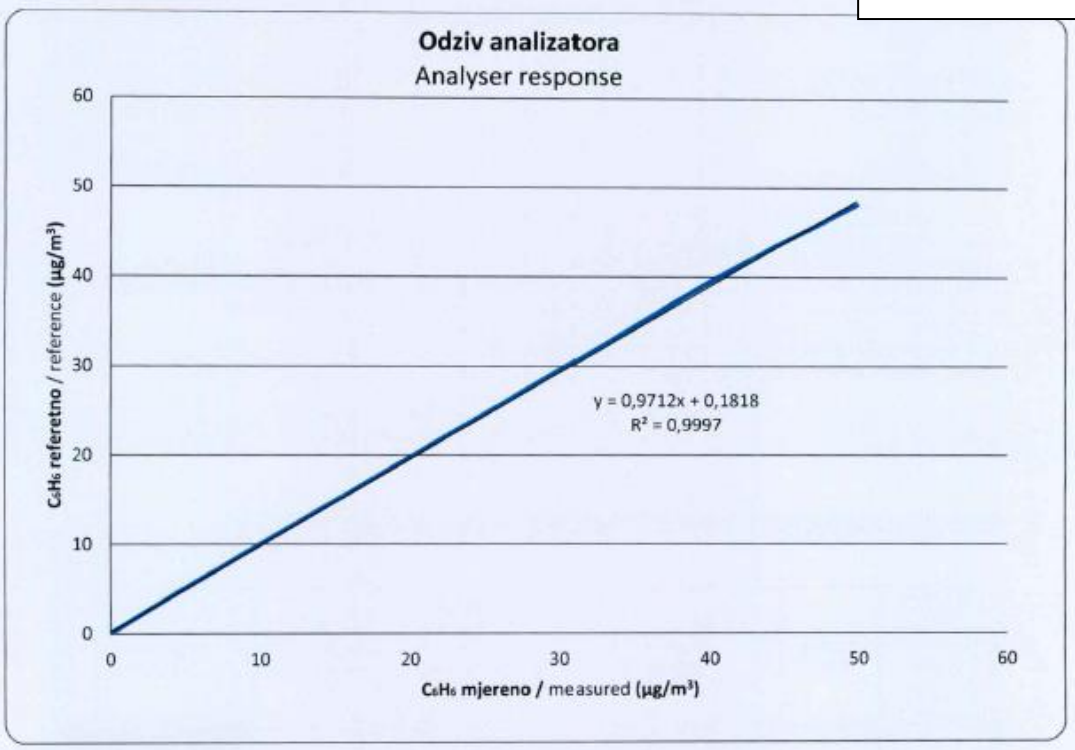
Broj prema Tablici 1 norme HRN EN 14662-3 Number according to Table 1 of the EN 14662-3	Oznaka Symbol	Karakteristika Characteristic	Rezultat provjere (μm^{-3} ili %) Result of the check (μm^{-3} or %)	Granice prihvatljivosti Acceptance limits	Sukladnost Compliance
1	s_{rz}	**ponovljivost na 1/10 GV (0,5 µg/m³)** repeatability at 0,5 µg/m³	**0,02**	≤ 0,20 μgm^{-3}	**Zadovoljava** *Complies*
2	$s_{r,ct}$	**ponovljivost na graničnoj vrijednosti** repeatability at limit value	**0,05**	≤ 0,25 μgm^{-3}	**Zadovoljava** *Complies*
3	r_{max}	**nelinearnost, najveće odstupanje** lack of fit, largest residual	**1,0 %**	≤ 5,0 %	**Zadovoljava** *Complies*
formula (3)	l_{det}	**granica detekcije** detection limit	**0,06**	N/A	
11	$D_{s,s}$	**kratkotrajni odmak na rasponu** short term drift at span value	**0,13**	≤ 2,0 μgm^{-2}	**Zadovoljava** *Complies*

ZAKLJUČAK / *CONCLUSION*

Analizator **zadovoljava** granice prihvatljivosti definirane normom HRN EN 14662-3:2015.
*Analyzer **complies** with the acceptance limits according to EN 14662-3:2015.*

9. ODZIV ANALIZATORA / *ANALYZER RESPONSE*

EKONERG



10. MJERNA NESIGURNOST / *MEASUREMENT UNCERTAINTY*

Izražena proširena mjerna nesigurnost umjeravanja prikazana je kao umnožak sastavljene mjerne nesigurnosti i faktora pokrivanja k=2, koji u slučaju normalne razdiobe odgovara približno 95%-tnoj vjerojatnosti pokrivanja. Sastavljena mjerna nesigurnost određena je u skladu s EA-4/02.

The reported expanded measurement uncertainty is stated as combined standard uncertainty multiplied by coverage factor k=2 which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard measurement uncertainty has been determinated in accordance with EA-4/02.

11. NAPOMENA / *NOTE*

Korisnik analizatora odgovoran je umjeravati ga u prikladnim vremenskim razmacima.
The user is obligated to have the analyzer recalibrated at appropriate intervals.

---------- *kraj potvrde o umjeravanju (end of calibration certificate)* ----------

Participating Laboratory	Istituto Superiore per la Protezione e Ricerca Ambientale Area Metrologia
Acronym	ISPRA
Person(s) responsible	dr. Damiano Centioli
Contact e-mails:	damiano.centioli@irerambiente.it fabio.cadoni@irerambiente.it
Telephone contact:	+390650073214; +390650073227

ISPRA

Characteristic of your BTEX analyser

Trademark	ORION S.r.l./SRI
Model:	Orion BTX2000/SRI 8610C
Version:	
Year of manufacture:	2006

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

Operating system:	windows			
Cycle time, min:	29 + 1 min standby			
Adsorbent material:	TENAX GR,			
Sampling control	pump			
Sampling temperature, °C	ambient			
Sample volume, ml				
Number of adsorbent tube	1			
Desorption temperature, °				
Desorption time, sec				
Desorption flow, ml/min				
Cryo-trap detail				
Trapping temperature, °C	35			
Desorption temperature, °C	200	Desorption time, se	210	
Desorption flow, ml/min	20	split flow, ml/min		
Stripper column				
Analytical column	packed RESTEK cat.# 80129			
phase:	5% RT1200/5% Bentone on 100/120 Silcoport			
length, m:	2			
diameter (ID) mm:	2			
thickness (µm):				
analytical conditions:	T = 80°C hold for 29 min			

Traceability of your calibration Standard

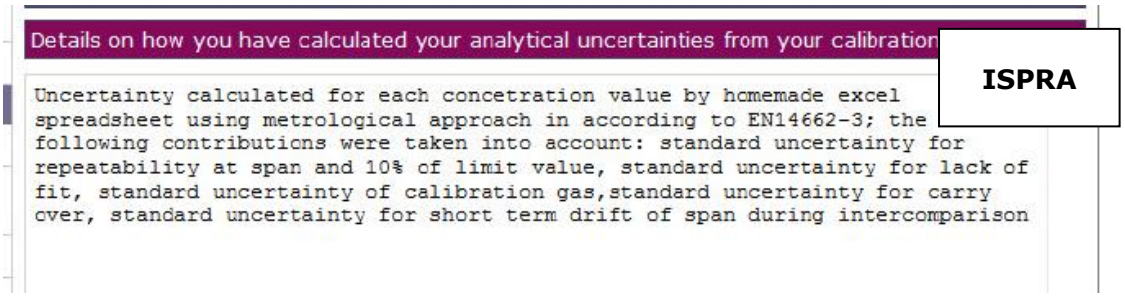
Certified reference material (CR	gaseous CRM according ISO6142 by SIAD S.p.A.	
Certified by	SIAD S.p.A. accredited calibration lab n. LAT n.143	
Certified number:	G035519 23/05/2019	
Compound	oncentration, ppb (mol/mo	Expanded Uncertainty, ppb(mol/mol
Benzene	9.98	0.20
Toluene	9.98	0.2
Ethyl-benzene	9.98	0.28
m-Xylene	10.01	0.41
p-Xylene	9.99	0.37
o-Xylene	10	0.38

Other methods

Dilution of CRM	RM* at nominal concentration 400 ppb diluted by ORION OGD2000 dilution system calibrated by accredited lab n. LAT n. 159
Static Injection	
Permeation	

Additional comments

*RM by SIAD S.p.A. Certified number: 14474 (not accredited)
Concentration ppb: benzene 410 ±32 , toluene 395 ±31, Ethyl-benzene 409±32, m-xylene 392±31, p-xylene 391 ±31 , o-xylene 395±31


Details on how you have calculated your analytical uncertainties from your calibration
Uncertainty calculated for each concetration value by homemade excel spreadsheet using metrological approach in according to EN14662-3; the following contributions were taken into account: standard uncertainty for repeatability at span and 10% of limit value, standard uncertainty for lack of fit, standard uncertainty of calibration gas,standard uncertainty for carry over, standard uncertainty for short term drift of span during intercomparison

ISPRA

SIAD

Laboratorio di Metrologia
S.S. 525 del Brembo, 1
24040 Osio Sopra (BG)
e-mail: ricerca@siad.eu
http://www.siad.eu

Centro di Taratura LAT N° 143
Calibration Centre
Laboratorio Accreditato di Taratura

ACCR

LAT N° 143

ISPRA

CERTIFICATO DI TARATURA LAT 143 G035519
Certificate of Calibration

- data di emissione *date of issue*	2019-05-23
- cliente *customer*	ORION SRL ISPRA IST.SUP.PROT.RIC.AM VIA CAS 00144 ROMA RM
- destinatario *receiver*	-
- richiesta *application*	RF 238902
- in data *date*	2019-04-19
Si riferisce a *referring to*	
- oggetto *item*	Miscela Gassosa: ISO 6142-1:2015 Classe 1
- costruttore *manufacturer*	SIAD S.p.A. - Centro LAT N° 143
- modello *model*	G-CGM
- matricola *serial number*	260420
- data di ricevimento oggetto *date of receipt of item*	-
- data delle misure *date of measurement*	2019-05-16
- registro di laboratorio *laboratory reference*	058

Il presente certificato di taratura è emesso in base all'accreditamento LAT N° 143 rilasciato in accordo ai decreti attuativi della legge n. 273/1991 che ha istituito il Sistema Nazionale di Taratura (SNT). ACCREDIA attesta le capacità di misura e di taratura, le competenze metrologiche del Centro e la riferibilità delle tarature eseguite ai campioni nazionali e internazionali delle unità di misura del Sistema Internazionale delle Unità (SI). Questo certificato non può essere riprodotto in modo parziale, salvo espressa autorizzazione scritta da parte del Centro.

