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

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Contents

Abstract

This report presents the results of the sixth inter-laboratory comparison for BTEX automatic analysers performed at the JRC Ispra from the 26th to the 29th of September 2022. Twelve 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 13528:2022 methodologies for the evaluation of inter-laboratory proficiency assessment and the recommendation of the protocol N_{37} of the AQUILA network. Participating laboratories were identified as requested by the afore-mentioned protocol.

The robust average value calculated according to ISO 13528:2022 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 scores, Z' scores, P_A scores, biases 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). For benzene and toluene, average repeatability and reproducibility values were about 6.5 ± 0.5 % and 15 ± 2 %, respectively. Ethyl-benzene, m,p-xylene and o-xylene showed higher repeatability values of around 9.7 ± 0.2 %, while their values of reproducibility were about 35 ± 3 %.

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1 Introduction

This BTEX inter-laboratory comparison exercise is the sixth exercise carried out by the Joint Research Centre aiming to fulfil the QA/QC programme for the harmonisation 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 26th to the 29th September 2022. Participants were required to register and provide a detailed description of their instrumentation. As agreed within the AQUILA protocol, participating laboratories are identified in the report. In this exercise, the average robust value was adopted as the reference value of the inter-laboratory comparison. The evaluated concentration range was that used during the previous comparison exercise.

In this report, statistics of r scores, Z' scores, E_n scores, P_A scores were processed for the evaluation of the laboratory performance. The report also provides additional information regarding linearity test, blank levels, overall repeatability and reproducibility values and robustness of the method in the context of the comparison exercise.

2 Inter-laboratory comparison strategy

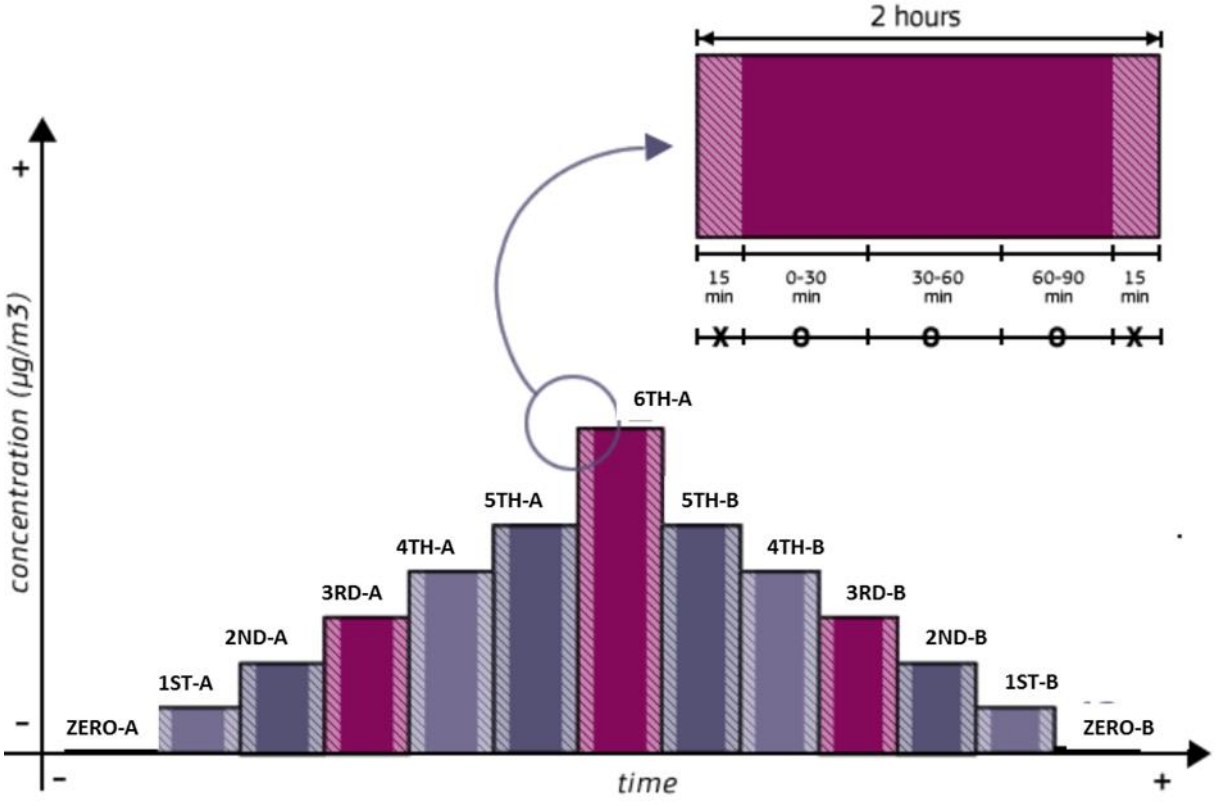
The reporting of results from the participating laboratories was done by uploading the requested information on the JRC web site application at http://interlabo-comparison.jrc.ec.europa.eu. This included the characteristics of the BTEX analyser, description of the calibration method and traceable reference 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 are resumed in section 2.1.

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**). A stable concentration interval of 1.5 h for the comparison of the measurements is highlighted in a darker tonality in **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.

Reference concentration was derived from the robust average concentration of the exercise. Whereas, ERLAP results were included in the comparison and managed as any other participant. Furthermore, laboratories were requested to estimate and report the uncertainties associated with the average concentration of each level.

Concentrations were expressed in µg/m3 at 20 °C and 1 atm. Conversion factors from ppb (v/v) to µg/m3 for reporting results were agreed before the inter-laboratory comparison (see Annex 5: Conversion factor for data reporting: **Table A 19**).

Figure 1. Time versus concentration steps along the exercise



Source: Pérez Ballesta et al. EUR30239

2.1 Participating laboratories and instrumentation

Twelve 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 instrument and analytical parameters used by each laboratory. CHMI participated with an online analyser (CHMI1) and a pumped tube sampling system (CHMI2) that reported fewer concentration levels due to sampling restrictions. Furthermore, Both DLI and SHI reported data from two online instruments identified by the corresponding number after the laboratory acronym. Instead UBA and IPH-S that participated with two instruments of the same characteristic only reported the results from one of them.

From the fifteen instruments in comparison, five had a flame ionization detector (FID), while the others ten 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
CHMI	Czech Hydrometeorological Institute	Czech Republic	Jan Silhavy, Martin Beck
DHZ-TES	Croatian Meteorological and Hydrological Service	Croatia	Borna Bozikovic, Dominik Piskor
DLI	Department of Labour Inspection	Cyprus	Christos Kiza, Christakis Papadopoulos
EKONERG	Energy and Environmental Protection Institute	Croatia	Hercog Predrag, Marijo Bilic
EPA	Environmental Protection Agency	Ireland	Kevin Delaney, Ken Murphy
ERA	Environment & resources Authority	Malta	Rosalie Camilleri, Carmel Bonnici
IPH-S	Institute of Public Health of Belgrade	Serbia	Andrej Šoštarić, Slaviša Mladenović
ISCIII	Instituto de Salud Carlos III	Spain	Jose Miguel de Miguel
ISPRA	Istituto Superiore per la Protezione e Ricerca Ambientale	Italy	Diego Capobianco, Fabio Cadoni
SHI	Slovak Hydrometeorological Institute	Slovakia	Peter Holoman, Terezia Udvarosova, Samuel Vincze
UBA	Umweltbundesamt	Germany	Vesela Petkova-Krasteva, Wilma Travnicek
JRC	Joint Research Centre – ERLAP	European Commission	Andrea Baú, Pascual Pérez Ballesta,

Source: JRC, 2023

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

Code	Analyser	Cycle time, min	Detector	Column: Length, i.d.[1], film thickness Operational conditions	Adsorbent, Sampled volume Desorption conditions
CHMI	Syntech Spectras GC955 6.0.9.1 (2015)	15	PID	Synspec, 15 m, .32 mm i.d., 1 µm 50°C (3 min), 10°C/min,70°C (5 min)	Tenax GR, 20 ml, 180 °C
CHMI2	n.a.[2]	n.a.[2]	FID	n.a.[2]	Carbopack-X
DHZ-TES	Chromatotec GC866 FID airmoVOC (2019)	15	FID	MXT 30 XE: 30 m, 0.28 mm i.d. 1 µm --	Carbotrap, 425 ml 350°C for 180 s
DLI	SynSpeck GC955 601 9601-PX2XXC	15	PID	SY-1, 13 m, 0.32 mm i.d., 1 µm 50 °C (3 min), 70 °C (5-12 min), 50 °C (14-15 min)	Tenax GR 40-60, 4 x 23.33 ml 185 °C for 60 s at 1.5 ml/min
DLI2	SynSpeck GC955 601 9601-PX2XXC	15	PID	SY-1, 13 m, 0.32 mm i.d., 1 µm 50 °C (3 min), 70 °C (5-12 min), 50 °C (14-15 min)	Tenax GR 40-60, 4 x 23.33 ml 185 °C for 60 s at 1.5 ml/min
EKONERG	Chromatotec AirmoVOC GC866 (2018)	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
EPA	SYNTECH Analyser GC 955, (2019)	15	PID	AT-5, 13 m, 0.32 mm, 1µm 45°C (4 min),14°C/min, 80°C (1 min)	Tenax GR 35/60, 210 ml 180°C for 60 s, 1.5 ml/min
ERA	SYNSPEC Analyser GC 955, Vers. 601 (2018)	15	PID	AT-5: 13 m, 0.32 mm, 1 µm 50°C (3 min), 10°C/min,70°C (7 min)	Tenax GR, 4 x 23.33 ml 180°C for 26 s, 1.5 ml/min
IPH-S	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)	Tenax GR, 210 ml 180°C for 60 s, 1.5 ml/min
ISCIII	Syntech Spectras GC955-601 9601-PX2XXC (2022)	15	PID	Synspec, (2+13) m, .32 mm i.d., 1 µm 50°C (3 min), 70°C (5-12 min), 50°C (14-15 min)	Tenax GR 35-60 mesh, 175°C for 1.5 s
ISPRA	AMA GC5000 BTX FID	30	FID	AMAsep 1 30 m , 0.32 mm i.d., 1.5 µm 50°C 3 min., 8°C/min, 130°C 5 min	Carbotrap 230 °C for 3 min at 3 ml/min
SHI	Syntech Spectras GC955 Model 601, 2019	15	PID	Synspec SY-1, 15 m, .32 mm i.d., 1 µm 50°C (3 min),70°C (5-12 min), 50°C (14-15 min)	Tenax GR 180°C
SHI2	Syntech Spectras GC955 Model 601, 2019	15	PID	Synspec SY-1, 15 m, .32 mm i.d., 1 µm 50°C (3 min),70°C (5-12 min), 50°C (14-15 min)	Tenax GR 180°C
UBA	SPECTRA GC 955, (2008)	15	PID	AT-5: 13 m, 0.32 mm, 1 µm 50°C (4.5 min), 70°C (6.8-13.5 min)	Tenax GR, 77.3 ml 180°C for 3 min, 2 ml/min
JRC	Agilent 8890 GC UNITY-AirServer-xr + Kori XR	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)	Ozone precursors trap, 900 ml. 300 °C, 3 min, 20 ml/min

([1]) i.d.: internal diameter
([2]) n.a.: information not available

Source: JRC, 2023

Table 3. Reference material used by the participating laboratories

Laboratory	Reference Material[1]	Benzene	Toluene	Ethyl-benzene	m-Xylene	p-Xylene	o-Xylene	Producer	Certified by	Certification date
		ppb(m/m)[2]	ppb(m/m)[2]	ppb(m/m)[2]	ppb(m/m)[2]	ppb(m/m)[2]	ppb(m/m)[2]			
CHMI	Press. Cyl.	9.92 ± 0.2	9.65 ± 0.25	--	--	--	--	NPL	NPL	n.a.[3]
DHZ-TES	Press. Cyl. D.D.: Orion OGD2000	498 ± 15	501 ± 15	504 ± 15	500 ± 15	500 ± 15	499 ± 15	VSL	VSL	28-05-2024
DLI	Press. Cyl.	5.00 ± 0.20	5.03 ± 0.20	5.06 ± 0.20	5.02 ± 0.20	5.02 ± 0.20	5.01 ± 0.20	NPL	NPL	10/11/2024
EKONERG	Press. Cyl. D.D. MCZ CGM200	961 ± 35	958 ±35	902 ± 39	1758 ± 78		835±35		Hungary Meteorogy Service	01/04/2022
EPA	Press. Cyl.	10.00 ± 0.31	9.98 ± 0.25	9.99 ± 0.25	20.0 ± 0.6		10.04± 0.26	NPL	NPL	24/05/2021
ERA	Press. Cyl. D.D.: MGC101 SN 3728 Environment s.a.	197.20 ± 3.9	197.20 ± 5.9	197.7 ± 8.9	197.20± 8.9	197.5± 8.9	197.1± 8.9	SIAD	Accredia	30/03/2022
IPH-S	Press. Cyl	2.16	2.24	2.14	2.06	2.06	2.06	MESSER	MESSER	27/06/2022
ISCIII	Press. Cyl.	994 ± 34.79	--	--	--	--	--	Swiss Calibration Service	--	--
UBA	Press. Cyl. DD: Sonimix from LNI	1980 ± 99	4960 ± 248	960 ± 48	976 ± 49	-	994 ± 50	Riessner Gase	Riessner Gase	10/08/2022
ISPRA	Press. Cyl.	10.06 ± 0.20	10.07±0.30	9.99±0.45	21.50 ± 0.90		10.90 ± 0.45	SIAD	SIAD	10/06/2022
SHI	Press. Cyl.	1.04 ± 0.03, 4.96 ± 0.10, 9.93 ± 0.3	1.06 ± 0.03, 4.79 ± 0.12, 9.65 ± 0.25	1.12 ± 0.03, 5.18 ± 0.13, 10.44 ± 0.27	2.17 ± 0.06, 10.08 ± 0.26, 20.3 ± 0.6		1.00 ± 0.03, 4.96 ± 0.13, 9.99 ± 0.25	NPL	NPL	04/05/2022, 24/02/2022, 25/03/2022
JRC	Press. Cyl.	4.00 ± 0.08	3.89 ± 0.10	4.21 ± 0.11	8.18 ± 0.21		4.02 ± 0.11	NPL	NPL	23/03/2022

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

Source: JRC, 2023

2.2 Reference values and uncertainties

Based on the experience from previous inter-laboratory comparison exercise, the robust average value calculated according to ISO 13528:2022 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.

Prior to the calculation of the robust average, the h and K statistics were applied to identify potential laboratory outliers to be excluded from the analysis. The number of outliers identified for each compound and laboratory (see Annex 7: **Figure A 19**) was not sufficient to justify the exclusion of any laboratory from the robust test. Therefore, outliers were smoothed using the robust averaging approach. The h and K statistics are shown in Annex 7.

In line with ISO 13528:2022, the standard uncertainty assigned to the robust value of the proficiency test, u_{pt}, was estimated as:

$$u_{pt} = \frac{1.25 \cdot s^*}{\sqrt{p}} \quad \text{Eq. 1}$$

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. In this comparison robust average and estimated uncertainty will be adopted as reference value, C_{ref}, and associated uncertainty, u_{ref}, respectively.