This certificate of calibration is issued in compliance with the accreditation LAT N° 143 granted according to decrees connected with Italian law No. 273/1991 which has established the National Calibration System. ACCREDIA attests the calibration and measurement capability, the metrological competence of the Centre and the traceability of calibration results to the national and international standards of the International System of Units (SI). This certificate may not be partially reproduced, except with the prior written permission of the issuing Centre.

I risultati di misura riportati nel presente Certificato sono stati ottenuti applicando le procedure di taratura citate alla pagina seguente, dove sono specificati anche i campioni o gli strumenti che garantiscono la catena di riferibilità del Centro e i rispettivi certificati di taratura in corso di validità. Essi si riferiscono esclusivamente all'oggetto in taratura e sono validi nel momento e nelle condizioni di taratura, salvo diversamente specificato.

The measurement results reported in this Certificate were obtained following the calibration procedures given in the following page, where the reference standards or instruments are indicated which guarantee the traceability chain of the laboratory, and the related calibration certificates in the course of validity are indicated as well. They relate only to the calibrated item and they are valid for the time and conditions of calibration, unless otherwise specified.

Le incertezze di misura dichiarate in questo documento sono state determinate conformemente alla Guida ISO/IEC 98 e al documento EA-4/02. Solitamente sono espresse come incertezza estesa ottenuta moltiplicando l'incertezza tipo per il fattore di copertura *k* corrispondente ad un livello di fiducia di circa il 95%. Normalmente tale fattore *k* vale 2.

The measurement uncertainties stated in this document have been determined according to the ISO/IEC Guide 98 and to EA-4/02. Usually, they have been estimated as expanded uncertainty obtained multiplying the standard uncertainty by the coverage factor k corresponding to a confidence level of about 95%. Normally, this factor k is 2.

Direzione tecnica
Approving Officer
Ing. Giorgio Bissolotti

Participating Laboratory	Air Quality Section, Department of Labour Ins
Acronym	AQS DLI
Person(s) responsible	Christos Kizas & Christos Papadopoulos
Contact e-mails:	ckizas@dli.mlsi.gov.cy, cpapadopoulos@dli.mlsi.gov.cy
Telephone contact:	00357-22-405674, 00357-22-405683

DLI

Characteristic of your BTEX analyser

Trademark	Chromatotec
Model:	airmoVOC(BTEX)
Version:	
Year of manufacture:	2018

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:			yes		
Other gases used:					yes

Operating system:	MS-Windows
Cycle time, min:	15
Adsorbent material:	TENAX GR, Carbopack B, CARBOPACK X, CARBOPACK C
Sampling control	critical orifice
Sampling temperature, °C	ambient
Sample volume, ml	482.35
Number of adsorbent tubes	1
Desorption temperature, °C	380
Desorption time, sec	120
Desorption flow, ml/min	
Cryo-trap detail	N/A
Trapping temperature, °C	
Desorption temperature, °C	
Desorption time, se	
Desorption flow, ml/min	
split flow, ml/min	
Stripper column	
Analytical column	MXT 30 CE
phase:	
length, m:	30
diameter (ID) mm:	0.28
thickness (µm):	1
analytical conditions:	Oven 45 - 165 °C, 3-4 l/min H_2 flow (carrier gas), FID Air 180 ml/min H_2 27 ml/min

Traceability of your calibration Standard

Certified reference material (C	VSL Primary Reference Gas Mixture (BTEX in nitrogen)
Certified by	VSL, Dutch Metrology Institute
Certified number:	C1336210,04

Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	681 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
Toluene	683 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
Ethyl-benzene	693 x 10^{-9} mol/mol	21 x 10^{-9} mol/mol
m-Xylene	665 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
p-Xylene	662 x 10^{-9} mol/mol	20 x 10^{-9} mol/mol
o-Xylene	686 x 10^{-9} mol/mol	21 x 10^{-9} mol/mol

Other methods

Dilution of CRM	Sabio 4010, Range: ~ 1 - 20 ppb

DLI

CERTIFICATE

Number C1336210.04

Reference material of BTEX in nitrogen

Description	Primary reference gas mixture (PRM), cylinder number APEX1223926. The cylinder contains a mixture of BTEX in nitrogen. The PRM is contained in a passivated aluminium cylinder. The cylinder has a water volume of 5 L and is pressurized to 12.1 MPa. Cylinder outlet conforms to DIN 1 specifications.
Method of preparation	Gravimetric preparation in accordance with ISO 6142-1:2015.
Result	The results are presented on page 2. The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95 %. The standard uncertainty of measurement has been determined in accordance with the GUM 'Evaluation of measurement data - Guide to the expression of uncertainty in measurement'.
Traceability	The values on this certificate are traceable to VSL Primary Standards.
Safety information	The cylinder should be handled with care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of gaseous materials.
Instructions for use	The gas mixture can be used to validate and/or calibrate analytical methods and equipment. Do not use the cylinder in case the cylinder pressure is below 1 MPa. Further instructions regarding the handling of calibration gases can be found in ISO 16664:2017.
Expiry date	This certificate is valid until 7 October 2020.

Delft, 27 November 2017
VSL B.V.

J.I.T. van Wijk
Senior Metrologist

VSL B.V.
Thijsseweg 11, 2629 JA Delft (NL)
P.O. Box 654, 2600 AR Delft (NL)
T +31 15 269 15 00
F +31 15 261 29 71

Details on how you have calculated your analytical uncertainties from your calibration data

The uncertainties were calculated as follows:
- Using a home made software (excel worksheet) we calculated the uncertainty due to dilution. This includes the uncertainty of the gas standard, the uncertainty of the primary flow-meter used for the calibration of the Mass Flow Controllers of the Calibrator (Sabio 4010), the uncertainties of the MFCs etc.
- To calculate the final uncertainty we introduce the above uncertainty into a home made software (excel worksheet) prepared according to the requirements of the EN 14662-3: 2015.

Characteristic of your BTEX analyser

GIOS

Trademark	Syntech Spectras
Model:	GC955-601
Version:	
Year of manufacture:	2018

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:	-	yes	-		-
Other gases used:					yes

Operating system:	Windows		
Cycle time, min:	15 min		
Adsorbent material:	TENAX GR		
Sampling control	Piston - pump		
Sampling temperature, °C	Ambient temperature		
Sample volume, ml	35		
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	26		
Desorption flow, ml/min	1.5		
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, se	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	SY-5 15m, 0.32 mm ID, 1 µm film, 2m,		
Analytical column	Synspec		
phase:			
length, m:	12		
diameter (ID) mm:	0.32		
thickness (µm):	1		
analytical conditions:	50°C (1-3min), 10°C/min, 70°C (5-12min),-8°C/min,50°C(13,5-15min)		

Traceability of your calibration Standard

Certified reference material (C	AirLiqude	
Certified by	AirLiqude	
Certified number:	9512517018	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	1142.00	57.00
Toluene	1184.00	118
Ethyl-benzene	1274	127
m+p-Xylene	1200	120.00
	1218	122
o-Xylene	1232	123

Other methods	
Dilution of CRM	MCZ CGM2000
Static Injection	

AIR LIQUIDE

GIOS

TEST REPORT

AIR LIQUIDE Deutschland GmbH
Bataverstrasse 47
47809 KREFELD

ORDER DATA	
Determination of C_6H_6, C_8H_{10}, C_7H_8, C_8H_{10}, C_9H_{10} and C_9H_{10} in AIR	Certificate No. 9512517018
Customer : AIR LIQUIDE POLSKA SP ZOO Al.Pilsudskiego 92 41-308 DABROWA GORNICZA	Date of receipt: 31.07.2017

TEST

[X] Test Report acc. to DIN EN ISO/IEC 17025	[ ] Amendment / Addition	[ ] Correction

Test item:
1 Aluminium gas cylinder (11 L), Cylindar No. : 1046

Test Parameter(s)			Test Method:
Determination of			
BENZENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID
ETHYL BENZENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID
TOLUENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID
M-XYLENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID
O-XYLENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID
P-XYLENE	1,10	Mol-ppm	GAS-CHROMATOGRAPHY-FID