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

Table 4. Reference concentrations 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	0.89	9.45	3.16	9.29	0.37	31.28
2ND-A	2.58	4.31	8.57	5.39	1.57	20.32
3RD-A	5.05	3.60	16.54	4.58	3.20	15.06
4TH-A	10.00	2.86	32.83	5.36	6.59	10.33
5TH-A	15.05	2.40	49.87	7.25	9.66	7.99
6TH-A	20.12	2.05	64.98	7.03	13.21	5.13
5TH-B	15.31	2.00	50.87	6.43	10.12	7.05
4TH-B	10.37	2.23	34.83	4.75	6.90	10.23
3RD-B	5.32	3.41	18.23	4.62	3.37	14.45
2ND-B	2.65	4.72	9.70	6.23	1.64	19.73
1ST-B	0.94	7.76	3.96	10.45	0.45	23.89

Level	m,p-Xylene	uncertainty (1σ)	o-Xylene	uncertainty (1σ)
	Conc., µg/m³	%	Conc., µg/m³	%
1ST-A	0.39	25.28	0.56	27.40
2ND-A	1.53	23.00	1.94	24.21
3RD-A	3.34	20.94	3.71	19.45
4TH-A	6.89	15.84	7.17	11.42
5TH-A	10.12	13.38	10.38	9.57
6TH-A	14.03	10.79	14.11	6.61
5TH-B	10.76	11.78	10.89	7.82
4TH-B	7.30	14.88	7.46	11.26
3RD-B	3.60	19.41	3.85	17.94
2ND-B	1.73	22.44	2.10	19.86
1ST-B	0.45	22.56	0.59	27.67

Source: JRC, 2023

2.3 Statistical considerations

2.3.1 Reported concentration and uncertainty

Laboratories were requested to provide, for each stable concentration interval level, three measurements values, the average concentration, and its associated uncertainty. Those average values and associated uncertainties were used as input values for the statistical evaluation of this exercise.

A comprehensive evaluation of the laboratory results should consider the combination of different scores, which allow the interpretation of outliers as well as possible corrective actions.

2.3.2 Linearity test

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

$$R_C = \overline{\mathrm{C}} - (\mathrm{a} + \mathrm{b} \cdot \mathrm{C_{ref}}) \qquad \text{Eq. 2}$$

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

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 concentration value, $\overline{\mathrm{C}}$, of p participants and the standard deviation of the average inter-laboratory values:

$$h_i = \frac{C_i - \bar{C}}{\sqrt{\frac{\sum (C_i - \bar{C})^2}{p-1}}} \qquad \text{Eq. 3}$$

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

$$k_i = \frac{s_i}{\sqrt{\frac{\sum s_i^2}{p}}} \qquad \text{q. 4}$$

Indicators for Mandel's statistics at the 1 and 5 % level of significance are given in the Annex 2: Indicators of Mandel's statistics. These values determine the outliers and stragglers, respectively.

As a result, the uncertainty of the inter-laboratory average concentration value 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 2, 2019]:

$$u = \sqrt{s_L^2 + s_r^2} = s_R \qquad \text{Eq. 5}$$

being

$$s_r^2 = \frac{1}{p} \sum_i^p s_i^2 \qquad \text{Eq. 6}$$

$$s_R^2 = \frac{1}{p-1} \sum_i^p \left(\overline{C}_i - \overline{C}\right)^2 + \left(1 - \frac{1}{n}\right) \cdot s_r^2 \qquad \text{Eq. 7}$$

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.*

For method robustness, 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 the robustness of the method, being robust ratios those lower than 2 [P. Pérez Ballesta et al., 2001].

2.3.4 Repeatability scores

A repeatability score derived from the ratio between reported laboratory uncertainty and the standard deviation for the proficiency assessment , $\sigma_{N37,}$, is used as an indication of the suitability of the reported uncertainty with respect to that expected for the proficiency assessment.

$$r\ score = \frac{u_{lab}}{\sigma_{N37}} \quad \text{Eq. 8}$$

By applying the same indicator of Mandel's k statistic $k_{p,n,1-\alpha}$, it is possible to identify straggles and outliers at the 5 % and 1 % level of significance, respectively, being *n* the number of replicated measurements of each laboratory, and p, representing the number of laboratories, is adopting the convergent value for k.

In agreement with AQUILA N37 document, the standard deviation for the proficiency assessment, σ_{N37}, is calculated as a function of the concentration level in µg/m³, *C*, by the following equation:

$$\hat{\sigma}_{N37} = 0.128 + 0.057 \cdot C \quad \text{Eq. 9}$$

2.3.5 Z' scores

As the estimated uncertainty for the reference value, u_{ref}, appears significant if compared to the uncertainty defined for the proficiency assessment ($u_{ref} > \sigma_{N37}$), the statistic Z' score is used for the identification of outliers.

This statistic is calculated as follows:

$$Z'score = \frac{C_{lab} - C_{ref}}{\sqrt{\hat{\sigma}_{N37}^2 + u_{ref}^2}} \quad \text{Eq. 10}$$

This statistic provides a criterion for identification of outliers independent of the comparison exercise performance, being critical values of 2.0 or 3.0 used to identify "warning" or "action" signals, respectively.

2.3.6 E_n scores

E_n scores were calculated according to the following equation:

$$\mathrm{E}_n = \frac{C_{lab} - C_{ref}}{\sqrt{U_{lab}^2 + U_{ref}^2}} \quad \text{Eq. 11}$$

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.

2.3.7 P_A scores

P_A score is a standardized performance score that represents the percentage of allowed deviation for each result. This score is based on the ratio between biases and performance criteria for the measurand. The score considers both the standard deviation for the proficiency assessment, as defined by the AQUILA N37 document, and the uncertainty of the reference value. The following equation is used to calculate the P_A score:

$$P_A = \frac{C_{lab} - C_{ref}}{\sqrt{(3 \cdot \hat{\sigma}_{N37})^2 + u_{ref}^2}} \quad \text{Eq. 12}$$

This score provides a criterion of acceptance, which is equivalent to $z \leq 3$, for the interval $-1 \leq P_A \leq 1$. This score can also be expressed as percentage. In that case, scores with absolute values higher than 100 % are rejected.

3 Results and discussion

3.1 Data reporting

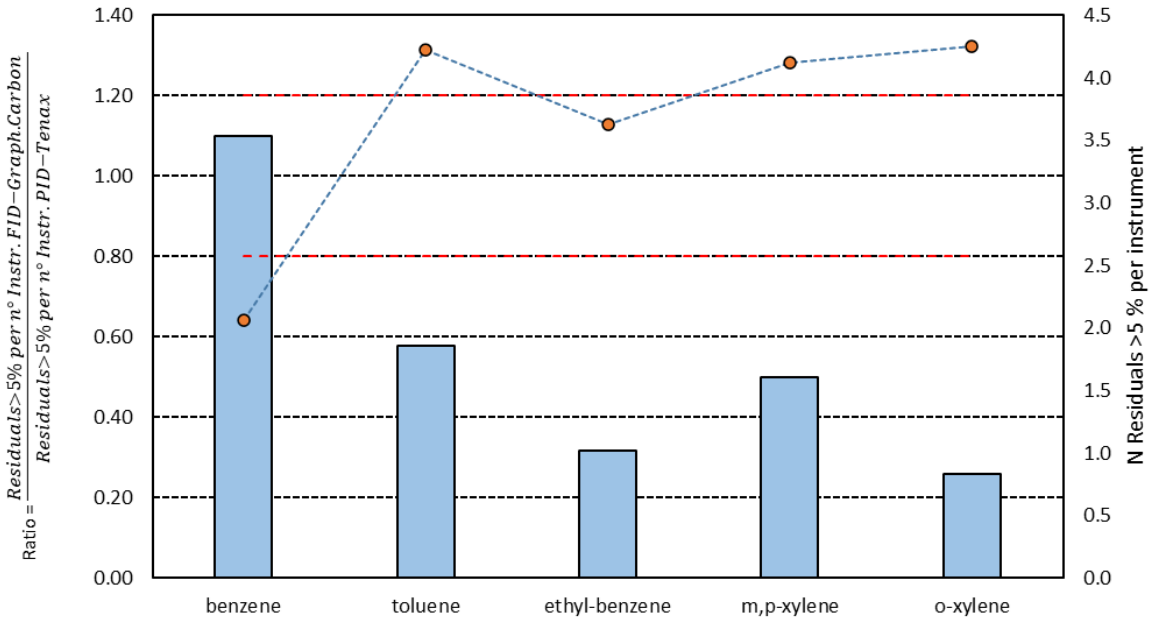
The laboratories were asked to provide three concentration values and the corresponding average and associated uncertainty for each compound and concentration level. They were instructed to exclude the first and last 15 minutes of each concentration step in order to avoid unstable concentrations. Additionally, they were required to provide details about the instrument used, the analytical method, the use of certified reference material for calibration, and the calculation of reported uncertainties. This information is summarized in section 2.1 and an example data collection sheet can be found in Annex 9.

DLI and SHI participated with two on-line automatic analysers, which were labelled as 1 or 2 in the report. CHMI2's data was based on pumped tubes. In this comparison exercise, EPA, EKONERG, CHMI2, and ISCIII only reported benzene, while CHMI and IPH-S reported both benzene and toluene. Only five of the invited participants (DLI, ERA, ISPRA, SHI, and UBA) reported all of the target compounds (BTEX), which resulted in a higher uncertainty associated with the reference value derived from the robust average of the comparison exercise

3.2 Linearity test

The analysis revealed that high residual values were frequently observed at the lowest concentration levels, particularly for the heaviest compounds: C_7-C_8 and for instruments using Tenax GR and PID detector (see **Figure 2**). Notably, instruments using Tenax GR were also equipped with PID detector, as instruments with a FID detector were using graphic charcoal adsorbent (Carbotrap, Carbopack-B or in combination with other adsorbents). **Table 5** to **Table 7** present the results of the linearity test conducted to determine the correlation between reported and the robust reference value. Residuals were calculated using Eq.2, and the percentage of residuals was shown for those with absolute values greater than 5 %. Absolute values with residuals greater than 10 % were highlighted in red.

Figure 2. Number of non-linear cases per adsorbent or detector



Source: JRC, 2023

Table 5. Linearity tests for benzene and toluene

BENZENE(1)	CHMI	CHMI2	DHZ-TES	DLI	DLI2	EKONERG	EPA	ERA	IPH-S	ISCIII	ISPRA	SHI	SHI2	UBA	ERLAP
1st -A	**-35**		OK	OK	9	**18**	**61**	**-29**	**17**	**-57**	**-18**	OK	5	**20**	**22**
2nd -A	**-11**		OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK	OK
3rd -A	OK	**-15**	OK	OK	OK	OK	-10	OK	OK	8	OK	OK	OK	OK	OK
4th -A	OK	OK	OK	OK	OK	OK	-7	OK	OK	OK	6	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
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
3rd -B	6		OK	OK	OK	OK	OK	5	-6	8	OK	OK	OK	-5	-6
2nd -B	OK	OK	OK	OK	OK	OK	OK	OK	8	OK	-7	OK	OK	OK	OK
1st -B	**-16**	**67**	OK	OK	**11**	**20**	**57**	**-18**	**12**	**-44**	**-22**	OK	6	9	5
TOLUENE(1)	CHMI	CHMI2	DHZ-TES	DLI	DLI2	EKONERG	EPA	ERA	IPH-S	ISCIII	ISPRA	SHI	SHI2	UBA	ERLAP
1st -A	**-45**			**29**	**30**			-9	**54**		**-17**	**-40**	**-57**	OK	**41**
2nd -A	-8			OK	OK			OK	**14**		OK	OK	-7	OK	11
3rd -A	-5			OK	OK			OK	OK		6	7	6	OK	OK
4th -A	OK			-5	OK			OK	OK		9	5	5	OK	OK
5th -A	OK			OK	OK			OK	OK		OK	OK	OK	8	OK
6th	OK			OK	OK			OK	OK		-6	OK	OK	OK	OK
5th -B	OK			OK	OK			OK	OK		OK	OK	OK	OK	OK
4th -B	5			OK	OK			OK	-7		OK	OK	6	OK	-6
3rd -B	8			OK	OK			OK	**-12**		OK	5	9	OK	-10
2nd -B	11			OK	OK			6	OK		**-10**	OK	OK	OK	-8
1st -B	**13**			**21**	**20**			OK	**26**		**-31**	**-35**	**-41**	**-14**	**16**

(1) Residual values in percentage

Source: JRC, 2023

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

ETHYLBENZENE (1)	CHMI	CHMI2	DHZ-TES	DLI	DLI2	EKONERG	EPA	ERA	IPH-S	ISCIII	ISPRA	SHI	SHI2	UBA	ERLAP
1st -A				**-60**	**-47**			**-110**			**-11**	**88**	**126**	**59**	**31**
2nd -A				OK	OK			OK			8	OK	-6	OK	6
3rd -A				7	6			OK			OK	-8	**-13**	OK	OK
4th -A				OK	OK			OK			OK	-5	-7	OK	OK
5th -A				OK	OK			OK			OK	OK	OK	**-11**	OK
6th				OK	OK			OK			OK	OK	OK	OK	OK
5th -B				OK	OK			OK			OK	OK	OK	OK	OK
4th -B				OK	OK			7			OK	-6	-5	OK	OK
3rd -B				**10**	8			5			OK	-8	-8	OK	-7
2nd -B				OK	OK			**9**			OK	OK	OK	OK	-9
1st -B				**-53**	**-32**			**-69**			**-12**	**95**	**114**	**42**	OK
M,P-XYLENE (1)	CHMI	CHMI2	DHZ-TES	DLI	DLI2	EKONERG	EPA	ERA	IPH-S	ISCIII	ISPRA	SHI	SHI2	UBA	ERLAP
1st -A				**-76**	**-33**			**-85**			**-26**	**112**	**138**	**39**	**23**
2nd -A				-8	-9			OK			9	6	OK	OK	**11**
3rd -A				OK	OK			8			5	-8	**-14**	-8	OK
4th -A				OK	OK			OK			OK	-6	-10	OK	OK
5th -A				OK	OK			OK			6	OK	OK	**-12**	5
6th				OK	OK			OK			OK	OK	OK	OK	OK
5th -B				OK	OK			OK			OK	OK	OK	OK	OK
4th -B				5	OK			OK			OK	-6	-6	OK	-7
3rd -B				7	OK			**14**			OK	-10	-9	OK	**-11**
2nd -B				-5	-6			6			OK	OK	OK	**14**	OK
1st -B				**-51**	**-21**			**-53**			**-33**	**88**	**123**	**25**	**25**

(1) Residual values in percentage

Source: JRC, 2023

Table 7. Linearity tests for o-xylene

O-XYLENE (1)	CHMI	CHMI2	DHZ-TES	DLI	DLI2	EKONERG	EPA	ERA	IPH-S	ISCIII	ISPRA	SHI	SHI2	UBA	ERLAP
1st -A				**-41**	**-53**			**-49**			OK	**97**	**107**	**71**	**16**
2nd -A				OK	**17**			OK			OK	OK	-6	OK	OK
3rd -A				5	**19**			-5			OK	**-11**	**-15**	-8	OK
4th -A				OK	OK			5			OK	OK	-7	OK	OK
5th -A				OK	OK			OK			6	OK	OK	**-13**	OK
6th				OK	OK			OK			OK	OK	OK	OK	OK
5th -B				OK	OK			OK			OK	OK	OK	OK	OK
4th -B				OK	OK			8			OK	OK	OK	OK	OK
3rd -B				10	9			OK			OK	**-10**	-9	-6	-6
2nd -B				-6	-6			OK			**-10**	-7	-6	-8	**-11**
1st -B				**-27**	**-97**			**-17**			6	**89**	**109**	**63**	**17**