SAMPLING
Gas Withdrawal by Pressure Reducer / Needle Valve

ATTACHMENTS
Air Liquide Certificate of Analysis

Durch die DAkkS Deutsche Akkreditierungsstelle GmbH
akkreditiertes Prüflaboratorium
Die Akkreditierung gilt für die in der Urkunde
aufgeführten Prüfverfahren

DAkkS Deutsche Akkreditierungsstelle D-PL-14641-01-00

Participating Laboratory	Vlaamse Milieumaatschappij
Acronym	VMM
Person(s) responsible	Jan Petré, Tine Fierens
Contact e-mails:	j.petre@vmm.be, t.fierens@vmm.be
Telephone contact:	003232166108

VMM

Characteristic of your BTEX analyser

Trademark	Chromatotec
Model:	Airmo BTEX
Version:	Mcerts-A21022
Year of manufacture:	2018

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:	no	no	yes	no	yes
Other gases used:					

Operating system:	Win 7 embedded
Cycle time, min:	15 min
Adsorbent material:	2 phases C6
Sampling control	sampling pump, critical orifice 76 µm
Sampling temperature, °C	ambient temp
Sample volume, ml	+/- 450 ml
Number of adsorbent tubes	1
Desorption temperature, °	380°C
Desorption time, sec	120 sec
Desorption flow, ml/min	3-4 ml/min
Cryo-trap detail	
Trapping temperature, °C	
Desorption temperature, °C	
Desorption time, se	
Desorption flow, ml/min	
split flow, ml/min	
Stripper column	
Analytical column	MTEX 30 CE
phase:	
length, m:	30 m
diameter (ID) mm:	0.28 mm
thickness (µm):	1 µm
analytical conditions:	Initial 43°C->45°C gradient 2°/min, duration 60 sec Final temp 45->165°C, gradient 15°/min, duration 480 sec

Traceability of your calibration Standard

Certified reference material (C	system MFCair 10 sl/min, MFCbtex 100 sml/min) from certified high concer
Certified by	VMM-lab: certified standard and dilution system
Certified number:	

Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	4.89	
Toluene	4.89	
Ethyl-benzene	4.917	
m+p-Xylene	4.846	
o-Xylene	4.917	

Other methods	
Dilution of CRM	AirQrate, 400 ppb dilution system

Details on how you have calculated your analytical uncertainties from your calibrati

VMM

Measurement uncertainties were calculated according to EN 14662-3. Th
following items were included among other things:
- Uncertainty of reference standards/primary gas mixture (see also certificate of calibration);
- Uncertainty of travelling standard;
- Uncertainty of BTEX analyzer.

The expanded uncertainty (U) equals two times the combined uncertainty (u).

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS 4002

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D994146R

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **Flanders Environment Agency (VMM)**

ADDRESS: Vlaamse Milieumaatschappij, Afdeling Lucht, Milieu en Communicatie, Kronenburgstraat 45 bus B3, 2000 Antwerpen, Belgium

CALIBRATION DATE: 11 January 2018

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	205.7 ± 4.2
Toluene	206 ± 6
Ethylbenzene	207 ± 6
m-xylene + *p*-xylene	204 ± 7
o-xylene	207 ± 6
1,2-dichloroethane	200 ± 10
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID and MS)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

NPL cannot guarantee the stability of 1,2-dichloroethane

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2017090132 **Date of issue:** 17 January 2018

Signed: (Authorised Signatory)

Name: Dr PJ Brewer (on behalf of NPLML)

Checked by:

Page 1 of 1

Participating Laboratory	EPA Ireland
Acronym	EPA
Person(s) responsible	Kevin Delaney, Joe Reilly
Contact e-mails:	k.delaney@epa.ie , d.burke@epa.ie
Telephone contact:	

EPA

Characteristic of your BTEX analyser

Trademark	Syntech
Model:	Syntech GC955
Version:	600
Year of manufacture:	2008

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:		yes			
Other gases used:					

Operating system:	Windows XP		
Cycle time, min:	15 min		
Adsorbent material:	Tenax GR 35/60		
Sampling control	sample pump/piston pump		
Sampling temperature, °C	Ambient		
Sample volume, ml	210		
Number of adsorbent tubes	1		
Desorption temperature, `	180		
Desorption time, sec	60		
Desorption flow, ml/min	1.5		
Cryo-trap detail	na		
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, se	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	Length 2m. Same as the analytical column.		
Analytical column	Altech - p/n:13710, AT-5		
phase:	(5% Phenyl)-95% Methylpolysiloxane		
length, m:	13		
diameter (ID) mm:	0.32		
thickness (µm):	1.0		
analytical conditions:	Initial Temp of 45°C, hold for 4 mins. Ramp to 80°C over the next 6.5mins. Hold at 80°C for 1 min. Return to 45°C.		

Traceability of your calibration Standard

Certified reference material (C	Gas Mixture	
Certified by	NPL	
Certified number:	2019010381	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	9.88	0.20
Toluene	9.61	0.25
Ethyl-benzene	10.39	0.26
m+p-Xylene	20.2	0.60
o-Xylene	9.94	0.25

Other methods	
Dilution of CRM	na

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EPA

Certificate of Calibration

UKAS 4002

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D386627R

CUSTOMER: **Environmental Protection Agency**

ADDRESS: Seville Lodge, Callan Road, Kilkenny, Ireland

CALIBRATION DATE: 21 May 2019

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)		
Benzene	9.88	±	0.20
Toluene	9.61	±	0.25
Ethylbenzene	10.39	±	0.26
m-xylene + *p*-xylene	20.2	±	0.6
o-xylene	9.94	±	0.25
Nitrogen	Balance		

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 115 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2019010381 **Date of issue:** 24 May 2019

Signed: (Authorised Signatory)

Name: Dr R J C Brown (on behalf of NPLML)

Checked by:

Participating Laboratory	Ricardo Energy & Environment
Acronym	REE
Person(s) responsible	James Dernie + Luke Doman
Contact e-mails:	james.dernie@ricardo.com
Telephone contact:	01235 75 3643

REE

Characteristic of your BTEX analyser

Trademark					
Model:	Environnement VOC71M				
Version:	NA				
Year of manufacture:	2005				
	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:		yes			
Other gases used:					
Operating system:	Windows				
Cycle time, min:	15				
Adsorbent material:	Trap - Carbotrap, Focusing tube - Carbopack B				
Sampling control	Internal trap with critical orifice				
Sampling temperature, °C	Ambient				
Sample volume, ml	1050				
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	Supalco SPB 624				
phase:	Proprietry, bonded				
length, m:	13				
diameter (ID) mm:	0.32				
thickness (µm):	1.8				
analytical conditions:					

Traceability of your calibration Standard

Certified reference material (CRM	NPL	
Certified by	NPL	
Certified number:		
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	4.00	0.08
Toluene	4.00	0.08
Ethyl-benzene	4.00	0.08
m+p-Xylene	8.00	0.16
o-Xylene	4.00	0.08

NATIONAL PHYSICAL LABORATORY

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REE

Certificate of Calibration

4002

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D035753R

CUSTOMER: **Ricardo – AEA Ltd**

ADDRESS: The Gemini Building, Fermi Avenue, Harwell, Oxfordshire, OX11 0QR, United Kingdom

CALIBRATION DATE: 08 March 2019

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)	Component	Amount fraction / (nmol/mol)
Ethane	4.00 ± 0.10	2-methylpentane	4.14 ± 0.11
Ethene	3.92 ± 0.10	Hexane	4.14 ± 0.11
Propane	3.94 ± 0.08	Isoprene	4.13 ± 0.09
Propene	3.92 ± 0.10	Heptane	4.15 ± 0.09
2-methylpropane	4.02 ± 0.11	Benzene	3.92 ± 0.10
Butane	3.98 ± 0.08	2,2,4-trimethylpentane	3.90 ± 0.08
Ethyne	4.13 ± 0.21	Octane	3.91 ± 0.08
trans-but-2-ene	4.00 ± 0.08	Toluene	3.81 ± 0.10
But-1-ene	3.97 ± 0.16	Ethylbenzene	4.12 ± 0.11
cis-but-2-ene	3.99 ± 0.08	*m*-xylene + *p*-xylene	8.01 ± 0.21
2-methylbutane	3.93 ± 0.08	*o*-xylene	3.94 ± 0.10
Pentane	3.95 ± 0.08	1,3,5-trimethylbenzene	3.76 ± 0.10
1,3-butadiene	4.03 ± 0.09	1,2,4-trimethylbenzene	3.98 ± 0.10
trans-pent-2-ene	3.97 ± 0.08	1,2,3-trimethylbenzene	3.78 ± 0.10
Pent-1-ene	4.03 ± 0.09	Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 120 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2018070344-2 **Date of issue:** 15 March 2019

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

Participating Laboratory	Ambient air testing laboratory, Croatian hydrometeorological service
Acronym	LIKZ
Person(s) responsible	Lovro Hrust
Contact e-mails:	hrust@cirus.dhz.hr
Telephone contact:	+385914565685