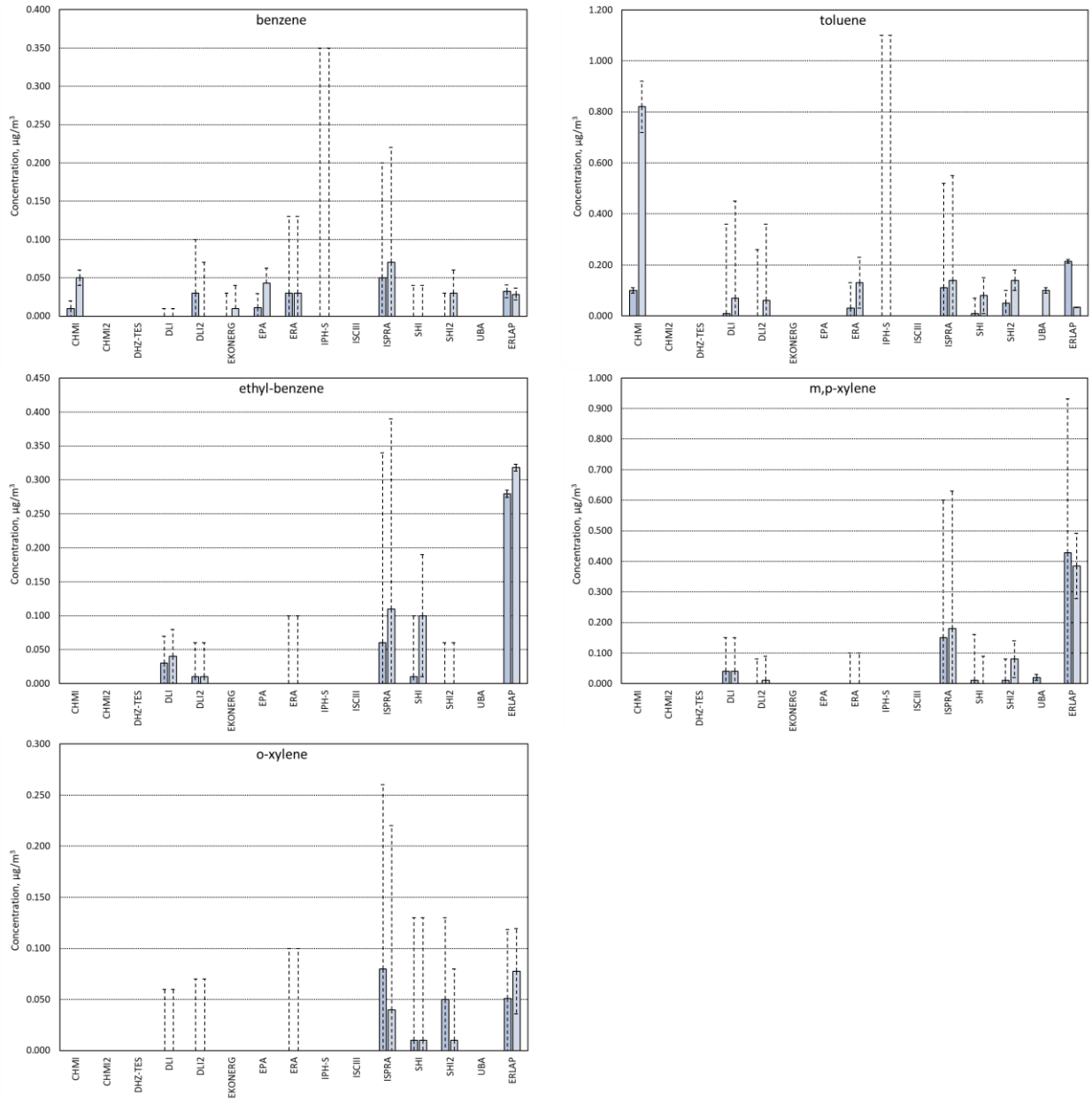
(1) Residual values in percentage

Source: JRC, 2023

3.3 Blank levels

Figure 3 depicts 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 1.7 % to 19.3 % of the reference concentrations at the first concentration level. These blank values were found to be at the same level of uncertainty associated with the first concentration level.

Figure 3. Reported blank levels

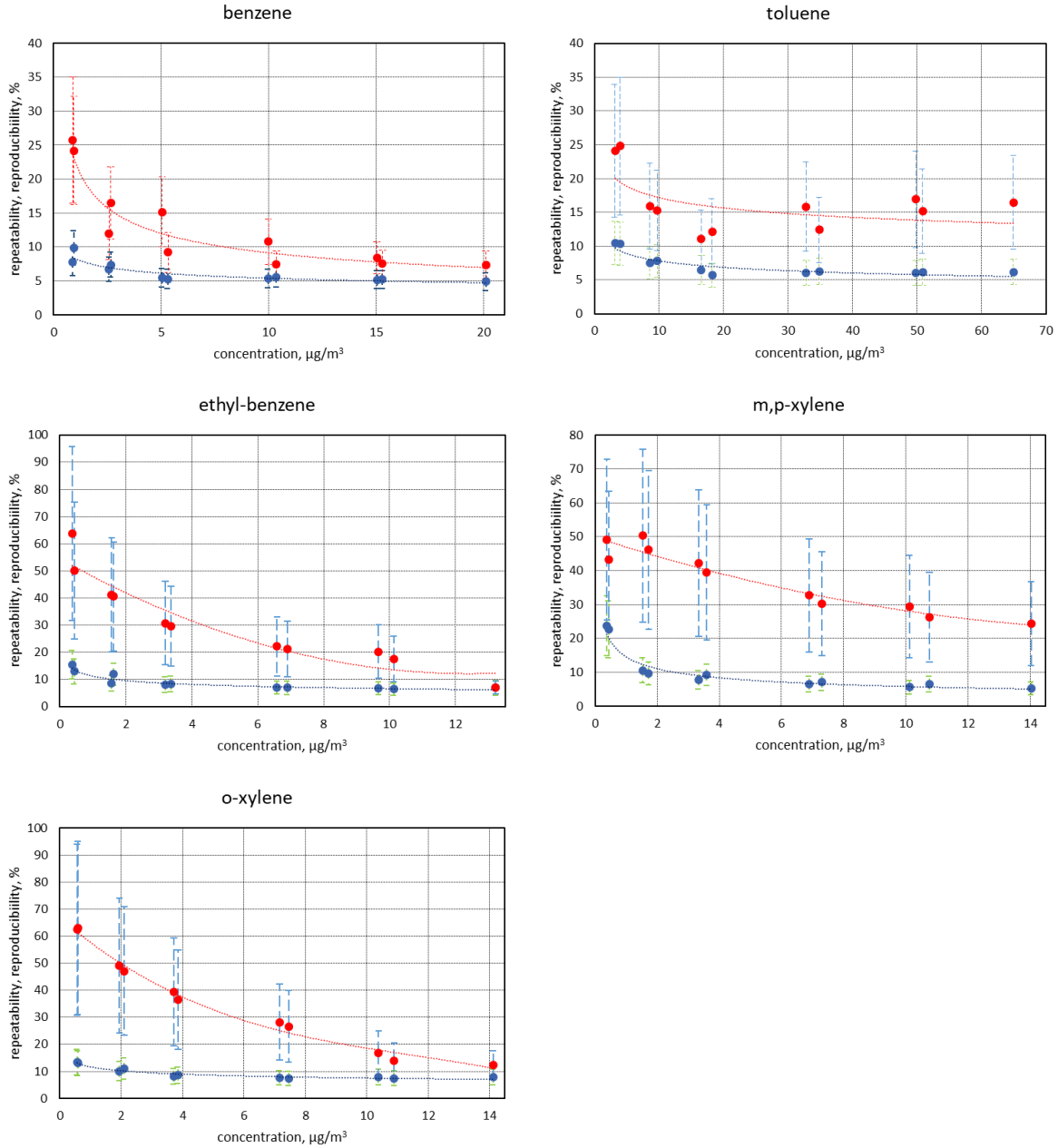


Source: JRC, 2023

3.4 Outliers, repeatability, reproducibility and robustness of the method

As outlined in the previous section 2.3.3, repeatability and reproducibility standard deviation were calculated based on the converged results obtained after eliminating outliers using the k and h statistics (see Annex 7). The repeatability, reproducibility standard deviation values are presented in **Figure 4**, while **Figure 5** illustrates the corresponding robustness values for each compound and concentration level. Notably, the repeatability values represent the average of the uncertainties reported by the participating laboratories at each level, whereas the reproducibility values are associated with the method's uncertainty in this exercise. The figures reveal that the values of repeatability and reproducibility tend to increase with decreasing concentration levels. Additionally, the gamma values also exhibit a similar trend (**Figure 5**), although to a lesser extent.

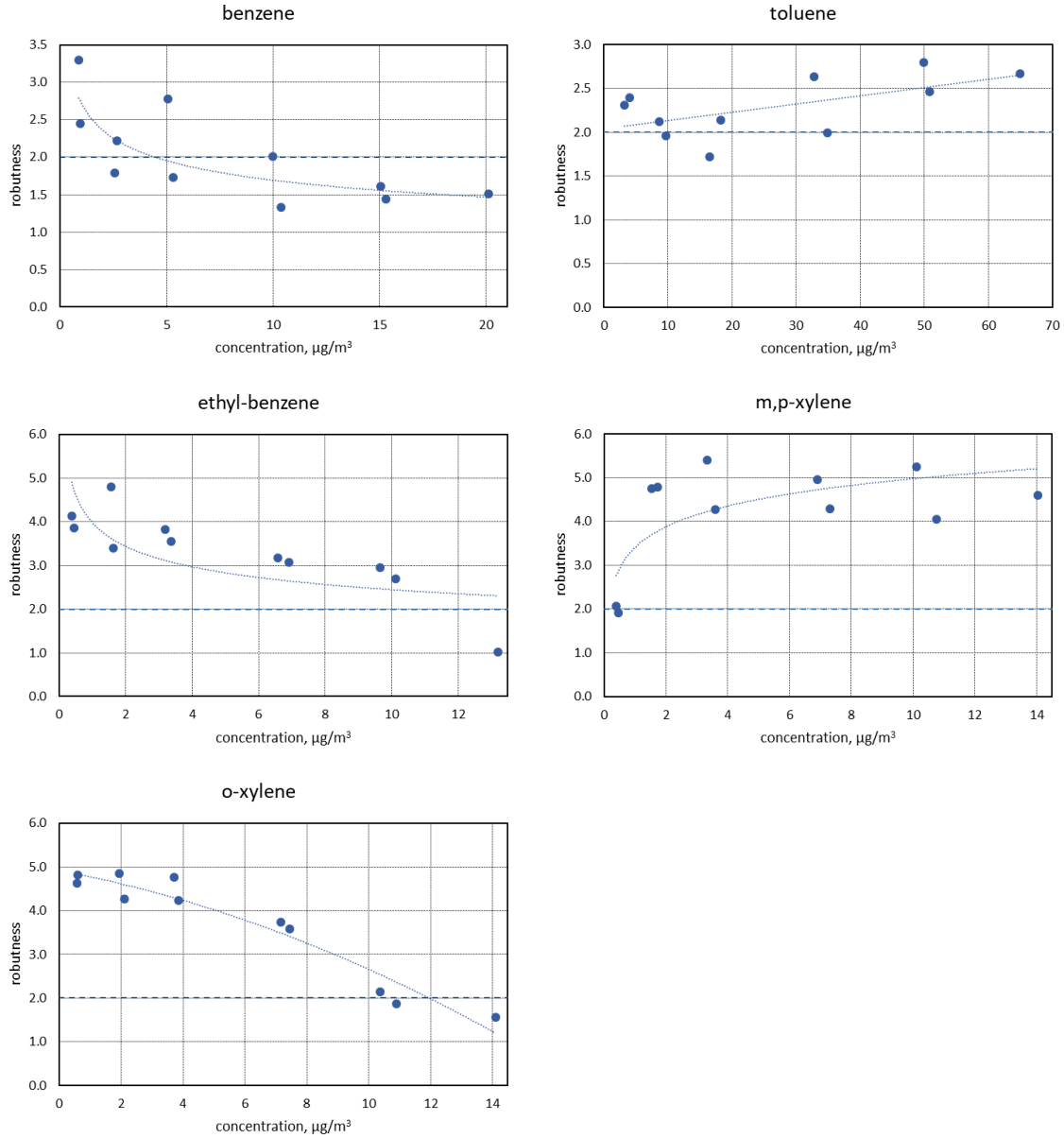
Figure 4. Repeatability and reproducibility of the inter-laboratory exercise



--•-- Repeatability, --•-- Reproducibility, |------| 2 stdev

Source: JRC, 2023

Figure 5. Robustness of the inter-laboratory exercise



Source: JRC, 2023

In comparison to the previous inter-laboratory exercise (EUR 30239 EN), an increase in the reproducibility values was observed. This was also reflected in the robustness values, which significantly exceeded the recommended value of 2, as shown in **Table 8**.

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

	Repeatability, %([1,2])	Reproducibility, %([1,2])	Robustness (γ)([1,2])
Benzene	6.25	13.11	2.02
Toluene	7.15	16.60	2.32
Ethyl-benzene	9.17	31.79	3.33
m,p-Xylene	10.39	37.76	4.15
o-Xylene	9.45	36.61	3.69

([1]) Outliers excluded in the analysis
([2]) Repeatability, reproducibility and robustness values of previous inter-laboratory exercises are provided in Annex 4: Tables A 2 to A 5

Source: JRC, 2023

3.5 N37 and minimum standard deviation compatible with the reproducibility of the proficiency assessment

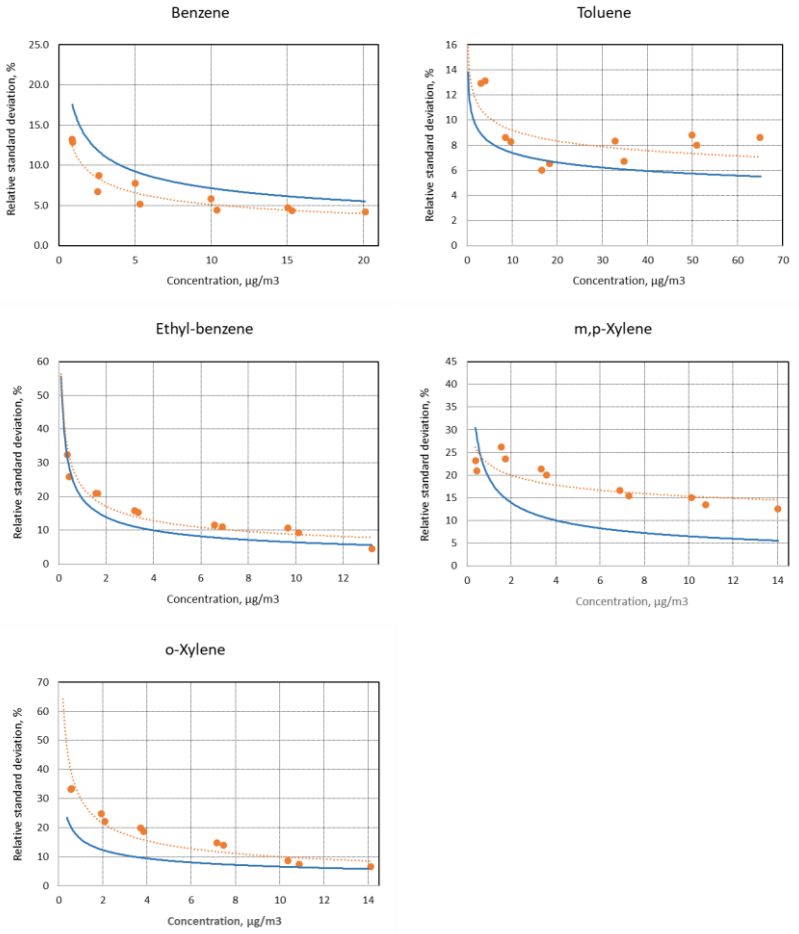
To make a realistic choice of a prescriptive standard deviation for proficiency assessment, i.e. $\hat{\sigma}_{N37}$, it is important to ensure that the ratio between the between-laboratory standard deviation of the comparison, s_L, and the one derived from the assigned value, is less than 2. This ratio determines the definition of a minimum standard deviation, $\hat{\sigma}_m$, that is compatible with the method reproducibility, as shown in the following equation:

$$\hat{\sigma}_m = \sqrt{\left(\frac{s_L}{2}\right)^2 + \frac{s_r^2}{n}} \qquad \text{Eq. 13}$$

where n is represented the number of replicated measurements.

Figure 6 shows the minimum relative standard deviation, $\frac{\hat{\sigma}_m}{C_{ref}} \cdot 100$, which is compatible with the reproducibility of the exercise, as well as the relative standard deviation, , $\frac{\hat{\sigma}_{N37}}{C_{ref}} \cdot 100$, for proficiency assessment. Therefore, the N37 criteria will align with the reproducibility of the exercise if $\hat{\sigma}_{N37} \leq \hat{\sigma}_{N37}$. As seen in **Figure 6**, this condition is met for benzene and partially for the other compounds. This indicates that N37 is a more stringent approach to identify outliers than the use of the minimum relative standard deviation. However, the use of N37 is justified because it establishes a uniform criterion for evaluation across inter-laboratory exercises.

Figure 6. N37 and minimum standard deviation compatible with the reproducibility of the proficiency assessment



Relative standard deviation from AQUILA N37 proposal, $\frac{\hat{\sigma}_{N37}}{C_{ref}} . 100$

Minimum relative standard deviation compatible with the reproducibility of the exercise, $\frac{\hat{\sigma}_m}{C_{ref}} . 100$

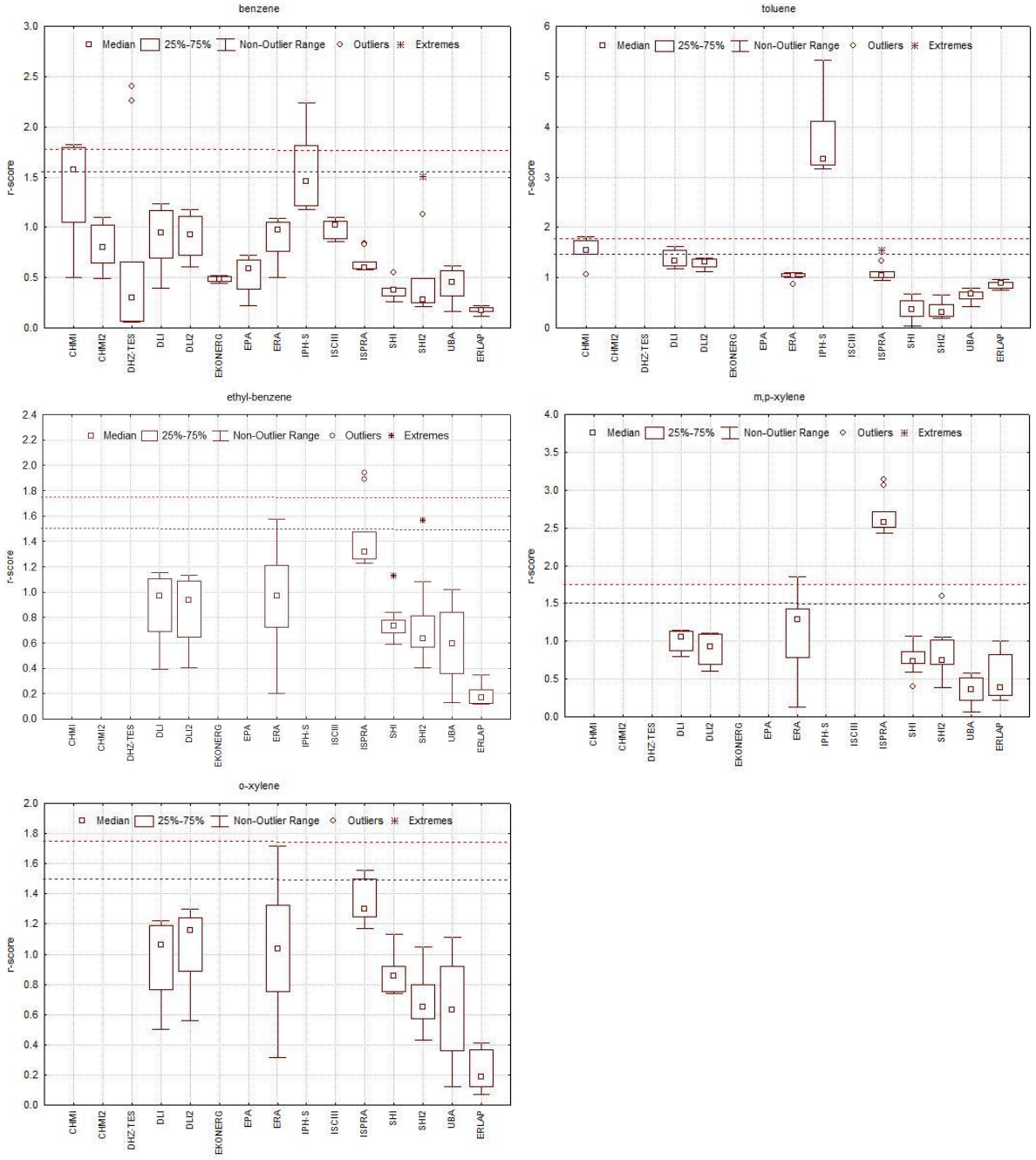
Source: JRC, 2023

3.6 r score, Z' score, P_A and E_n score

The laboratory test performance was evaluated individually using the r score (repeatability score), Z' score, and E_n score, all of which were derived from the N37 standard deviation for proficiency test, σN37.

For a quick overview of the results, a multi-plot-box representing the afore-mention statistics for concentration level and compounds are illustrated in **Figure 7**, **Figure 8** and **Figure 9**. Instead, level detailed graphs are given in Annex 8.

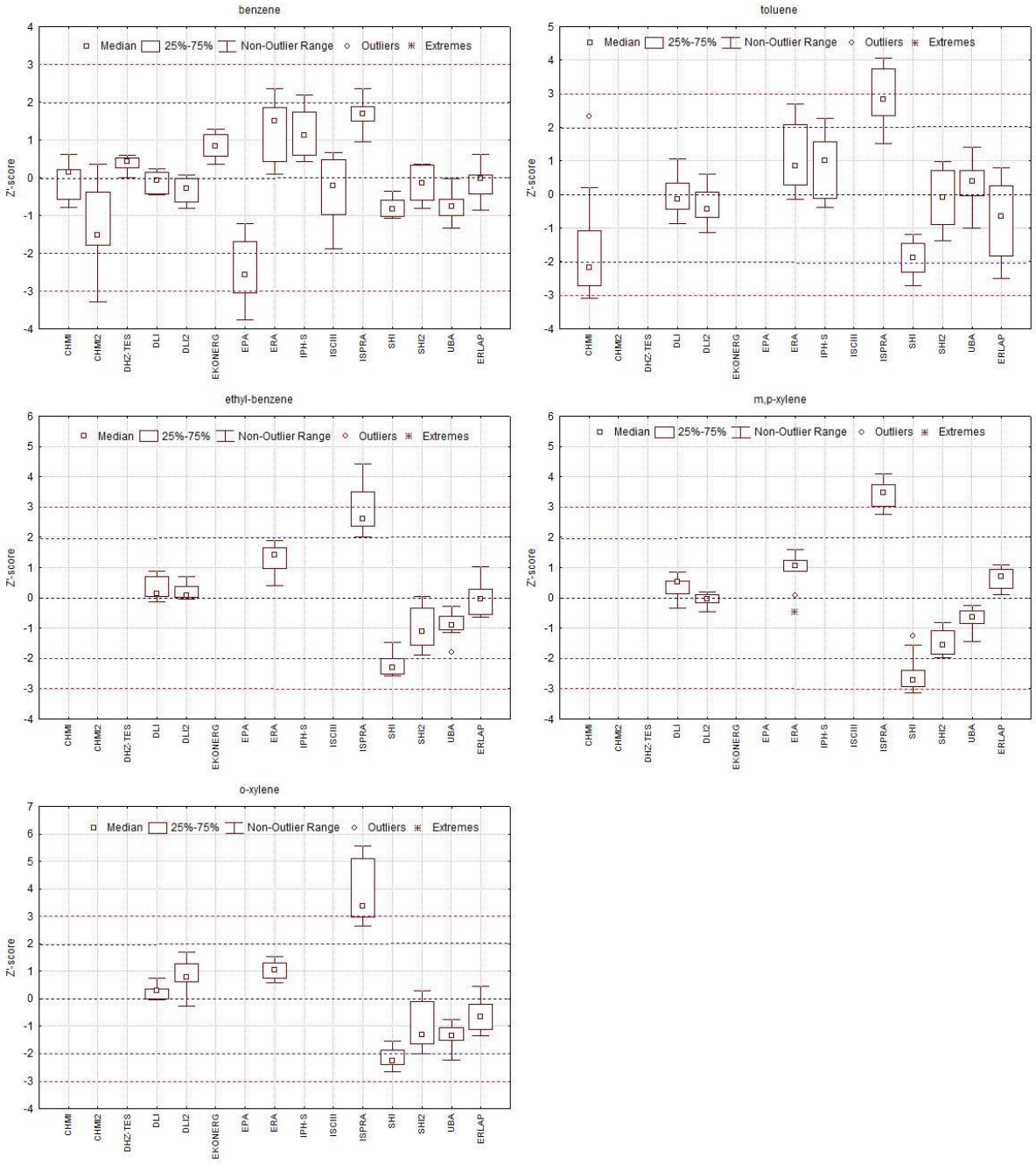
Figure 7. r score for the inter-laboratory comparison exercise



-------- action signal ------- warning signal

Source: JRC, 2023

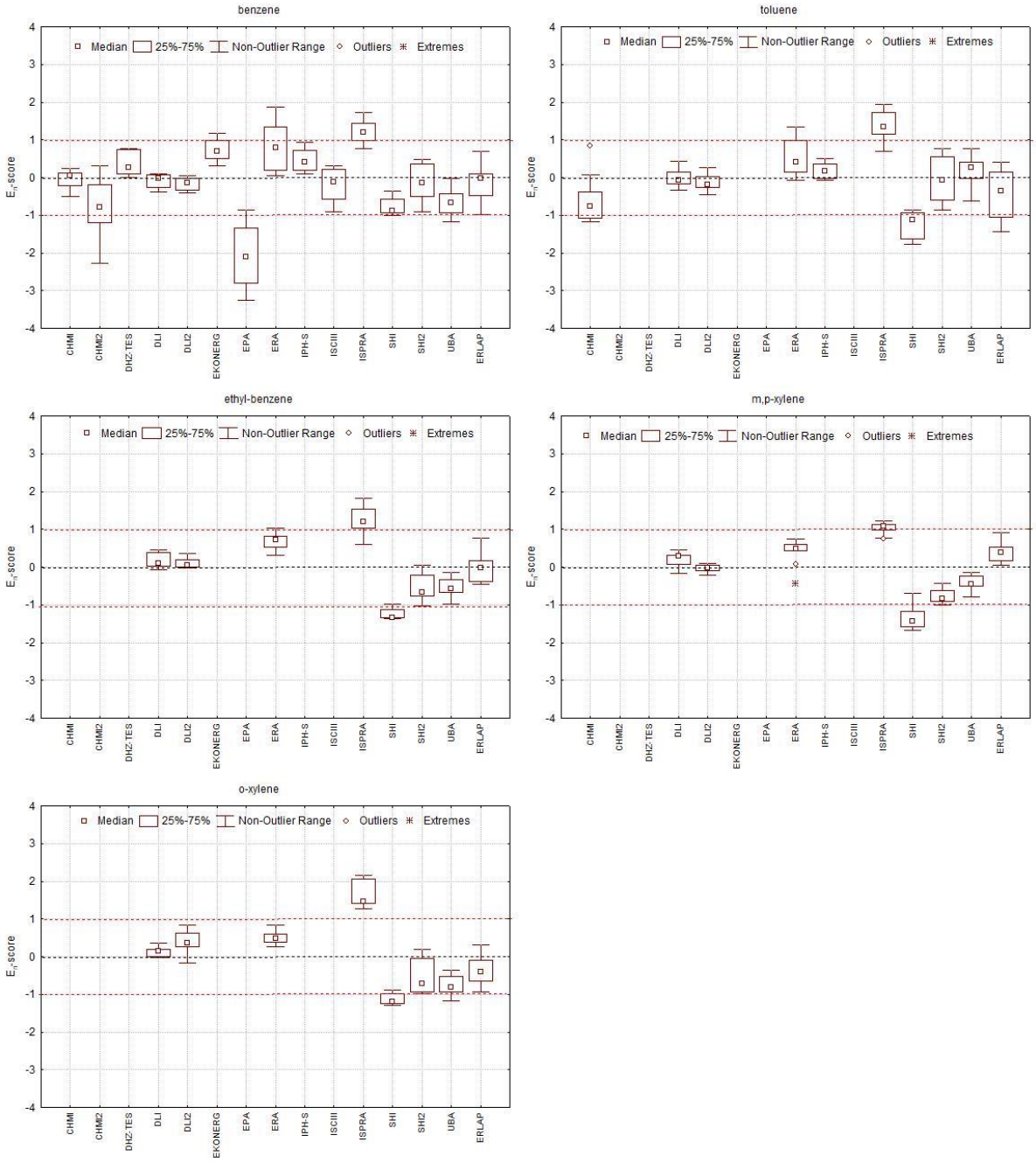
Figure 8. Z' scores for the inter-laboratory comparison exercise



-------- action signal ------- warning signal

Source: JRC, 2023

Figure 9. E_n score for the inter-laboratory comparison exercise



-------- action signal

Source: JRC, 2023

Tabulated results of the inter-laboratory comparison are presented in **Table 9** to **Table 13**. For each laboratory and concentration level, these tables provide reported concentrations with expanded uncertainties, biases, P_A, r scores, Z' scores, and E_n scores. P_A and E_n scores with absolute values equal to or greater than 1 are highlighted in red to indicate an action signal. Absolute values of Z' scores between 2 and 3 are considered warning signals, while those greater than 3 are action signals, being highlighted in blue and red, respectively. Notably, the P_A action should agree or be very close to Z' scores with absolute values greater than 3. Finally, acceptance values of r scores are highlighted in blue and red for the 95% and 99% confidence levels.