LIKZ

Characteristic of your BTEX analyser

Trademark	Chromatotec
Model:	GC 866 FID airmoVOC
Version:	BTEX (Model A21022)
Year of manufacture:	2019

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

Operating system:	Windows 7		
Cycle time, min:	15		
Adsorbent material:	CARBOTRAP		
Sampling control	ntrol unit (sample volume calculated) with one critical orifice, linked to a sa		
Sampling temperature, °C	ambient		
Sample volume, ml	calculated, appx. 425ml		
Number of adsorbent tubes	–		
Desorption temperature, `	350 °C		
Desorption time, sec	180		
Desorption flow, ml/min	–		
Cryo-trap detail	–		
Trapping temperature, °C	–		
Desorption temperature, °C	–	Desorption time, se	–
Desorption flow, ml/min	–	split flow, ml/min	–
Stripper column	–		
Analytical column	MXT 30 XE		
phase:	solid		
length, m:	30		
diameter (ID) mm:	0.28		
thickness (µm):	1		
analytical conditions:	–		

Traceability of your calibration Standard

Certified reference material (CRM	Gas cylinder	
Certified by	National Physical laboratory, U.K.	
Certified number:	D600074	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(nmol/mol)
Benzene	12.18	0.25
Toluene	11.85	0.30
Ethyl-benzene	12.81	0.33
m-Xylene	24.90	0.70
p-Xylene		
o-Xylene	12.26	0.31
Other methods		
Dilution of CRM	–	
Static Injection	–	
Permeation	–	

Details on how you have calculated your analytical uncertainties from your calibration data

LIKZ

Uncertainties were estimated based on previous research of instru
characteristics and using literature data from type approval of t
instrument. For some values such as repeatability and linearity, it was
concluded that it is best to use linear equation to describe particular
partial uncertainty, i.e. there is a part not dependent on measured
concentration and dependent on measured concentration. All estimated
contributions due to various effects were added by using rule for combining
measurement uncertainties. Final combined measurement uncertainty was
reported, together with expanded uncertainty. For expanded uncertainty it
was assumed coverage factor of k=2, based on normal distribution and
coverage of 95% of probability of a result being in reported interval one

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS 4002

NPL PRIMARY REFERENCE MATERIAL
Cylinder Number: D600074

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CUSTOMER: **Messer Croatia Plin d.o.o.**

ADDRESS: Industrijska 1, HR - 10290 Zaprešic, Croatia

CALIBRATION DATE: 26 June 2018

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	12.18 ± 0.25
Toluene	11.85 ± 0.30
Ethylbenzene	12.81 ± 0.33
m-xylene + *p*-xylene	24.9 ± 0.7
o-xylene	12.26 ± 0.31
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2018020364-5 **Date of issue:** 11 July 2018

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

Page 1 of 1

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

Participating Laboratory	Environmental protection Agency	**AAA**
Acronym	AAA	
Person(s) responsible	J. Molis, R. Kybartas	
Contact e-mails:	j.molis@aaa.am.lt , rolandas.kybartas@aaa.am.lt	
Telephone contact:	+37068617501, +37068617504	

Characteristic of your BTEX analyser

Trademark	AMA Instruments				
Model:	GC 5000				
Version:	BTX				
Year of manufacture:	2017				
	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:		x			
Other gases used:			x		x
Operating system:	Windows 7				
Cycle time, min:	30				
Adsorbent material:	Carbotrap				
Sampling control	Pump/MFC				
Sampling temperature, °C	30				
Sample volume, ml	300				
Number of adsorbent tubes	1				
Desorption temperature, `	230				
Desorption time, sec	180				
Desorption flow, ml/min					
Cryo-trap detail					
Trapping temperature, °C					
Desorption temperature, °C		Desorption time, se			
Desorption flow, ml/min		split flow, ml/min			
Stripper column					
Analytical column	AMAsep 1				
phase:					
length, m:	30				
diameter (ID) mm:	0.32				
thickness (µm):	1.5				
analytical conditions:	50°C hold 3min., ramp 50°C - 130°C 15 min.,hold 5min.				

Traceability of your calibration Standard

Certified reference material (C	NPL	
Certified by	NPL	
Certified number:	121444SG	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	4830	130
Toluene	4670	120
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		
Other methods		
Dilution of CRM	Umwelttechnik MCZ GmbH Dilution 35-12670 times	

Details on how you have calculated your analytical uncertainties from your calibrati

AAA

$Un = \sqrt{(((Cnn,0\text{-}30 - Cavrg.)^2 + (Cn,30\text{-}60 - Cavrg.)^2 + (Cn,0\text{-}30 - Cav}$
$+ 4\ (un,0\text{-}30^2\ + un,30\text{-}60^2\ + un,60\text{-}90^2\ )/3)$

Un - expanded for stage.

u for concetration C incorporates :

Min reading /2
Zero reading
calibration gas: u% calgas/100 x C
largest residual from linear regresion: Lres.%/100 x C/SQRT 3

NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

NPL CALIBRATED GAS MIXTURE

Cylinder Number: 121444SG

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CUSTOMER: **BOC Ltd**

ADDRESS: The Priestley Centre, The Surrey Research Park, Guildford, GU2 7XY, United Kingdom

CALIBRATION DATE: 06 February 2019

CERTIFIED AMOUNT FRACTIONS:

Component	Amount fraction / (µmol/mol)
Benzene	4.83 ± 0.13
Toluene	4.67 ± 0.12
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHOD: Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: NPL cannot guarantee the stability of this mixture

PRESSURE: Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 20180802.63 **Date of issue:** 08 February 2019

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

Page 1 of 1

Participating Laboratory	DCMR Milieudienst Rijnmond
Acronym	DCMR
Person(s) responsible	Ed van der Gaag
Contact e-mails:	ed.vandergaag@dcmr.nl
Telephone contact:	0031 (0) 102468679

DCMR

Characteristic of your BTEX analyser

Trademark	Environnement SA (ENVEA)
Model:	VOC72M
Version:	PID
Year of manufacture:	2017

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:	no	yes	no	no	no
Other gases used:					

Operating system:	android
Cycle time, min:	20
Adsorbent material:	CARBOPACK
Sampling control	pump, micro capillary tube
Sampling temperature, °C	25
Sample volume, ml	220
Number of adsorbent tubes	1
Desorption temperature, `	380
Desorption time, sec	<3sec
Desorption flow, ml/min	
Cryo-trap detail	
Trapping temperature, °C	
Desorption temperature, °C	
Desorption flow, ml/min	
Stripper column	
Analytical column	
phase:	a-polar
length, m:	15
diameter (ID) mm:	0.25
thickness (µm):	1
analytical conditions:	20-170

Traceability of your calibration Standard

Certified reference material (CRM	YES, PRM	
Certified by	VSL	
Certified number:	C1303010	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	12.00	0.50
Toluene	12.00	0.5
Ethyl-benzene	12.1	0.5
m+p-Xylene	24	0.50
o-Xylene	11.8	0.5

Participating Laboratory	DCMR Milieudienst Rijnmond
Acronym	DCMR
Person(s) responsible	Ed van der Gaag
Contact e-mails:	ed.vandergaag@dcmr.nl
Telephone contact:	0031 (0) 102468679

DCMR2

Characteristic of your BTEX analyser

Trademark	AMA instruments GmbH
Model:	GC 5000 BTX
Version:	FID
Year of manufacture:	2017

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

Operating system:	windows 7 (10)		
Cycle time, min:	20		
Adsorbent material:	tenax		
Sampling control	pump, MFC		
Sampling temperature, °C	30		
Sample volume, ml	300		
Number of adsorbent tubes	1		
Desorption temperature, `	350		
Desorption time, sec	<9sec		
Desorption flow, ml/min			
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, se	
Desorption flow, ml/min		split flow, ml/min	
Stripper column			
Analytical column	AMAsep 1 - FUSED silica capillary		
phase:			
length, m:	30		
diameter (ID) mm:	0.32		
thickness (µm):	1.5		
analytical conditions:	30-210		

Traceability of your calibration Standard

Certified reference material (CRM	YES, PRM	
Certified by	VSL	
Certified number:	C1303010	
Compound	Concentration, ppb (mol/mo	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	12.00	0.50
Toluene	12.00	0.5
Ethyl-benzene	12.1	0.5
m+p-Xylene	24	0.50
o-Xylene	11.8	0.5

VSL
Dutch Metrology Institute

CERTIFIC

DCMR

Number C1303010

Reference material of BTEX in nitrogen

Description: Primary reference gas mixture (PRM), cylinder number APEX1170581.
The cylinder contains a mixture of BTEX in nitrogen.
The PRM is contained in a passivated aluminium cylinder. The cylinder has a water volume of 5 L and is pressurized to 11.6 MPa.
Cylinder outlet conforms to DIN 1 specifications.

Method of preparation: Gravimetric preparation in accordance with ISO 6142-1:2015.

Result

Component	Amount fraction [mol/mol]	Uncertainty [mol/mol]
Benzene	12.0×10^{-9}	0.5×10^{-9}
Toluene	12.0×10^{-9}	0.5×10^{-9}
o-xylene	11.8×10^{-9}	0.5×10^{-9}
ethylbenzene	12.1×10^{-9}	0.5×10^{-9}
m-xylene	11.9×10^{-9}	0.5×10^{-9}
p-xylene	12.1×10^{-9}	0.5×10^{-9}

The reported uncertainty of measurement is based on the standard uncertainty multiplied by a coverage factor $k = 2$, which for a normal distribution corresponds to a coverage probability of approximately 95%. The standard uncertainty has been determined in accordance with the GUM '*Evaluation of measurement data - Guide to the Expression of Uncertainty in Measurement*'.