Furthermore, it is important to interpret E_n scores and r scores together, as a high reported uncertainty can compensate for a high bias input in the E_n score. On the other hand, P_A and Z' scores are not influenced by the uncertainty reported by the laboratory, as they adopt the prescriptive standard deviation for proficiency assessment, σ_{N37}, as a fixed parameter in the score. These two parameters can be used to identify actions where E_n score or Z' score are not sensitive.

Biases are given in percentage and are directly comparable with the uncertainty of the performance test and the reference through the P_A score. The results of the laboratory comparison are presented in terms of deviation (%) in Annex 6: Scattering of Laboratory Results, **Figure A 11**.

Therefore, under these criteria, the tables below provide a clear overview of the instrument performance of each participant. The interpretation and actions to be taken based on the results are the responsibility of each laboratory and are outside the scope of this report.

Table 9. r-scores, Z'-scores, E_n scores, PA, bias and reported expanded uncertainty of the participants: benzene

Compound	CHMI							CHMI2							DHZ-TES						
benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.77	23.4	-13.8	-0.22	-0.50	-0.62	0.50								0.98	87.8	9.7	0.15	0.10	0.44	**2.40**
2nd-A	2.41	24.1	-6.6	-0.20	-0.27	-0.57	1.05								2.69	13.4	4.2	0.13	0.26	0.37	0.65
3rd-A	5.13	24.6	1.7	0.06	0.06	0.19	1.52	3.56	15.2	**-29.4**	**-1.14**	**-2.28**	**-3.28**	0.65	5.32	4.9	5.4	0.21	0.61	0.60	0.31
4th-A	10.10	24.4	1.0	0.05	0.04	0.14	**1.76**	8.67	15.0	-13.3	-0.61	-0.93	-1.76	0.93	10.44	1.9	4.4	0.20	0.73	0.59	0.14
5th-A	14.50	24.4	-3.6	-0.18	-0.15	-0.52	**1.80**	13.69	14.8	-9.0	-0.45	-0.63	-1.29	1.02	15.59	0.9	3.6	0.18	0.74	0.52	0.07
6th-A	19.06	24.4	-5.3	-0.27	-0.22	-0.79	**1.83**								20.76	0.7	3.2	0.16	0.77	0.48	0.05
5th-B	14.87	24.3	-2.9	-0.14	-0.12	-0.42	**1.81**	14.90	14.8	-2.7	-0.13	-0.18	-0.39	1.10	15.59	0.9	1.8	0.09	0.45	0.27	0.07
4th-B	10.53	24.5	1.5	0.07	0.06	0.21	**1.79**								10.45	1.9	0.7	0.03	0.15	0.10	0.14
3rd-B	5.61	24.2	5.4	0.21	0.21	0.62	**1.58**								5.32	4.9	0.0	0.00	0.00	0.00	0.30
2nd-B	2.82	24.1	6.3	0.19	0.23	0.54	1.22	2.11	18.0	-20.5	-0.62	**-1.19**	-1.78	0.68	2.74	13.1	3.3	0.10	0.20	0.28	0.64
1st-B	0.97	24.7	3.4	0.06	0.11	0.16	0.66	1.01	17.8	7.7	0.13	0.31	0.37	0.50	1.02	80.4	8.8	0.15	0.10	0.42	**2.26**
Compound	DLI							DLI2							EKONERG						
benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.81	17.3	-9.3	-0.15	-0.38	-0.42	0.39	0.89	24.7	-0.4	-0.01	-0.01	-0.02	0.61	1.12	14.3	25.4	0.40	0.97	1.15	0.45
2nd-A	2.45	15.5	-5.1	-0.15	-0.30	-0.44	0.69	2.43	16.5	-5.8	-0.18	-0.33	-0.51	0.73	2.80	9.3	8.5	0.26	0.64	0.74	0.47
3rd-A	4.92	15.0	-2.5	-0.10	-0.15	-0.28	0.89	4.72	15.7	-6.5	-0.25	-0.40	-0.72	0.89	5.35	7.5	6.0	0.23	0.56	0.67	0.48
4th-A	9.66	15.3	-3.4	-0.15	-0.21	-0.45	1.06	9.38	15.4	-6.2	-0.28	-0.40	-0.82	1.03	10.62	6.6	6.2	0.29	0.69	0.83	0.50
5th-A	14.97	15.4	-0.5	-0.03	-0.03	-0.07	1.17	14.37	15.2	-4.5	-0.22	-0.29	-0.64	1.11	16.21	6.3	7.7	0.38	0.93	1.11	0.52
6th-A	20.33	15.4	1.1	0.05	0.07	0.16	1.23	19.77	15.2	-1.7	-0.09	-0.11	-0.26	1.18	21.68	6.2	7.8	0.40	0.99	1.17	0.53
5th-B	15.55	15.3	1.6	0.08	0.10	0.23	1.19	15.06	15.1	-1.6	-0.08	-0.10	-0.24	1.14	16.23	6.3	6.0	0.30	0.78	0.88	0.51
4th-B	10.43	15.3	0.5	0.03	0.03	0.08	1.11	10.16	15.2	-2.1	-0.10	-0.13	-0.28	1.07	10.80	6.7	4.1	0.19	0.50	0.57	0.50
3rd-B	5.36	15.3	0.7	0.03	0.04	0.08	0.95	5.11	15.7	-4.0	-0.16	-0.24	-0.45	0.93	5.49	7.7	3.2	0.13	0.30	0.36	0.49
2nd-B	2.70	14.8	1.8	0.05	0.10	0.15	0.72	2.65	16.6	-0.1	0.00	-0.01	-0.01	0.79	2.78	9.4	4.8	0.14	0.35	0.41	0.47
1st-B	0.88	18.2	-6.2	-0.10	-0.27	-0.30	0.44	0.95	23.2	1.3	0.02	0.05	0.06	0.61	1.19	13.4	26.9	0.45	**1.17**	1.29	0.44
Compound	EPA							ERA							IPH-S						
benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.57	14.0	-35.7	-0.57	**-1.71**	-1.61	0.22	1.26	14.3	41.0	0.65	**1.49**	1.85	0.50	1.01	79.2	13.0	0.21	0.14	0.59	**2.24**
2nd-A	1.56	**14.2**	-39.5	**-1.19**	**-3.25**	**-3.44**	0.40	3.10	13.5	20.1	0.61	**1.09**	1.75	0.76	2.90	34.5	12.4	0.37	0.31	1.08	**1.82**
3rd-A	3.34	**14.7**	-33.9	**-1.32**	**-2.80**	**-3.77**	0.59	5.73	13.6	13.6	0.53	0.80	1.51	0.94	5.43	22.8	7.6	0.30	0.30	0.85	1.49
4th-A	7.69	**10.8**	-23.1	**-1.06**	**-2.28**	**-3.06**	0.60	10.46	13.8	4.6	0.21	0.30	0.62	1.03	11.22	16.2	12.2	0.56	0.64	1.62	1.30
5th-A	12.89	11.1	-14.3	-0.71	**-1.35**	**-2.05**	0.73	15.14	13.7	0.6	0.03	0.04	0.09	1.06	16.91	14.2	12.4	0.61	0.74	1.77	1.22
6th-A	18.48	9.4	-8.1	-0.42	-0.85	-1.22	0.68	20.34	13.7	1.1	0.06	0.08	0.17	1.09	23.04	13.0	14.5	0.75	0.94	**2.18**	1.18
5th-B	13.50	10.4	-11.8	-0.59	**-1.18**	-1.73	0.70	15.76	13.7	3.0	0.15	0.20	0.43	1.08	17.12	14.1	11.8	0.59	0.73	1.73	1.21
4th-B	8.44	9.4	-18.6	-0.88	**-2.10**	**-2.56**	0.55	11.09	13.7	6.9	0.32	0.45	0.95	1.06	11.22	16.2	8.2	0.38	0.45	1.12	1.27
3rd-B	3.93	**13.0**	-26.1	**-1.03**	**-2.21**	**-2.97**	0.59	6.16	13.6	15.8	0.62	0.92	1.79	0.97	5.58	22.6	4.9	0.19	0.20	0.55	1.46
2nd-B	1.74	**11.1**	-34.3	**-1.04**	**-2.87**	**-2.97**	0.35	3.36	13.7	26.6	0.81	**1.35**	**2.31**	0.82	3.08	32.5	16.1	0.49	0.41	1.39	**1.79**
1st-B	0.61	23.3	-35.3	-0.59	**-1.63**	-1.69	0.39	1.40	14.3	49.3	0.82	**1.87**	**2.36**	0.55	1.02	78.4	8.8	0.15	0.10	0.42	**2.20**
Compound	ISCIII							ISPRA							SHI						
benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.52	73.1	-41.8	-0.66	-0.90	-1.89	1.06	1.23	24.4	37.7	0.60	0.98	1.70	0.84	0.73	16.4	-18.3	-0.29	-0.79	-0.83	0.34
2nd-A	2.54	22.8	-1.6	-0.05	-0.07	-0.14	1.05	3.14	11.5	21.7	0.65	**1.32**	1.89	0.65	2.33	7.7	-9.7	-0.29	-0.88	-0.84	0.33
3rd-A	5.34	16.1	5.8	0.23	0.32	0.65	1.03	6.04	8.3	19.7	0.77	**1.61**	**2.19**	0.60	4.78	6.7	-5.3	-0.20	-0.55	-0.59	0.38
4th-A	10.01	13.2	0.1	0.01	0.01	0.02	0.95	11.78	7.3	17.8	0.82	**1.73**	**2.37**	0.62	9.72	5.3	-2.8	-0.13	-0.36	-0.37	0.37
5th-A	14.38	12.2	-4.4	-0.22	-0.35	-0.63	0.89	16.86	7.0	12.1	0.60	**1.31**	1.73	0.60	14.51	4.3	-3.6	-0.18	-0.56	-0.51	0.31
6th-A	18.80	11.6	-6.6	-0.34	-0.57	-0.98	0.86	21.40	6.9	6.4	0.33	0.76	0.96	0.58	19.10	3.5	-5.1	-0.26	-0.96	-0.76	0.26
5th-B	14.54	12.1	-5.0	-0.25	-0.41	-0.73	0.88	16.89	7.0	10.3	0.52	**1.19**	1.51	0.59	14.55	4.1	-4.9	-0.25	-0.88	-0.72	0.30
4th-B	10.21	13.1	-1.6	-0.07	-0.11	-0.22	0.93	11.79	7.3	13.7	0.64	**1.45**	1.88	0.60	9.75	5.5	-6.0	-0.28	-0.88	-0.82	0.38
3rd-B	5.63	15.6	5.8	0.23	0.32	0.66	1.02	6.05	8.3	13.7	0.54	**1.18**	1.56	0.58	4.82	7.1	-9.4	-0.37	**-1.01**	-1.07	0.39
2nd-B	2.80	21.4	5.5	0.17	0.23	0.48	1.07	3.08	11.7	16.1	0.49	0.97	1.39	0.64	2.34	9.4	-11.8	-0.36	-0.94	-1.02	0.39
1st-B	0.66	60.6	-29.6	-0.49	-0.65	-1.42	1.10	1.23	24.4	31.2	0.52	0.88	1.49	0.83	0.73	27.4	-22.2	-0.37	-0.84	-1.06	0.55
Compound	SHI2							UBA							ERLAP						
benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.76	13.2	-14.9	-0.24	-0.68	-0.67	0.28	0.84	7.1	-6.0	-0.09	-0.30	-0.27	0.17	1.01	4.5	13.5	0.21	0.69	0.61	0.13
2nd-A	2.34	6.0	-9.3	-0.28	-0.91	-0.81	0.25	2.39	7.5	-7.4	-0.22	-0.67	-0.64	0.33	2.61	3.4	1.3	0.04	0.14	0.11	0.16
3rd-A	4.94	5.7	-2.1	-0.08	-0.23	-0.23	0.34	4.69	8.1	-7.1	-0.27	-0.68	-0.78	0.46	5.07	2.8	0.5	0.02	0.06	0.05	0.17
4th-A	10.24	3.7	2.4	0.11	0.36	0.32	0.27	9.44	7.8	-5.6	-0.26	-0.59	-0.74	0.53	9.99	2.6	-0.1	0.00	-0.02	-0.01	0.19
5th-A	15.40	3.2	2.3	0.12	0.40	0.34	0.25	15.03	8.1	-0.1	-0.01	-0.01	-0.02	0.62	15.08	2.6	0.2	0.01	0.04	0.03	0.20
6th-A	20.38	2.6	1.3	0.07	0.27	0.20	0.21	19.37	8.0	-3.7	-0.19	-0.43	-0.56	0.60	20.21	2.8	0.5	0.02	0.10	0.07	0.22
5th-B	15.69	3.2	2.5	0.12	0.48	0.37	0.25	14.51	7.9	-5.2	-0.26	-0.62	-0.76	0.57	15.01	2.7	-2.0	-0.10	-0.41	-0.29	0.21
4th-B	10.29	15.7	-0.8	-0.04	-0.05	-0.11	1.13	9.62	7.9	-7.3	-0.34	-0.85	-1.00	0.53	9.93	2.6	-4.3	-0.20	-0.85	-0.59	0.18
3rd-B	5.26	5.7	-1.2	-0.05	-0.13	-0.13	0.35	4.70	8.1	-11.7	-0.46	**-1.18**	-1.33	0.44	4.93	3.3	-7.4	-0.29	-0.99	-0.84	0.19
2nd-B	2.53	33.2	-4.7	-0.14	-0.14	-0.40	1.50	2.34	7.7	-11.8	-0.36	**-1.02**	-1.02	0.32	2.52	3.6	-4.9	-0.15	-0.48	-0.42	0.16
1st-B	0.82	22.0	-12.6	-0.21	-0.51	-0.60	0.50	0.79	7.6	-15.8	-0.26	-0.94	-0.76	0.17	0.91	4.6	-2.5	-0.04	-0.16	-0.12	0.12

([1])|PA| and |E_n scores| ≥ 1 are highlighted in red. |Z' score| between 2 and 3 in blue, being red those values higher than 3. r scores ≥ 95 % and 99 % confident level interval are highlighted in blue and red, respectively

Source: JRC, 2023

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

Compound	CHMI							CHMI2							DHZ-TES						
toluene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	2.70	24.4	-14.4	-0.42	-0.52	-1.07	1.07														
2nd-A	7.34	24.5	-14.4	-0.60	-0.61	-1.60	1.46														
3rd-A	12.99	24.3	-21.5	-1.00	**-1.01**	**-2.71**	1.48														
4th-A	24.60	24.4	-25.1	**-1.18**	**-1.18**	**-3.09**	**1.50**														
5th-A	36.46	24.4	-26.9	**-1.17**	**-1.17**	**-2.87**	1.50														
6th-A	48.83	24.4	-24.9	**-1.10**	**-1.08**	**-2.71**	**1.56**														
5th-B	39.37	24.4	-22.6	**-1.03**	-0.99	**-2.58**	**1.59**														
4th-B	28.96	24.4	-16.9	-0.82	-0.75	**-2.19**	**1.67**														
3rd-B	16.55	24.4	-9.2	-0.43	-0.38	-1.16	**1.73**														
2nd-B	9.90	24.4	2.0	0.08	0.07	0.22	**1.78**														
1st-B	5.23	24.5	31.9	0.94	0.83	**2.32**	**1.81**														
Compound	DLI							DLI2							EKONERG						
toluene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	2.97	33.7	-5.9	-0.17	-0.16	-0.44	**1.62**	2.98	28.9	-5.6	-0.16	-0.17	-0.41	1.40							
2nd-A	7.91	23.0	-7.7	-0.32	-0.33	-0.86	1.48	7.70	21.3	-10.2	-0.42	-0.46	-1.13	1.33							
3rd-A	15.95	15.9	-3.6	-0.17	-0.20	-0.45	1.19	15.23	15.8	-7.9	-0.37	-0.46	-1.00	1.12							
4th-A	32.46	15.3	-1.1	-0.05	-0.06	-0.14	1.24	31.59	15.3	-3.8	-0.18	-0.21	-0.46	1.21							
5th-A	51.01	15.2	2.3	0.10	0.11	0.24	1.30	49.42	15.3	-0.9	-0.04	-0.04	-0.10	1.27							
6th-A	71.27	15.3	9.7	0.43	0.44	1.05	1.42	68.54	15.3	5.5	0.24	0.26	0.60	1.37							
5th-B	53.46	15.2	5.1	0.23	0.25	0.58	1.34	52.23	15.3	2.7	0.12	0.13	0.31	1.32							
4th-B	35.76	15.2	2.7	0.13	0.15	0.35	1.29	35.02	15.3	0.5	0.03	0.03	0.07	1.27							
3rd-B	18.36	15.7	0.7	0.03	0.04	0.09	1.23	17.61	15.6	-3.4	-0.16	-0.19	-0.43	1.17							
2nd-B	9.29	22.6	-4.3	-0.17	-0.17	-0.45	**1.54**	9.09	20.9	-6.3	-0.26	-0.27	-0.67	1.39							
1st-B	3.75	29.9	-5.4	-0.16	-0.15	-0.39	**1.58**	3.70	25.9	-6.7	-0.20	-0.21	-0.48	1.36							
Compound	EPA							ERA							IPH-S						
toluene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								4.21	12.8	33.4	0.96	**1.32**	**2.48**	0.88	3.59	91.4	13.8	0.40	0.13	1.02	**5.33**
2nd-A								9.67	12.8	12.8	0.53	0.71	1.42	1.01	9.59	53.0	11.8	0.49	0.20	1.32	**4.12**
3rd-A								17.31	12.7	4.7	0.22	0.29	0.59	1.03	17.55	42.5	6.1	0.28	0.13	0.77	**3.48**
4th-A								33.01	12.7	0.6	0.03	0.03	0.07	1.05	36.90	35.9	12.4	0.59	0.30	1.53	**3.32**
5th-A								49.15	12.7	-1.4	-0.06	-0.08	-0.15	1.05	57.22	33.8	14.7	0.64	0.36	1.57	**3.26**
6th-A								66.76	12.7	2.7	0.12	0.14	0.30	1.11	78.48	32.8	20.8	0.92	0.49	**2.26**	**3.36**
5th-B								52.37	12.6	2.9	0.13	0.16	0.34	1.09	58.08	33.8	14.2	0.64	0.35	1.62	**3.24**
4th-B								37.13	12.6	6.6	0.32	0.40	0.86	1.11	37.10	36.0	6.5	0.32	0.17	0.85	**3.16**
3rd-B								20.23	12.6	11.0	0.52	0.66	1.39	1.09	17.71	42.5	-2.8	-0.13	-0.07	-0.36	**3.22**
2nd-B								11.59	12.6	19.4	0.79	1.00	**2.07**	1.07	9.36	53.4	-3.5	-0.14	-0.07	-0.38	**3.67**
1st-B								5.43	13.3	37.0	**1.09**	**1.34**	**2.69**	1.02	3.90	86.2	-1.6	-0.05	-0.02	-0.12	**4.75**
Compound	ISCIII							ISPRA							SHI						
toluene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								4.58	20.5	45.1	**1.30**	**1.29**	**3.35**	**1.53**	2.46	14.6	-22.0	-0.64	**-1.01**	-1.64	0.58
2nd-A								11.45	12.1	33.5	**1.39**	**1.73**	**3.73**	1.12	7.59	8.7	-11.5	-0.48	-0.87	-1.28	0.54
3rd-A								21.86	10.4	32.2	**1.50**	**1.94**	**4.06**	1.06	14.97	5.7	-9.5	-0.44	-0.90	-1.20	0.40
4th-A								43.25	9.9	31.8	**1.50**	**1.88**	**3.91**	1.08	27.85	3.6	-15.2	-0.72	**-1.36**	-1.87	0.25
5th-A								62.71	9.9	25.7	**1.12**	**1.35**	**2.74**	1.04	39.00	3.6	-21.8	-0.95	**-1.47**	**-2.32**	0.24
6th-A								73.99	9.8	13.9	0.61	0.77	1.51	0.95	48.74	0.6	-25.0	**-1.11**	**-1.78**	**-2.72**	0.04
5th-B								62.81	9.9	23.5	**1.07**	**1.33**	**2.68**	1.02	39.80	3.7	-21.8	-0.99	**-1.65**	**-2.48**	0.24
4th-B								42.44	9.9	21.8	**1.06**	**1.42**	**2.84**	1.00	29.18	3.4	-16.2	-0.79	**-1.64**	**-2.11**	0.24
3rd-B								22.31	10.4	22.4	**1.05**	**1.42**	**2.84**	0.99	16.10	5.5	-11.7	-0.55	**-1.12**	-1.48	0.38
2nd-B								11.85	12.0	22.1	0.90	**1.15**	**2.36**	1.04	8.38	8.6	-13.6	-0.56	-0.94	-1.45	0.53
1st-B								4.83	19.5	21.8	0.64	0.69	1.59	1.33	2.94	16.3	-25.8	-0.76	**-1.07**	-1.88	0.68
Compound	SHI2							UBA							ERLAP						
toluene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	2.87	11.1	-9.1	-0.26	-0.43	-0.67	0.52	3.07	8.5	-2.7	-0.08	-0.13	-0.20	0.42	2.45	24.0	-22.3	-0.64	-0.85	-1.65	0.96
2nd-A	8.80	5.9	2.6	0.11	0.21	0.29	0.42	8.89	8.3	3.7	0.15	0.27	0.41	0.60	7.93	14.6	-7.6	-0.31	-0.44	-0.84	0.94
3rd-A	17.49	3.9	5.8	0.27	0.57	0.73	0.32	17.71	8.2	7.1	0.33	0.56	0.89	0.68	16.10	11.8	-2.7	-0.12	-0.18	-0.33	0.89
4th-A	32.57	2.6	-0.8	-0.04	-0.07	-0.10	0.22	34.72	8.2	5.8	0.27	0.42	0.71	0.72	33.51	10.5	2.1	0.10	0.14	0.26	0.88
5th-A	45.46	3.0	-8.8	-0.38	-0.60	-0.94	0.23	56.50	8.4	13.3	0.58	0.77	1.42	0.80	51.78	10.2	3.8	0.17	0.21	0.41	0.89
6th-A	56.85	3.6	-12.5	-0.55	-0.87	-1.36	0.27	66.62	8.3	2.5	0.11	0.15	0.27	0.72	69.73	10.1	7.3	0.32	0.41	0.80	0.92
5th-B	46.84	3.0	-7.9	-0.36	-0.60	-0.90	0.23	52.33	8.3	2.9	0.13	0.19	0.33	0.71	51.41	10.2	1.1	0.05	0.06	0.12	0.87
4th-B	34.60	2.5	-0.7	-0.03	-0.07	-0.09	0.20	36.34	8.3	4.3	0.21	0.34	0.56	0.71	33.10	10.7	-5.0	-0.24	-0.36	-0.65	0.84
3rd-B	19.65	3.8	7.8	0.37	0.77	0.99	0.32	19.02	8.3	4.4	0.20	0.34	0.55	0.68	15.60	11.8	-14.4	-0.68	**-1.05**	-1.83	0.79
2nd-B	10.46	5.9	7.8	0.32	0.56	0.83	0.46	9.68	8.3	-0.2	-0.01	-0.02	-0.03	0.59	7.43	13.8	-23.4	-0.96	**-1.43**	**-2.50**	0.76
1st-B	3.77	12.2	-4.9	-0.14	-0.20	-0.36	0.65	3.42	8.8	-13.7	-0.40	-0.62	-1.00	0.42	2.67	21.2	-32.7	-0.96	**-1.29**	**-2.38**	0.80

([1])|PA| and |E_n scores| ≥ 1 are highlighted in red. |Z' score| between 2 and 3 in blue, being red those values higher than 3. r scores ≥ 95 % and 99 % confident level interval are highlighted in blue and red, respectively

Source: JRC, 2023

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

Compound	CHMI							CHMI2							DHZ-TES						
ethyl-benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A																					
2nd-A																					
3rd-A																					
4th-A																					
5th-A																					
6th-A																					
5th-B																					
4th-B																					
3rd-B																					
2nd-B																					
1st-B																					
Compound	DLI							DLI2							EKONERG						
ethyl-benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.41	29.3	10.2	0.08	0.15	0.20	0.40	0.38	31.6	2.2	0.02	0.03	0.04	0.40							
2nd-A	1.77	16.9	12.9	0.22	0.29	0.53	0.69	1.64	17.1	4.6	0.08	0.10	0.19	0.64							
3rd-A	3.62	16.0	13.2	0.32	0.38	0.74	0.93	3.51	16.0	9.8	0.23	0.28	0.55	0.90							
4th-A	6.69	15.8	1.6	0.05	0.06	0.12	1.05	6.61	15.4	0.3	0.01	0.01	0.03	1.01							
5th-A	9.70	15.7	0.4	0.01	0.02	0.04	1.12	9.69	15.3	0.3	0.01	0.01	0.03	1.09							
6th-A	13.06	15.6	-1.2	-0.05	-0.06	-0.14	1.16	13.16	15.2	-0.4	-0.02	-0.02	-0.05	1.13							
5th-B	10.04	15.5	-0.8	-0.03	-0.04	-0.08	1.11	10.08	15.3	-0.4	-0.02	-0.02	-0.04	1.09							
4th-B	7.04	15.6	2.0	0.06	0.08	0.15	1.05	7.03	15.4	1.8	0.06	0.07	0.14	1.04							
3rd-B	3.89	15.9	15.5	0.38	0.45	0.90	0.97	3.77	15.9	11.9	0.29	0.35	0.69	0.94							
2nd-B	1.91	16.8	16.6	0.29	0.38	0.70	0.72	1.78	16.9	8.7	0.15	0.20	0.36	0.68							
1st-B	0.47	25.5	5.2	0.05	0.10	0.12	0.39	0.46	30.4	3.0	0.03	0.05	0.07	0.46							
Compound	EPA							ERA							IPH-S						
ethyl-benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								0.45	13.3	21.0	0.15	0.33	0.41	0.20							
2nd-A								2.20	14.5	40.4	0.69	0.89	1.64	0.74							
3rd-A								3.91	13.8	22.3	0.53	0.65	1.25	0.87							
4th-A								7.92	15.4	20.2	0.66	0.73	1.57	1.21							
5th-A								11.03	18.3	14.1	0.53	0.54	1.33	1.49							
6th-A								14.26	19.5	7.9	0.35	0.34	0.94	1.58							
5th-B								11.55	13.9	14.1	0.56	0.66	1.42	1.13							
4th-B								8.41	14.3	21.8	0.71	0.81	1.72	1.15							
3rd-B								4.30	14.4	27.7	0.68	0.81	1.60	0.97							
2nd-B								2.38	13.4	45.3	0.80	1.03	1.90	0.72							
1st-B								0.63	12.7	41.0	0.36	0.80	0.98	0.26							
Compound	ISCIII							ISPRA							SHI						
ethyl-benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								0.75	77.3	101.7	0.75	0.61	2.00	1.94	0.01	1800.0	-97.3	-0.72	-1.23	-1.91	0.60
2nd-A								2.53	25.3	61.4	1.06	1.07	2.50	1.47	0.69	49.3	-56.0	-0.96	-1.21	-2.28	0.78
3rd-A								4.70	17.4	47.0	1.12	1.19	2.62	1.32	1.76	26.1	-44.9	-1.07	-1.35	-2.51	0.74
4th-A								9.15	13.8	38.9	1.26	1.38	3.03	1.25	4.50	16.4	-31.7	-1.03	-1.35	-2.47	0.73
5th-A								13.69	13.0	41.7	1.58	1.71	3.92	1.31	7.59	13.2	-21.5	-0.81	-1.13	-2.02	0.74
6th-A								18.13	12.8	37.2	1.66	1.83	4.42	1.32	10.73	11.2	-18.8	-0.84	-1.37	-2.23	0.68
5th-B								13.64	13.0	34.7	1.38	1.54	3.50	1.26	7.77	13.1	-23.3	-0.92	-1.34	-2.35	0.72
4th-B								9.25	13.8	34.0	1.11	1.23	2.67	1.23	4.71	16.6	-31.8	-1.04	-1.36	-2.50	0.75
3rd-B								4.75	17.3	41.0	1.01	1.09	2.37	1.28	1.88	28.7	-44.2	-1.09	-1.34	-2.55	0.84
2nd-B								2.57	24.9	56.9	1.01	1.03	2.38	1.45	0.74	67.6	-54.8	-0.97	-1.10	-2.29	1.13
1st-B								0.84	69.0	88.0	0.78	0.64	2.10	1.89	0.17	105.9	-61.9	-0.55	-0.99	-1.48	0.59
Compound	SHI2							UBA							ERLAP						
ethyl-benzene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.17	70.6	-54.3	-0.40	-0.77	-1.07	0.40	0.24	16.7	-35.5	-0.26	-0.56	-0.70	0.13	0.57	18.5	52.0	0.38	0.76	1.02	0.35
2nd-A	0.84	35.7	-46.4	-0.80	-1.03	-1.89	0.69	1.19	13.4	-24.1	-0.41	-0.57	-0.98	0.37	1.68	4.2	7.1	0.12	0.17	0.29	0.16
3rd-A	2.19	18.3	-31.5	-0.75	-0.97	-1.76	0.64	2.62	13.7	-18.0	-0.43	-0.56	-1.01	0.58	3.26	2.2	2.1	0.05	0.07	0.12	0.12
4th-A	5.59	11.1	-15.1	-0.49	-0.67	-1.18	0.62	5.94	13.8	-9.8	-0.32	-0.41	-0.76	0.81	6.55	1.9	-0.6	-0.02	-0.03	-0.05	0.12
5th-A	9.40	8.3	-2.7	-0.10	-0.15	-0.26	0.57	7.82	14.1	-19.1	-0.72	-0.97	-1.79	0.81	9.77	1.7	1.1	0.04	0.07	0.11	0.12
6th-A	13.28	6.8	0.5	0.02	0.04	0.06	0.51	12.91	13.9	-2.3	-0.10	-0.13	-0.27	1.02	12.60	2.4	-4.6	-0.21	-0.44	-0.55	0.17
5th-B	9.79	8.2	-3.3	-0.13	-0.20	-0.33	0.57	9.71	14.0	-4.1	-0.16	-0.21	-0.41	0.96	9.49	2.6	-6.3	-0.25	-0.44	-0.63	0.18
4th-B	6.06	10.9	-12.2	-0.40	-0.54	-0.96	0.63	6.36	13.8	-7.9	-0.26	-0.33	-0.62	0.84	6.37	2.1	-7.7	-0.25	-0.38	-0.61	0.13
3rd-B	2.52	20.6	-25.2	-0.62	-0.77	-1.46	0.81	2.76	13.8	-18.1	-0.44	-0.58	-1.04	0.59	3.07	3.9	-8.7	-0.21	-0.30	-0.50	0.19
2nd-B	1.03	46.6	-37.1	-0.66	-0.76	-1.55	1.08	1.19	13.4	-27.3	-0.48	-0.67	-1.14	0.36	1.50	6.7	-8.3	-0.15	-0.21	-0.35	0.23
1st-B	0.24	200.0	-46.3	-0.41	-0.39	-1.11	1.56	0.28	14.3	-37.3	-0.33	-0.77	-0.89	0.13	0.51	16.7	15.1	0.13	0.29	0.36	0.28