Traceability: The values on this certificate are traceable to VSL Primary Standards.

Safety information: The cylinder should be handled with care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of gaseous materials.

Instructions for use: The gas mixture can be used to validate and/or calibrate analytical methods and equipment.
Do not use the cylinder in case the cylinder pressure is below 1 MPa.
Further instructions regarding the handling of calibration gases can be found in ISO 16664:2017.

Expiry date: This certificate is valid until 1 July 2020.

Delft, 12 September 2017
VSL B.V.

J.I.T. van Wijk
Senior Metrologist

VSL Dutch Metrology Institute

Participating Laboratory	Agenzia provinciale per l'ambiente e la tutela de
Acronym	APPA BZ
Person(s) responsible	Oswald Vigl
Contact e-mails:	oswald.vigl@provinz.bz.it
Telephone contact:	338-1610525

APPA

Characteristic of your BTEX analyser

Trademark	Syntech Spectras
Model:	GC 955 - 600
Version:	Version 2
Year of manufacture:	2008

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

Operating system:	Windows Xpe		
Cycle time, min:	30		
Adsorbent material:	TENAX GR, 35-60 mesh, 8 cm		
Sampling control	Pump; MFC, Piston		
Sampling temperature, °C	50		
Sample volume, ml	3.3		
Number of adsorbent tubes	3		
Desorption temperature, `	175		
Desorption time, sec	1.5		
Desorption flow , ml/min			
Cryo-trap detail	...		
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, se	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	2 m		
Analytical column	Capillar column AT5; ID 0,32 mm; film 1µm		
phase:	95% dimethylpolysiloxane; 5% diphenylpolysiloxane		
length, m:	13 m		
diameter (ID) mm:	0.32		
thickness (µm):	1		
analytical conditions:	50,70,50		

Traceability of your calibration Standard

Certified reference material (C	SIAD	
Certified by	ACCREDIA	
Certified number:	G085017	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	189.8	3.8
Toluene	189.7	3.8
Ethyl-benzene	190.1	5.9
m-Xylene	190.7	4.2

Other methods

Dilution of CRM			
Static Injection			
Permeation	Horiba 360 Permeation System		
Compound	Permeation rates ng/min	Dilution Flow	Oven Temp.
Benzene	19.7	1,0 lt/min	50°C
Toluene	18.5	1,0 lt/min	50°C
Ethyl-benzene	33.4	1,0 lt/min	50°C
m-Xylene	40.0	1,0 lt/min	50°C
p-Xylene	19.7	1,0 lt/min	50°C
o-Xylene	16.8	1,0 lt/min	50°C

APPA

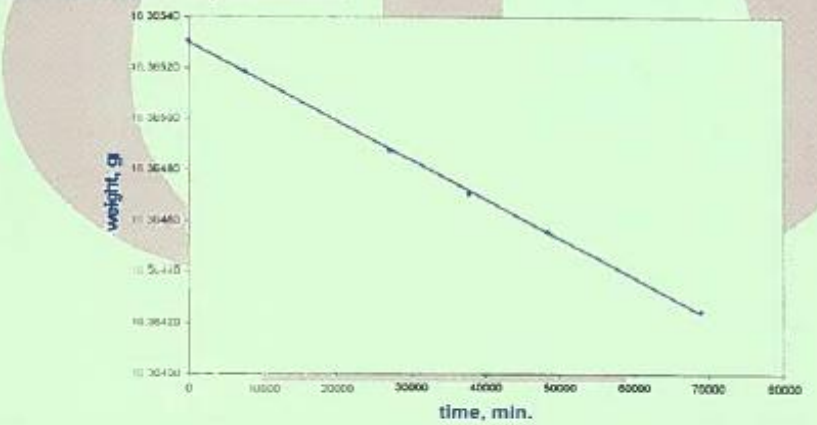
Certificato di Calibrazione

Si certifica che il tubo a permeazione **cod. D075SW4** serie **n. 15386** è caratterizzato dai seguenti parametri:

- **gas contenuto: Benzene**
- **temperatura di calibrazione: 50,0 °C**
- **velocità di permeazione: 15 ±2 ng/min**
- **vita media prevista a 15 ng/min: 3 anni**

La calibrazione è stata effettuata secondo la procedura **P3, sezione 3, protocollo U.S. EPA-600/R-12/531** ed in accordo al metodo descritto al **punto 4.1, appendice 11, allegato II del D.P.C.M. 28 marzo 1983**. Durante la calibrazione il tubo a permeazione è stato mantenuto, in una corrente di gas inerte e secco, ad una temperatura costante e controllata con una precisione di ±0,05 °C mediante catena termometrica certificata **S.I.T. Sistema Italiano di Taratura** (certificato n. 385-ST-11, Gefran S.p.A.). Il tubo è stato pesato ad intervalli di tempo regolari con una bilancia semi-micro analitica della precisione di ±0,01 mg (Sartorius BP210D s/n 70505503) e tarata con masse certificate S.I.T. (certificati n. 543/07, n. 544/07, n. 545/07, CIBE S.r.l.), fino a che i valori di velocità di permeazione non hanno raggiunto un livello di confidenza del 95%.

Il seguente grafico riporta la diminuzione del peso del tubo nel tempo, la pendenza della retta rappresenta la velocità di permeazione.



C(ppm) = C (ng /cc) x **0,313** a 298,15 °K; 101,3 kPa

Spadafora 29 Maggio 2015

ORDINE DEI CHIMICI DELLA PROVINCIA DI MESSINA
DOTT. IPSALE SALVATORE CHIMICO n. 241

ALBO DEI CHIMICI DI MESSINA n. 241

Ph. D. Salvatore Ipsale
Chimico - EurChem

EurChem
Certificato n. 550
European Chemist Registration Board

fine metrology S.r.l.s.
Via Vincenzo Monti 14 98048 Spadafora (ME) ITALY
☎ 0039 090-9941643 🖷 0039 090-9943700
http://www.finepermeation.it e-mail: fine@finepermeation.it

APPA

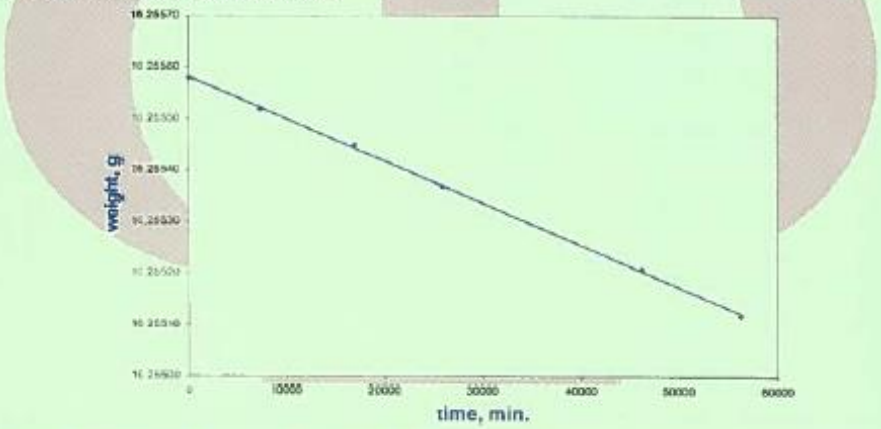
Certificato di Calibrazione

Si certifica che il tubo a permeazione **cod. D050SW4** serie **n. 15388** è caratterizzato dai seguenti parametri:

- **gas contenuto: Toluene**
- **temperatura di calibrazione: 50,0 °C**
- **velocità di permeazione: 10 ±2 ng/min**
- **vita media prevista a 10 ng/min: 3 anni**

La calibrazione è stata effettuata secondo la procedura **P3, sezione 3, protocollo U.S. EPA-600/R-12/531** ed in accordo al metodo descritto al **punto 4.1, appendice 11, allegato II del D.P.C.M. 28 marzo 1983**. Durante la calibrazione il tubo a permeazione è stato mantenuto, in una corrente di gas inerte e secco, ad una temperatura costante e controllata con una precisione di ±0,05 °C mediante catena termometrica certificata **S.I.T. Sistema Italiano di Taratura** (certificato n. 385-ST-11, Gefran S.p.A.). Il tubo è stato pesato ad intervalli di tempo regolari con una bilancia semi-micro analitica della precisione di ±0,01 mg (Sartorius BP210D s/n 70505503) e tarata con masse certificate **S.I.T.** (certificati n. 543/07, n. 544/07, n. 545/07, CIBE S.r.l.), fino a che i valori di velocità di permeazione non hanno raggiunto un livello di confidenza del 95%.

Il seguente grafico riporta la diminuzione del peso del tubo nel tempo, la pendenza della retta rappresenta la velocità di permeazione.