([1])|PA| and |E_n scores| ≥ 1 are highlighted in red. |Z' score| between 2 and 3 in blue, being red those values higher than 3. r scores ≥ 95 % and 99 % confident level interval are highlighted in blue and red, respectively

Source: JRC, 2023

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

Compound	CHMI							CHMI2							DHZ-TES						
m,p-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A																					
2nd-A																					
3rd-A																					
4th-A																					
5th-A																					
6th-A																					
5th-B																					
4th-B																					
3rd-B																					
2nd-B																					
1st-B																					
Compound	DLI							DLI2							EKONERG						
m,p-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.48	50.0	24.5	0.19	0.31	0.53	0.80	0.38	47.4	-1.4	-0.01	-0.02	-0.03	0.60							
2nd-A	1.76	21.6	14.7	0.24	0.28	0.55	0.88	1.47	20.4	-4.2	-0.07	-0.08	-0.16	0.70							
3rd-A	3.77	17.0	12.9	0.25	0.28	0.56	1.01	3.36	16.7	0.7	0.01	0.01	0.03	0.88							
4th-A	7.37	16.0	6.9	0.18	0.19	0.40	1.13	6.98	15.8	1.3	0.03	0.04	0.07	1.06							
5th-A	10.31	15.7	1.9	0.06	0.06	0.13	1.15	10.05	15.5	-0.7	-0.02	-0.02	-0.04	1.11							
6th-A	13.43	15.6	-4.3	-0.15	-0.16	-0.34	1.13	13.23	15.4	-5.7	-0.19	-0.22	-0.45	1.10							
5th-B	10.70	15.7	-0.6	-0.02	-0.02	-0.04	1.13	10.51	15.6	-2.3	-0.07	-0.08	-0.17	1.11							
4th-B	7.81	15.9	7.0	0.19	0.21	0.42	1.14	7.44	15.6	2.0	0.05	0.06	0.12	1.07							
3rd-B	4.13	16.9	14.8	0.31	0.34	0.69	1.05	3.76	16.5	4.5	0.10	0.11	0.21	0.93							
2nd-B	1.97	20.3	14.2	0.24	0.28	0.55	0.88	1.69	18.9	-2.1	-0.03	-0.04	-0.08	0.71							
1st-B	0.60	43.3	34.6	0.31	0.47	0.84	0.85	0.47	42.6	5.4	0.05	0.09	0.13	0.65							
Compound	EPA							ERA							IPH-S						
m,p-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								0.30	13.3	-22.2	-0.17	-0.43	-0.48	0.13							
2nd-A								1.91	17.8	24.5	0.39	0.48	0.91	0.79							
3rd-A								4.28	16.8	28.2	0.56	0.60	1.23	1.13							
4th-A								7.97	16.8	15.7	0.40	0.42	0.89	1.29							
5th-A								11.72	22.2	15.9	0.47	0.43	1.05	**1.84**							
6th-A								16.24	21.2	15.8	0.54	0.48	1.24	**1.85**							
5th-B								12.53	16.9	16.5	0.53	0.54	1.21	1.43							
4th-B								8.55	16.8	17.2	0.46	0.48	1.03	1.32							
3rd-B								4.83	17.8	34.3	0.72	0.75	1.60	1.29							
2nd-B								2.27	18.5	31.6	0.53	0.62	1.21	0.93							
1st-B								0.46	17.4	3.2	0.03	0.07	0.08	0.26							
Compound	ISCIII							ISPRA							SHI						
m,p-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								1.12	83.9	190.5	**1.50**	0.77	**4.11**	**3.13**	0.16	162.5	-58.5	-0.46	-0.69	-1.26	0.87
2nd-A								3.02	37.7	96.8	**1.55**	**1.11**	**3.59**	**2.65**	0.55	83.6	-64.2	**-1.03**	**-1.17**	**-2.38**	1.07
3rd-A								5.65	28.3	69.2	**1.37**	**1.09**	**3.01**	**2.51**	1.31	41.2	-60.8	**-1.20**	**-1.35**	**-2.64**	0.85
4th-A								10.81	24.8	56.9	**1.46**	**1.13**	**3.24**	**2.57**	3.41	21.7	-50.5	**-1.30**	**-1.51**	**-2.88**	0.71
5th-A								15.82	24.1	56.4	**1.66**	**1.22**	**3.74**	**2.71**	5.97	17.4	-41.0	**-1.21**	**-1.43**	**-2.72**	0.74
6th-A								20.66	23.8	47.3	**1.61**	**1.15**	**3.73**	**2.65**	8.81	15.2	-37.2	**-1.27**	**-1.58**	**-2.94**	0.72
5th-B								15.87	24.1	47.5	**1.52**	**1.11**	**3.48**	**2.58**	6.17	17.5	-42.7	**-1.36**	**-1.67**	**-3.13**	0.73
4th-B								10.98	24.8	50.5	**1.36**	**1.06**	**3.03**	**2.50**	3.63	22.0	-50.2	**-1.35**	**-1.58**	**-3.02**	0.74
3rd-B								5.73	28.3	59.3	**1.24**	1.00	**2.76**	**2.43**	1.40	50.0	-61.1	**-1.28**	**-1.41**	**-2.84**	1.05
2nd-B								3.10	37.4	79.7	**1.33**	0.99	**3.06**	**2.56**	0.54	33.3	-68.7	**-1.15**	**-1.49**	**-2.64**	0.40
1st-B								1.16	81.0	160.2	**1.42**	0.74	**3.89**	**3.06**	0.16	112.5	-64.1	-0.57	**-1.06**	-1.56	0.59
Compound	SHI2							UBA							ERLAP						
m,p-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.18	66.7	-53.3	-0.42	-0.90	-1.15	0.40	0.29	6.9	-24.8	-0.19	-0.49	-0.53	0.07	0.58	14.9	50.0	0.39	0.90	1.08	0.29
2nd-A	0.75	58.7	-51.1	-0.82	-0.94	-1.90	1.02	1.19	8.4	-22.4	-0.36	-0.48	-0.83	0.23	1.92	4.9	25.0	0.40	0.54	0.93	0.22
3rd-A	1.83	29.5	-45.2	-0.89	**-1.01**	-1.96	0.85	2.62	8.4	-21.5	-0.42	-0.51	-0.94	0.35	3.89	5.3	16.4	0.32	0.39	0.71	0.33
4th-A	4.84	15.7	-29.8	-0.76	-0.89	-1.70	0.73	6.05	8.3	-12.2	-0.31	-0.38	-0.70	0.48	7.91	3.0	14.8	0.38	0.46	0.84	0.23
5th-A	8.51	12.5	-15.9	-0.47	-0.55	-1.05	0.75	7.92	8.6	-21.7	-0.64	-0.79	-1.44	0.48	11.73	4.0	15.9	0.47	0.59	1.06	0.33
6th-A	12.58	10.2	-10.3	-0.35	-0.44	-0.82	0.69	13.28	8.1	-5.3	-0.18	-0.23	-0.42	0.58	15.41	4.6	9.9	0.34	0.45	0.78	0.38
5th-B	9.05	11.9	-15.9	-0.51	-0.62	-1.16	0.73	10.21	8.0	-5.1	-0.16	-0.21	-0.37	0.55	11.56	7.6	7.4	0.24	0.30	0.54	0.59
4th-B	5.42	15.9	-25.7	-0.69	-0.80	-1.54	0.79	6.78	8.3	-7.1	-0.19	-0.23	-0.43	0.51	7.76	11.3	6.4	0.17	0.20	0.38	0.81
3rd-B	2.21	31.7	-38.6	-0.81	-0.89	-1.79	1.05	2.95	8.1	-18.0	-0.38	-0.46	-0.84	0.36	3.76	17.7	4.6	0.10	0.11	0.21	1.00
2nd-B	0.90	80.0	-47.8	-0.80	-0.78	-1.84	1.59	1.62	6.2	-6.1	-0.10	-0.14	-0.24	0.22	1.78	24.4	2.9	0.05	0.06	0.11	0.96
1st-B	0.25	48.0	-43.9	-0.39	-0.84	-1.07	0.39	0.33	12.1	-26.0	-0.23	-0.56	-0.63	0.13	0.50	50.1	12.9	0.11	0.18	0.31	0.82

([1])|PA| and |E_n scores| ≥ 1 are highlighted in red. |Z' score| between 2 and 3 in blue, being red those values higher than 3. r scores ≥ 95 % and 99 % confident level interval are highlighted in blue and red, respectively

Source: JRC, 2023

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

Compound	CHMI							CHMI2							DHZ-TES						
o-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A																					
2nd-A																					
3rd-A																					
4th-A																					
5th-A																					
6th-A																					
5th-B																					
4th-B																					
3rd-B																					
2nd-B																					
1st-B																					
Compound	DLI							DLI2							EKONERG						
o-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.56	28.6	-0.3	0.00	-0.01	-0.01	0.50	0.78	25.6	38.9	0.38	0.59	0.98	0.62							
2nd-A	2.09	18.2	7.6	0.13	0.15	0.28	0.80	2.84	17.6	46.3	0.76	0.84	1.70	1.05							
3rd-A	4.12	16.5	11.0	0.23	0.26	0.51	1.00	5.06	16.2	36.3	0.76	0.81	1.69	1.21							
4th-A	7.50	16.3	4.7	0.15	0.16	0.34	1.14	7.94	16.1	10.8	0.34	0.37	0.79	1.19							
5th-A	10.56	16.3	1.7	0.06	0.07	0.15	1.19	11.33	16.1	9.1	0.32	0.35	0.77	1.26							
6th-A	14.08	16.2	-0.2	-0.01	-0.01	-0.02	1.22	15.08	16.0	6.9	0.29	0.32	0.74	1.30							
5th-B	10.89	16.3	0.0	0.00	0.00	0.00	1.19	11.58	16.1	6.3	0.25	0.27	0.61	1.24							
4th-B	7.82	16.4	4.9	0.15	0.17	0.36	1.16	7.99	16.0	7.2	0.23	0.25	0.53	1.16							
3rd-B	4.43	16.7	14.9	0.33	0.37	0.74	1.06	4.84	16.5	25.6	0.57	0.62	1.27	1.15							
2nd-B	2.19	17.4	4.2	0.08	0.10	0.18	0.77	2.55	17.3	21.4	0.40	0.48	0.93	0.89							
1st-B	0.66	27.3	12.2	0.12	0.19	0.31	0.56	0.53	34.0	-9.9	-0.10	-0.16	-0.25	0.56							
Compound	EPA							ERA							IPH-S						
o-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								0.69	14.5	22.8	0.22	0.40	0.58	0.31							
2nd-A								2.43	14.8	25.2	0.41	0.49	0.93	0.75							
3rd-A								4.18	14.4	12.6	0.26	0.30	0.59	0.88							
4th-A								8.48	16.7	18.4	0.57	0.61	1.34	1.32							
5th-A								11.66	17.7	12.3	0.44	0.45	1.04	1.43							
6th-A								15.08	21.2	6.9	0.29	0.26	0.74	**1.72**							
5th-B								12.23	14.6	12.3	0.48	0.54	1.18	1.19							
4th-B								9.00	15.1	20.7	0.65	0.71	1.54	1.23							
3rd-B								4.61	15.6	19.6	0.44	0.48	0.98	1.04							
2nd-B								2.61	14.6	24.2	0.46	0.56	1.05	0.77							
1st-B								0.89	15.7	51.3	0.52	0.85	1.32	0.43							
Compound	ISCIII							ISPRA							SHI						
o-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A								1.29	31.0	129.6	**1.28**	**1.44**	**3.28**	1.25	0.22	109.1	-60.8	-0.60	-0.88	-1.54	0.75
2nd-A								3.42	17.0	76.1	**1.25**	**1.34**	**2.80**	1.22	0.79	55.7	-59.3	-0.97	**-1.11**	**-2.18**	0.92
3rd-A								6.11	14.4	64.6	**1.36**	**1.42**	**3.00**	1.30	1.88	31.9	-49.4	**-1.04**	**-1.17**	**-2.30**	0.88
4th-A								11.40	13.7	59.1	**1.85**	**1.87**	**4.33**	1.45	4.84	19.0	-32.5	**-1.01**	**-1.24**	**-2.38**	0.86
5th-A								16.66	13.4	60.5	**2.14**	**2.10**	**5.12**	**1.56**	8.09	14.8	-22.1	-0.78	-0.99	-1.87	0.83
6th-A								21.44	13.3	52.0	**2.18**	**2.15**	**5.56**	**1.53**	11.36	12.1	-19.5	-0.82	**-1.18**	**-2.09**	0.74
5th-B								16.67	13.4	53.1	**2.05**	**2.05**	**5.10**	1.50	8.32	14.4	-23.6	-0.91	**-1.23**	**-2.27**	0.80
4th-B								11.45	13.6	53.6	**1.69**	**1.74**	**3.97**	1.41	5.06	19.0	-32.1	**-1.02**	**-1.24**	**-2.38**	0.87
3rd-B								6.17	14.6	60.1	**1.34**	**1.40**	**2.99**	1.29	2.05	31.2	-46.8	**-1.04**	**-1.18**	**-2.33**	0.92
2nd-B								3.39	17.1	61.3	**1.15**	**1.27**	**2.66**	1.17	0.81	69.1	-61.4	**-1.16**	**-1.28**	**-2.66**	1.13
1st-B								1.36	30.9	131.2	**1.32**	**1.45**	**3.37**	1.30	0.22	109.1	-62.6	-0.63	-0.91	-1.61	0.74
Compound	SHI2							UBA							ERLAP						
o-xylene	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores	Concentration, µg/m³	U, %	bias, %	P_A	En	Z'-scores	r-scores
1st-A	0.22	90.9	-60.8	-0.60	-0.93	-1.54	0.62	0.28	14.3	-50.2	-0.49	-0.91	-1.27	0.12	0.66	3.6	17.3	0.17	0.31	0.44	0.07
2nd-A	0.98	38.8	-49.5	-0.81	-0.95	-1.82	0.80	1.14	15.8	-41.3	-0.68	-0.84	-1.52	0.38	1.84	3.8	-5.1	-0.08	-0.10	-0.19	0.15
3rd-A	2.41	19.1	-35.1	-0.74	-0.86	-1.63	0.68	2.51	15.9	-32.4	-0.68	-0.80	-1.51	0.59	3.43	2.4	-7.5	-0.16	-0.19	-0.35	0.12
4th-A	6.17	11.3	-13.9	-0.43	-0.56	-1.02	0.65	5.91	15.9	-17.5	-0.55	-0.67	-1.28	0.88	6.52	1.7	-9.0	-0.28	-0.39	-0.66	0.10
5th-A	10.30	8.3	-0.8	-0.03	-0.04	-0.07	0.60	7.64	16.0	-26.4	-0.93	**-1.18**	**-2.23**	0.85	9.67	2.5	-6.8	-0.24	-0.35	-0.58	0.17
6th-A	14.49	6.2	2.7	0.11	0.18	0.29	0.48	13.12	15.9	-7.0	-0.29	-0.35	-0.75	1.12	12.32	2.9	-12.7	-0.53	-0.94	-1.36	0.19
5th-B	10.79	8.0	-0.9	-0.04	-0.05	-0.09	0.57	9.91	15.9	-9.0	-0.35	-0.42	-0.86	1.06	9.57	4.0	-12.1	-0.47	-0.76	-1.16	0.26
4th-B	6.70	11.3	-10.1	-0.32	-0.41	-0.75	0.69	6.41	15.9	-14.0	-0.44	-0.53	-1.04	0.92	6.35	6.3	-14.8	-0.47	-0.64	-1.10	0.36
3rd-B	2.78	20.9	-27.9	-0.62	-0.72	-1.39	0.83	2.71	16.2	-29.7	-0.66	-0.79	-1.48	0.63	3.24	8.9	-15.8	-0.35	-0.43	-0.79	0.41
2nd-B	1.13	46.0	-46.2	-0.87	-0.99	**-2.00**	1.05	1.14	15.8	-45.7	-0.86	**-1.13**	-1.98	0.36	1.70	10.6	-19.2	-0.36	-0.47	-0.83	0.36
1st-B	0.29	48.3	-50.7	-0.51	-0.84	-1.30	0.43	0.28	21.4	-52.4	-0.53	-0.93	-1.34	0.19	0.69	18.4	17.7	0.18	0.30	0.45	0.39