C(ppm) = C (ng /cc) x **0,265** a 298,15 °K, 101,3 kPa

Spadafora 29 Maggio 2015

ORDINE DEI CHIMICI DELLA PROVINCIA DI MESSINA
DOTT. IPSALE SALVATORE CHIMICO n. 241

ALBO DEI CHIMICI DI MESSINA
n 241

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http://www.finepermeation.it e-mail: fine@finepermeation.it

APPA

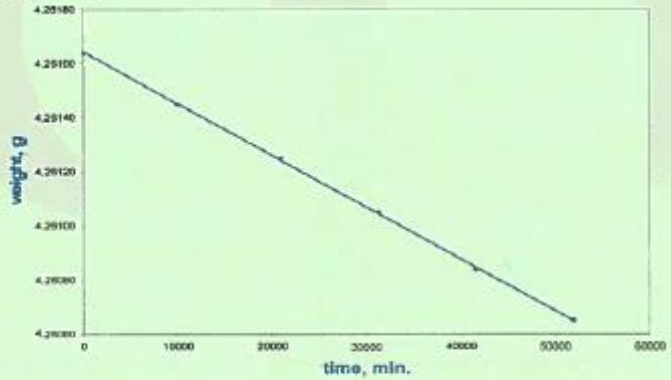
Calibration Certificate

This is to certify that the permeation tube **code STD50 serial n. A147** has the parameters recorded below:

- **chemical fill: Ethylbenzene**
- **calibration temperature: 50,0 °C**
- **permeation rate: 19 ±2 ng/min**
- **average useful life expected at 19 ng/min: 3 years**

Calibration has been performed, using the method described in the protocol **U.S. EPA-600/R-97/121, Section 3, procedure P3**, by keeping the permeation tube in a constant temperature chamber purged by a zero gas weighing periodically until a stable weight loss per unit of time has been achieved. Temperature is measured with a SIT-traceable thermoresistance (certificate n. 23868 by Gefran S.p.A., Italy) and controlled with ±0.05 °C accuracy. The weight loss is determined on a semi-micro analytical balance accurate to ±0.01 mg (Sartorius BP210D s/n 70505503) and calibrated using SIT-traceable masses reference standards (certificates n. 543/07, n. 544/07, n. 545/07 by CIBE S.r.l., Italy). Gravimetric permeation rate determinations are continued until the standard error reaches 95% confidence level.

Following graphic shows weight loss versus time, the slope of the best fitting straight line gives the permeation rate.



C(ppm) = **C** (ng /cc) x **0,230** at 298,15 °K; 101,3 kPa

Spadafora 18 March 2011

ORDINE DEI CHIMICI DELLA PROVINCIA DI MESSINA
DOTT. IPSALE SALVATORE CHIMICO n. 241

Ph.D. Salvatore Ipsale
European Chemist *

Φ fine permeation tubes
Via Nuova Grangiara, 15 98048 Spadafora (ME) ITALY
tel.: +39 (090) 9941643 fax:+39 (090) 9943700

* Certificate n. 550 by European Chemist Registration Board

APPA

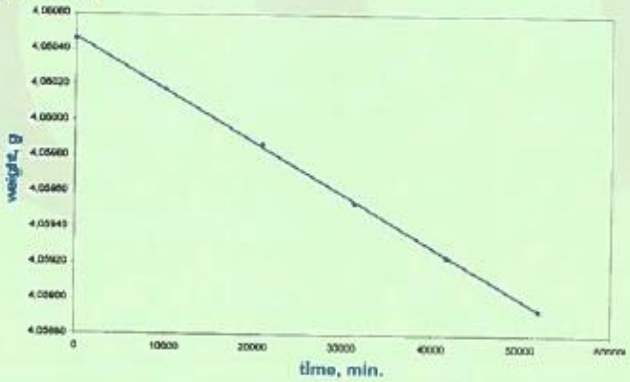
Calibration Certificate

This is to certify that the permeation tube **code STD40 serial n. A141** has the parameters recorded below:

- **chemical fill: m-Xilene**
- **calibration temperature: 50,0 °C**
- **permeation rate: 29 ±2 ng/min**
- **average useful life expected at 29 ng/min: 3 years**

Calibration has been performed, using the method described in the protocol **U.S. EPA-600/R-97/121, Section 3, procedure P3**, by keeping the permeation tube in a constant temperature chamber purged by a zero gas weighing periodically until a stable weight loss per unit of time has been achieved. Temperature is measured with a SIT-traceable thermoresistance (certificate n. 23868 by Gefran S.p.A., Italy) and controlled with ±0.05 °C accuracy. The weight loss is determined on a semi-micro analytical balance accurate to ±0.01 mg (Sartorius BP210D s/n 70505503) and calibrated using SIT-traceable masses reference standards (certificates n. 543/07, n. 544/07, n. 545/07 by CIBE S.r.l., Italy). Gravimetric permeation rate determinations are continued until the standard error reaches 95% confidence level.

Following graphic shows weight loss versus time, the slope of the best fitting straight line gives the permeation rate.



C(ppm) = C (ng /cc) x 0,230 at 298,15 °K; 101,3 kPa

Spadafora 18 March 2011

ORDINE DEI CHIMICI DELLA PROVINCIA DI MESSINA
dott. IPSALE SALVATORE CHIMICO n. 241

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* Certificate n. 550 by European Chemist Registration Board

APPA

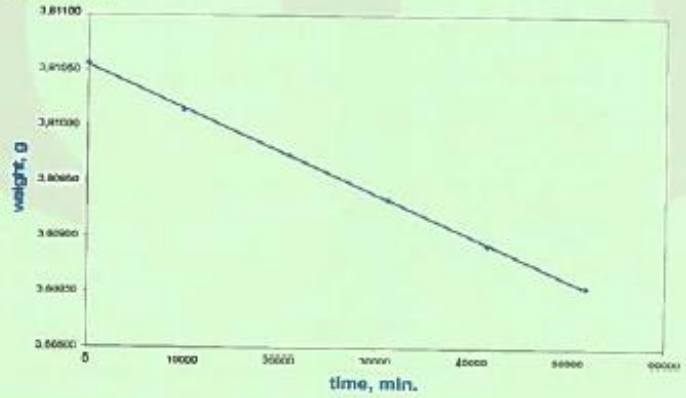
Calibration Certificate

This is to certify that the permeation tube **code STD35 serial n. A145** has the parameters recorded below:

- **chemical fill: p-Xilene**
- **calibration temperature: 50,0 °C**
- **permeation rate: 39 ±2 ng/min**
- **average useful life expected at 39 ng/min: 3 years**

Calibration has been performed, using the method described in the protocol **U.S. EPA-600/R-97/121, Section 3, procedure P3**, by keeping the permeation tube in a constant temperature chamber purged by a zero gas weighing periodically until a stable weight loss per unit of time has been achieved. Temperature is measured with a SIT-traceable thermoresistance (certificate n. 23868 by Gefran S.p.A., Italy) and controlled with ±0.05 °C accuracy. The weight loss is determined on a semi-micro analytical balance accurate to ±0.01 mg (Sartorius BP210D s/n 70505503) and calibrated using SIT-traceable masses reference standards (certificates n. 543/07, n. 544/07, n. 545/07 by CIBE S.r.l., Italy). Gravimetric permeation rate determinations are continued until the standard error reaches 95% confidence level.

Following graphic shows weight loss versus time, the slope of the best fitting straight line gives the permeation rate.



C(ppm) = C (ng /cc) x **0,230** at 298,15 °K; 101,3 kPa

Spadafora 18 March 2011

ORDINE DEI CHIMICI DELLA PROVINCIA DI MESSINA
DOTT. IPSALE SALVATORE CHIMICO n. 241

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APPA

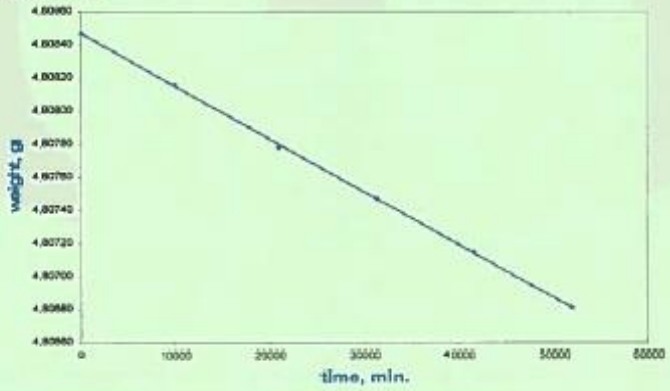
Calibration Certificate

This is to certify that the permeation tube **code STD70 serial n. A143** has the parameters recorded below:

- **chemical fill: o-Xilene**
- **calibration temperature: 50,0 °C**
- **permeation rate: 32 ±2 ng/min**
- **average useful life expected at 32 ng/min: 3 years**

Calibration has been performed, using the method described in the protocol **U.S. EPA-600/R-97/121, Section 3, procedure P3**, by keeping the permeation tube in a constant temperature chamber purged by a zero gas weighing periodically until a stable weight loss per unit of time has been achieved. Temperature is measured with a SIT-traceable thermoresistance (certificate n. 23868 by Gefran S.p.A., Italy) and controlled with ±0.05 °C accuracy. The weight loss is determined on a semi-micro analytical balance accurate to ±0.01 mg (Sartorius BP210D s/n 70505503) and calibrated using SIT-traceable masses reference standards (certificates n. 543/07, n. 544/07, n. 545/07 by CIBE S.r.l., Italy). Gravimetric permeation rate determinations are continued until the standard error reaches 95% confidence level.

Following graphic shows weight loss versus time, the slope of the best fitting straight line gives the permeation rate.



C(ppm) = C (ng /cc) x **0,230** at 298,15 °K; 101,3 kPa

Spadafora 18 March 2011

ORDINE DEI CHIMICI DELLA PROVINCIA DI MESSINA
DOTT. IPSALE SALVATORE CHIMICO n. 241

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* Certificate n. 550 by European Chemist Registration Board

Participating Laboratory	Slovak Hydrometeorological Institut
Acronym	SHMU
Person(s) responsible	Peter Holoman
Contact e-mails:	peter.holoman@shmu.sk
Telephone contact:	+421-2-59415364

SHMU

Characteristic of your BTEX analyser

Trademark	Syntech Spectras
Model:	GC955
Version:	Model 601
Year of manufacture:	2015

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:	-	yes	-	-	-
Other gases used:	-	-	-	-	-

Operating system:	Windows		
Cycle time, min:	15		
Adsorbent material:	TENAX GR,		
Sampling control	Piston - pump		
Sampling temperature, °C	25		
Sample volume, ml			
Number of adsorbent tubes	3		
Desorption temperature, `	180		
Desorption time, sec			
Desorption flow , ml/min			
Cryo-trap detail			
Trapping temperature, °C			
Desorption temperature, °C		Desorption time, se	
Desorption flow, ml/min		split flow, ml/min	
Stripper column	capillar		
Analytical column	capillar, Synspec SY-1		
phase:	SY-1		
length, m:	15		
diameter (ID) mm:	0.32		
thickness (µm):	1		
analytical conditions:	50°C (0-3min.) -> 70°C (3 - 5min.), 70°C (5 - 12min) -> 50°C (12-14min), 50°C (14-15min)		

Traceability of your calibration Standard

Certified reference material (C	NPL Primary Reference Material	
Certified by	NPL UK	
Certified number:	2017090429-1; 2017090429-2;	
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	1; 5; (10);	0.021; 0.10; (-)
Toluene		
Ethyl-benzene		
m+p-Xylene		
o-Xylene		

NATIONAL PHYSICAL LABORATORY
Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

SHMU

Certificate of Calibration

UKAS
4002

NPL PRIMARY REFERENCE MATERIAL

Cylinder Number: D517549

CUSTOMER: **Messer Tatragas spol. s.r.o**

ADDRESS: Vlcie hrdlo 1, 824 11 Bratislava 23, Slovakia

CALIBRATION DATE: 21 November 2017

AMOUNT FRACTION:

Component	Amount fraction / (nmol/mol)
Benzene	5.00 ± 0.10
Nitrogen	Balance

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2017090429-2 **Date of issue:** 15 December 2017

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by: N. Allen

Participating Laboratory	Institute of Public Health of Belgrad
Acronym	IPH
Person(s) responsible	Andrej Sostaric
Contact e-mails:	andrej.sostaric@zdravlje.org.rs
Telephone contact:	381 11 13 94 185, 381 11 20 78 792

IPH_S

Characteristic of your BTEX analyser

Trademark	SYNTECH SPECTRAS
Model:	GC 955
Version:	601
Year of manufacture:	2009

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

Operating system:	Windows XP
Cycle time, min:	15 min
Adsorbent material:	Tenax GR
Sampling control	piston pump + MFC
Sampling temperature, `C	Ambient
Sample volume, ml	210
Number of adsorbent tubes	one
Desorption temperature, `	180 C
Desorption time, sec	60
Desorption flow, ml/min	1.5
Cryo-trap detail	
Trapping temperature, `C	
Desorption temperature, `C	
Desorption time, se	
Desorption flow, ml/min	
split flow, ml/min	
Stripper column	identical with analytical column, 2m lenght
Analytical column	AT624
phase:	(6% Cyanopropylphenyl)-94% methylpolysiloxane
length, m:	15
diameter (ID) mm:	0.32
thickness (µm):	1
analytical conditions:	0 C (3 min),50-70 C ,10C/min, 70C (5-12 min), 70-50 C ,10C/min, 50C (14-15 m

Traceability of your calibration Standard

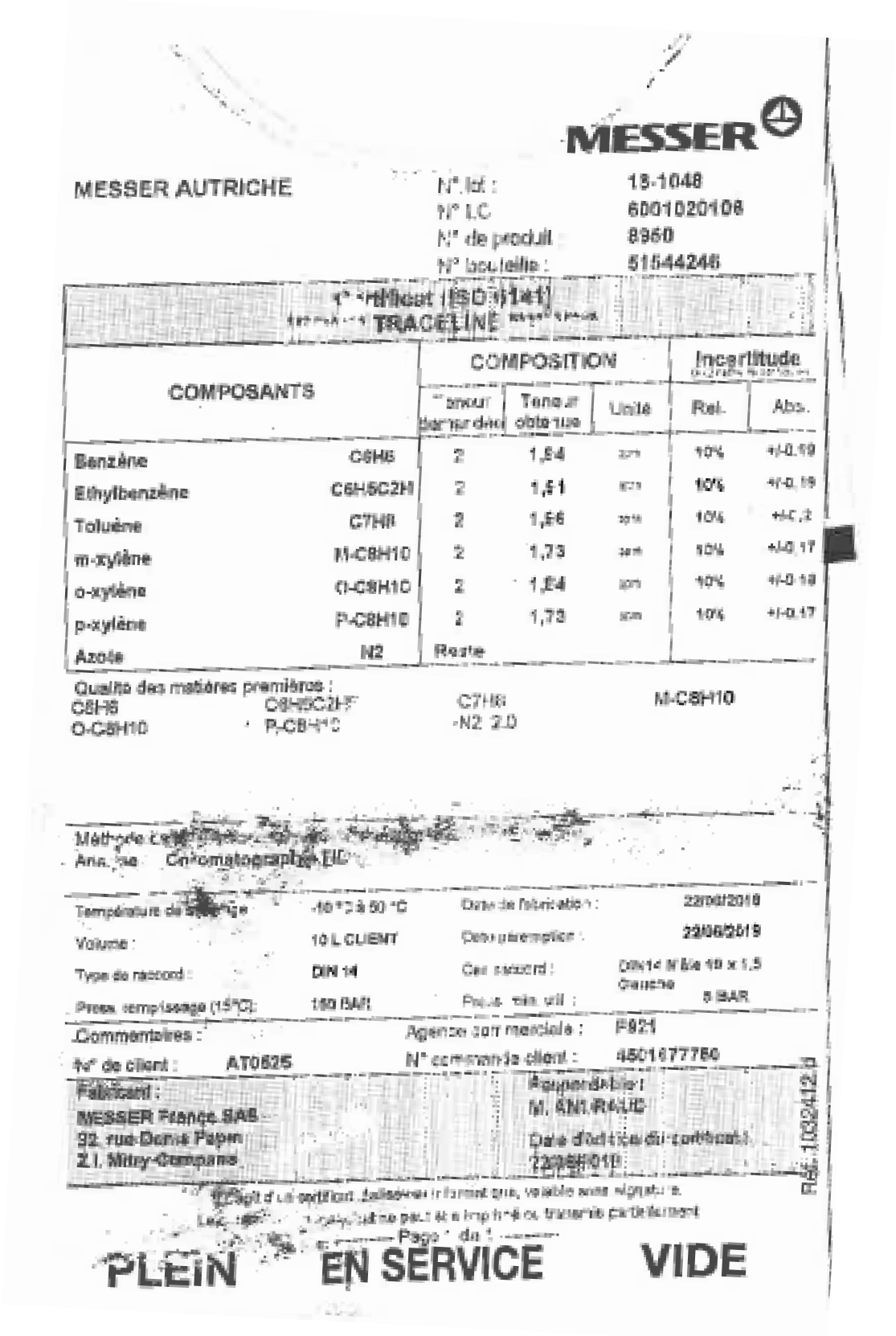
Certified reference material (C		
Certified by		
Certified number:		
Compound	Concentration, ppb (mol/mol	Expanded Uncertainty, ±ppb(mol/mol)
Benzene		
Toluene		
Ethyl-benzene		
m-Xylene		
p-Xylene		
o-Xylene		

Other methods

Dilution of CRM	containing 2ppm of BTEX is diluted by dinamic dilution system ASGU 370

Details on how you have calculated your analytical uncertainties from your calibrati	IPH_S

Uncertainties were calculated in accordance with EN 14662-3:2015.



MESSER

MESSER AUTRICHE

N° lot : 15-1048
N° LC 6001020108
N° de produit : 8960
N° bouteille : 51544246

TRACELINE

COMPOSANTS		COMPOSITION			Incertitude	
		Valeur par sur doc	Teneur obtenue	Unité	Rel.	Abs.
Benzène	C6H6	2	1,84	ppm	10%	+/-0.19
Ethylbenzène	C6H5C2H	2	1,51	ppm	10%	+/-0.15
Toluène	C7H8	2	1,86	ppm	10%	+/-0.2
m-xylène	M-C8H10	2	1,73	ppm	10%	+/-0.17
o-xylène	O-C8H10	2	1,84	ppm	10%	+/-0.18
p-xylène	P-C8H10	2	1,73	ppm	10%	+/-0.17
Azote	N2	Reste				

Qualité des matières premières :
C6H6 C6H5C2H5 C7H8 M-C8H10
O-C8H10 P-C8H10 N2 2.0

Méthode [illegible]
Analyse Chromatographie GC

Température de stockage :	-10 °C à 50 °C	Date de fabrication :	22/06/2019
Volume :	10 L CUIVRE	Date péremption :	22/06/2029
Type de raccord :	DIN 14	Cap raccord :	DIN14 W 8x 19 x 1,5 Gauche
Press. remplissage (15°C) :	150 BAR	Press. tare vil :	5 BAR
Commentaires :		Agence commerciale :	F821
N° de client :	AT0625	N° commande client :	4501677760

Fabricant :
MESSER France SAS
32, rue Denis Papin
Z.I. Mitry-Compans

Responsable :
M. ENRIQUE

Date d'édition du certificat :
22/06/2019

Réf. 1032412.0

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[illegible] ne peut être imprimé ou transmis partiellement
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PLEIN EN SERVICE VIDE

ERLAP

Acronym	ERLAP
Person(s) responsible	A. Bau' ,Pascual Perez Ballesta
Contact e-mails:	pascual.ballesta@ec.europa.eu, andrea.bau@ec.europa.eu
Telephone contact:	_+39033278-(5322) (5353)

Characteristic of your BTEX analyser

Trademark	Agilent + Perkin-Elmer
Model:	Agilent 6890 + ATD-50 PE
Version:	
Year of manufacture:	2005

	Helium	Nitrogen	Hydrogen	Carbon dioxi	Air
Carrier gas:	yes	yes	yes		yes
Other gases used:					

Operating system:	Windows 10
Cycle time, min:	30 min
Adsorbent material:	TENAX GR, Carbopack B, CARBOPACK X, CARBOPACK C
Sampling control	Pump/MFC
Sampling temperature, °C	Ambient
Sample volume, ml	200mL (20-800 ML)
Number of adsorbent tubes	1
Desorption temperature, `	300
Desorption time, sec	180
Desorption flow, ml/min	20

Cryo-trap detail	Perkin Elmer	Air Toxics, special preperation		
Trapping temperature, °C	-25			
Desorption temperature, °C	300	Desorption time, sec	300	
Desorption flow, ml/min	50	split flow, ml/min		

Stripper column	
Analytical column	DB1 and Al2O3 KCl dean-switch system
phase:	
length, m:	50
diameter (ID) mm:	0.32
thickness (µm):	1.2
analytical conditions:	40°C hold 5min., 6°C/min. to 200°C hold 15min

Traceability of your calibration Standard

Certified reference material (CRM	Primary Reference Gas Mixture	
Certified by	NPL	
Certified number:	Cylinder Number D386674	
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)
Benzene	3.99	±0.08
Toluene	3.99	±0.10
Ethyl-benzene	3.99	±0.10
m+p-Xylene	7.98	±0.20
o-Xylene	3.97	±0.10

Other methods	
Dilution of CRM	
Static Injection	
Permeation	

Additional comments

sampling volume during the exercise 300 ml.
multipoint calibration with volumes ranged from 20 to 800 ml

ERLAP

NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

Certificate of Calibration

UKAS REFERENCE MATERIALS 4002

PRIMARY REFERENCE GAS MIXTURE

Cylinder Number: D38 6674

This certificate is issued in accordance with the laboratory accreditation requirements of the United Kingdom Accreditation Service. It provides traceability of measurement to the SI system of units and/or to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes. This certificate may not be reproduced other than in full, except with the prior written approval of the issuing laboratory.

CUSTOMER: **European Commission – Joint Research Centre**

ADDRESS: Institute for Environment and Sustainability, Via E. Fermi, 1, I-21020 Ispra (VA), Italy

CALIBRATION DATE: 29 June 2016

AMOUNT FRACTIONS:

Component	Amount fraction / (nmol/mol)
Benzene	3.99 ± 0.08
Toluene	3.99 ± 0.10
Ethylbenzene	3.99 ± 0.10
m-xylene + *p*-xylene	7.98 ± 0.20
o-xylene	3.97 ± 0.10
Nitrogen	Balance

The reported expanded uncertainties are based on standard uncertainties multiplied by a coverage factor $k = 2$, providing a coverage probability of approximately 95 %. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

METHODS: Preparation: gravimetry; Analysis: gas chromatography (FID)

TRACEABILITY: The values on this certificate are traceable to NPL Primary Standards

EXPIRY: Certificate valid for 2 years from the date of issue

PRESSURE: Fill pressure: 100 bar; Minimum utilisation pressure: 10 bar

STORAGE: No special precautions are required

HANDLING: Refer to ISO 16664

OUTLET: DIN 477 No. 1 valve

INTENDED USE: Calibration standard

Reference: 2016040285 **Date of issue:** 1 July 2016

Signed: (Authorised Signatory)

Name: Dr P J Brewer (on behalf of NPLML)

Checked by:

CIPM MRA

This certificate is consistent with the capabilities that are included in Appendix C of the MRA drawn up by the CIPM. Under the MRA, all participating institutes recognise the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C (for details see http://www.bipm.org).

List of abbreviations and definitions

AAA	Environmental Protection Agency (Lithuania)
APPA	Agenzia Provinciale Per l'Ambiente e la Tutela del Clima
AQUILA	Air quality reference laboratories
BTEX	Benzene, toluene, ethyl-benzene, xylene
CG	Gas chromatograph
DCMR	DCMR Milieudienst Rijnmond
Conc.	Concentration
D.D.	Dynamic Dilution
DLI	Department of Labour Inspection. Ministry of Labour and Social Insurance (Cyprus)
EC	European Commission
EKONERG	Energy and Environmental Protection Institute (Croatia)
EPA	Environmental Protection Agency (Ireland)
ERLAP	European Reference Laboratory of Air Pollution
EU	European Union
U %	Relative Expanded Uncertainty
FID	Flame ionization detector
GIOS	Chief Inspectorate of Environmental Protection (Poland)
H.C.	Hydrocarbons
i.d.	Internal diameter
IPH_S	Institute of Public Health of Belgrade (Serbia)
ISO	International Standard Organisation
ISPRA	Istituto Superiore per la Protezione e Ricerca Ambientale - Area Metropologia (Italy)
JRC	Joint Research Centre
LIKZ	Laboratory Croatian Hydrological and Laboratory Service (Croatia)
l.s.	level of significance
LV	Limit value
QAQC	Quality assurance quality control
n.a.	Not available
NPL	National Physical Laboratory (United Kingdom)
NRL	National Reference Laboratory
PID	Photo ionization detector
ppb (m/m)	Concentration part per billion, molar fraction
Press. Cyl.	Pressurised cylinder
P.T.	Permeation tubes
REE	Agency Ricardo Energy and Environment (United Kingdom)
RSD	Relative standard deviation, %
SHMU	Slovak Hydrometeorological Institute (Slovakia)

stdev	standard deviation
Tr. Std.	Travelling standard
U	Expanded Uncertainty
VMM	Vlaamse Milieumaatschappij, (Belgium)
VSL	National Metrology Institute. (The Netherlands)

$\overline{C}$	Average concentration value
$\overline{C}_i$	Average concentration value of I measurements
$\overline{\overline{C}}$	Inter-laboratory average concentration
$\overline{C}_i^*$	Robust average value
C_{ref}	Reference concentration value
C_8	refers to hydrocarbons with 8 atoms of carbon
E_n	$E_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}}$
k_i	Mandel-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
$\sum\overline{\lvert Residuals\rvert} = \sum_i^{Levels}\left(\overline{\lvert bias\rvert}_i \cdot C_{ref_i}/100\right)$:	sum of average absolute residuals
s^*	Standard deviation of the robust average value $\overline{C}_i^*$
s_{bias}	Standard deviation of the bias, $\overline{C}_i^* - C_{ref}$
$S_{\bar{c}_i}$	Standard deviation of the average inter-laboratory value
s_i	Standard deviation of the sample i.
s_L^2	Inter-laboratory variance or between-laboratory variance
S_{LN37}	$\boldsymbol{s_{L_{N37}}} = \sqrt{\hat{\boldsymbol{\sigma}}_{\boldsymbol{N37}}^{\boldsymbol{2}} - \frac{\boldsymbol{s_r^2}}{\boldsymbol{n}}}$: 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
u	Uncertainty of the method
u_{Cref}	Uncertainty associated with the reference concentration value C_{ref}
u_{pt}	Standard uncertainty of the robust value of the proficiency test
Z	$\frac{C_{lab} - C_{ref}}{\hat{\sigma}_m}$: Z-scores statistic

$\mu g/m^3$	Micrograms per cubic meter
α	Level of significance
γ	$\gamma = s_R/s_r$, gamma value
σ	Standard deviation
$\hat{\sigma}$	Standard deviation for proficiency assessment
$\hat{\sigma}_m$	$\hat{\boldsymbol{\sigma}}_{\boldsymbol{m}} = \sqrt{(\mathbf{0.5} \cdot \boldsymbol{s_L})^2 + \frac{s_r^2}{n}}$: minimum standard deviation of proficiency assessment coherent with method reproducibility
$\hat{\sigma}_{N37}$	Standard deviation for proficiency assessment prescript by AQUILA network
$(1-\alpha)$	Confidence level

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