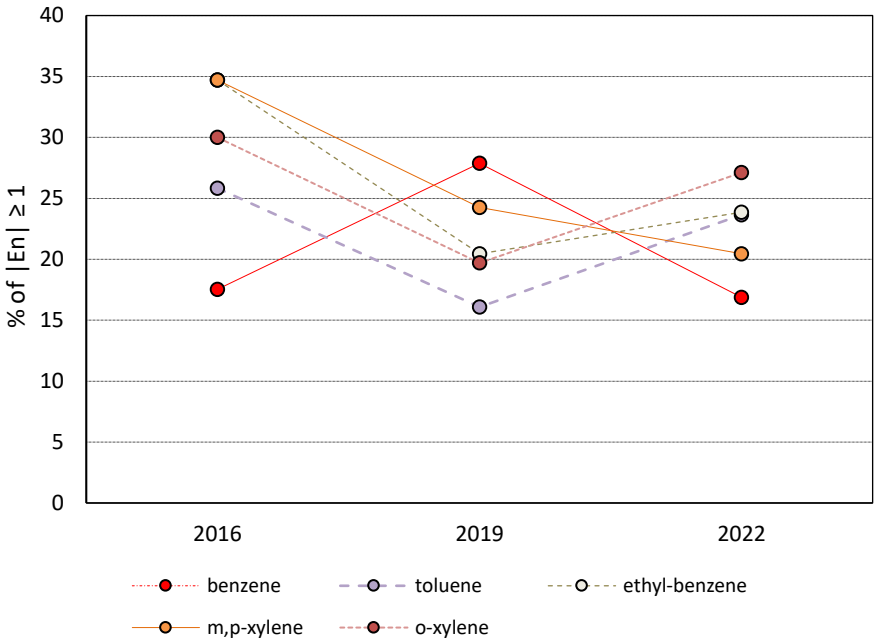
([1])|PA| and |E_n scores| ≥ 1 are highlighted in red. |Z' score| between 2 and 3 in blue, being red those values higher than 3. r scores ≥ 95 % and 99 % confident level interval are highlighted in blue and red, respectively

Source: JRC, 2023

Out of the 11 laboratories, only 6 participated in the last inter-laboratory comparison (EUR 30239 EN, 2020). Among the total participants, only 7 reported on toluene, and 5 reported on C_8 compounds.

Regarding the last comparison, there was a slight improvement in the percentage of E_n score outliers for benzene and m,p-xylene. However, this was accompanied by an increase in reported uncertainties, which suggests that the method may not have actually improved (refer to **Figure 10**). In contrast, the outlier percentage for the other compounds increased significantly compared to the previous exercise. This was also reflected in the reproducibility value of the exercise, especially for ethyl-benzene and o-xylene, indicating a deterioration in the quantification of these compounds and approaching the results from 2016, prior to the reduction in concentration levels used for the 2019 comparison.

Figure 10. Comparison of proficiency test exercises 2016 and 2019



Source: JRC, 2023

4 Conclusions

Despite the participation of fewer laboratories in this exercise (11 compared to 13 in the previous one), the number of replicated instrumentation increased significantly. In the previous exercise, only one laboratory participated with replicated instrumentation, while in this exercise, five laboratories brought replicated instrumentation. However, it's worth noting that two of these laboratories reported results from only one instrument, and another laboratory involved a pumped tube system with off-line analysis.

The repeatability values obtained in this comparison exercise were similar to those reported in the last inter-laboratory comparison in 2019, with values ranging from 6% to 10% and increasing with the carbon number. However, the reproducibility values were only comparable to the previous exercise for benzene and toluene, at around 13 % and 16 %, respectively. In contrast, the C_8 compounds showed a significant increase in reproducibility values, exceeding 30 %. This was also reflected in the deterioration of the method robustness for these compounds, with γ values greater than 3.

Lastly, it's worth noting that the reported statistics (r score, Z' score, and P_A) were referenced against the prescribed standard deviation for the proficiency assessment, σ_{N37}. These scores confirmed a decrease in the measurement quality of aromatic compounds with a carbon number $>C_7$, as well as a slight improvement in benzene measurement.

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List of abbreviations and definitions

AQUILA	Air quality reference laboratories
BTEX	Benzene, toluene, ethyl-benzene, xylene
CG	Gas chromatograph
CHMI	Czech Hydrometeorological Institute (Czech Republic)
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)
ERA	Environment & resources Authority (Malta)
ERLAP	European Reference Laboratory of Air Pollution
EU	European Union
FID	Flame ionization detector
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 (Italy)
l.s.	level of significance
LV	Limit value
P_A	score $P_A = \frac{C_{lab} - C_{ref}}{\sqrt{(3 \cdot \hat{\sigma}_{N37})^2 + u_{ref}^2}}$
QA/QC	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)	Part per billion, molar fraction
Press. Cyl.	Pressurised cylinder
P.T.	Permeation tubes
RSD	Relative standard deviation, %
SHI	Slovak Hydrometeorological Institute (Slovakia)
stdev	standard deviation
STEOL	Star Trek Entrerprise Organic Laboratory
Tr. Std.	Travelling standard
U	Expanded Uncertainty
U %	Relative Expanded Uncertainty

UBA	Umweltbundesamt (Germany)
VSL	National Metrology Institute (The Neatherland)
$\overline{C}$	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_7	refers to hydrocarbons with 7 atoms of carbon
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 or number of inter-laboratory measurements
s^*	Standard deviation of the robust average value
s_{bias}	Standard deviation of the bias
$s_{\bar{c}_i}$	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
$s_{L_{N37}}$	$s_{L_{N37}} = \sqrt{\hat{\sigma}_{N37}^2 - \frac{s_r^2}{n}}$: between laboratory standard deviation from the prescript conditions of proficiency assessment of AQUILA network.
s_r^2	Repeatability variance or intra-laboratory variance
s_R^2	Reproducibility variance
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 assessment
$\mu g/m^3$	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
$\hat{\sigma}_m$	minimum standard deviation of proficiency assessment coherent with method reproducibility
$\hat{\sigma}_{N37}$	Standard deviation for proficiency assessment prescript by AQUILA network
(1-α)	Confidence level

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Annexes

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

Sept. 26th: Arrival of participants and installation of equipment: 14:00 to 17:30

Sept. 27th: Calibration and Synchronization: 9:00 – 13:30 / Measurements starting: 14:30

Sept. 28th: End of measurements: 15:30 / Calibration 15:30 – 17:30

Sept.29th: Dismantling of equipment and departure of participants.

Annex 2. Indicators of Mandel's statistic

Table A 14. k and h values

Number of Laboratories	k values at of s.l. ([1])				h values at s.l. ([1])	
	3 replicates		5 replicates			
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

([1]) s.l. : significance level

Source: ISO 5725-2 (2019)

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:

$$\bar{C}_i^* = \frac{\sum C_i^*}{p} \qquad \text{Eq. A 14}$$

$$s^* = 1.134 \cdot \sqrt{\frac{\sum (C_i - \bar{C}_i^*)^2}{(p-1)}} \qquad \text{Eq. A 15}$$

Where recurrent values are calculated from these equations:

$$C_i^* = \begin{cases} \bar{C}_i^* - 1.5 \cdot s^* \text{ if } C_i < \bar{C}_i^* - 1.5 \cdot s^* \\ \bar{C}_i^* + 1.5 \cdot s^* \text{if } C_i > \bar{C}_i^* + 1.5 \cdot s^* \\ C_i \qquad\qquad \text{otherwise} \end{cases} \qquad \text{Eq. A 16}$$

The initial values are calculated as:

$$\bar{C}_i^* = \text{ median of } C_i \ (i = 1, 2, \ldots p) \qquad \text{Eq. A 17}$$

$$s^* = 1.483 \cdot \text{ median of } |C_i - \bar{C}_i^*| \ (i = 1, 2, \ldots p) \qquad \text{Eq. A 18}$$

Annex 4. Repeatability, reproducibility and robustness of previous comparison exercises

Table A 15. Average repeatability, reproducibility and gamma values: 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

Source: Pérez Ballesta et al. EUR 23792EN, 2009

Table A 16. Average repeatability, reproducibility and gamma values: 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

Source: Pérez Ballesta et al. EUR 27012EN, 2014

Table A 17. Average repeatability, reproducibility and gamma values: 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

Source: Pérez Ballesta et al. EUR 28692 EN, 2017

Table A 18. Average repeatability, reproducibility and gamma values: 5th 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

Source: Pérez Ballesta et al. EUR 30239 EN, 2020

Annex 5. Conversion factors for data reporting

Table A 19. µg/m^3 to ppb (v/v) conversion factors

	Conversion factor, µg/m^3 / ppb (v/v)
Benzene	3.25
Toluene	3.83
Ethyl-benzene	4.41
Xylenes	4.41

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

Source: Pérez Ballesta et al. EUR 30239 EN, 2020

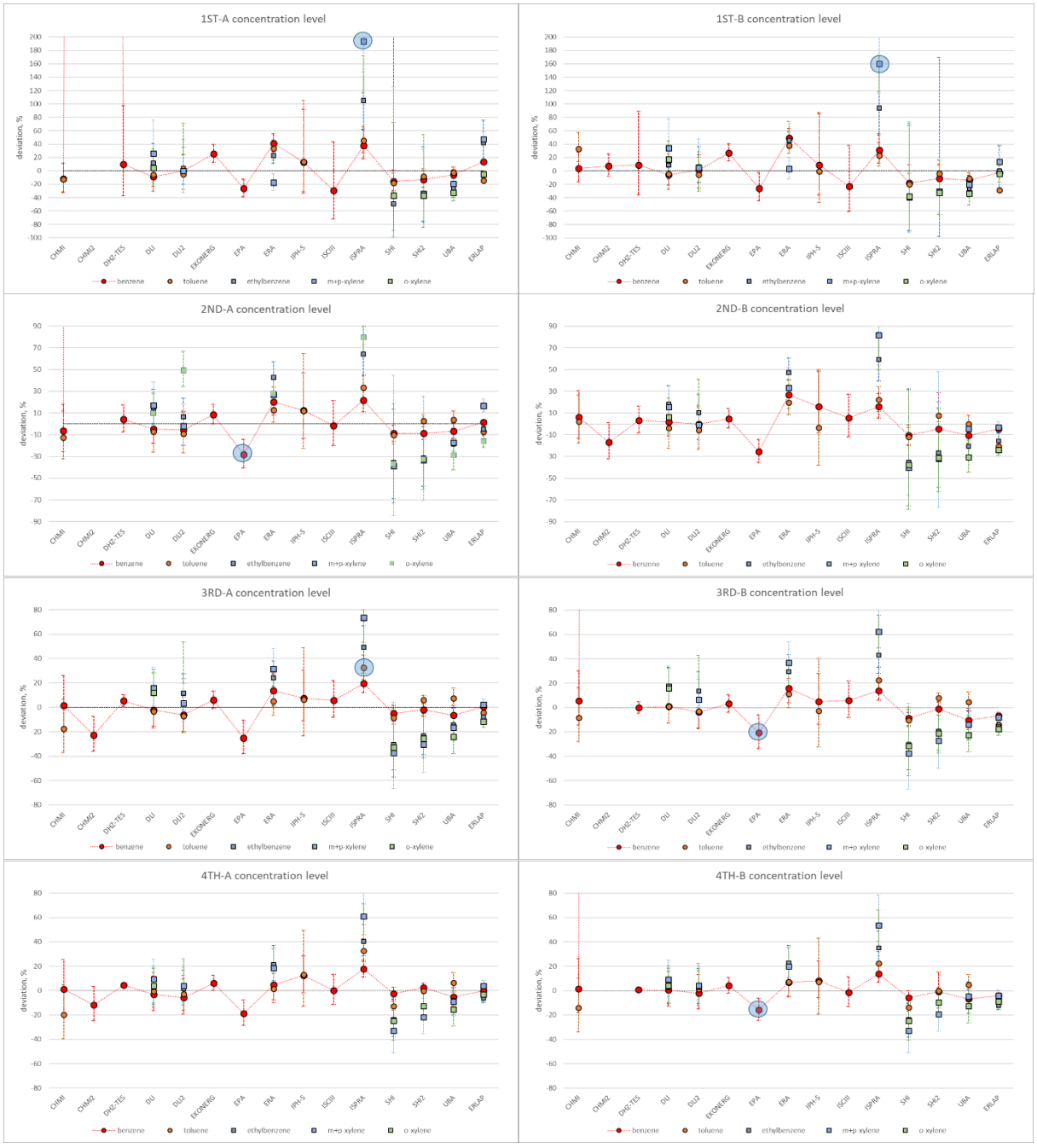
Annex 6. Scattering of Laboratory Results

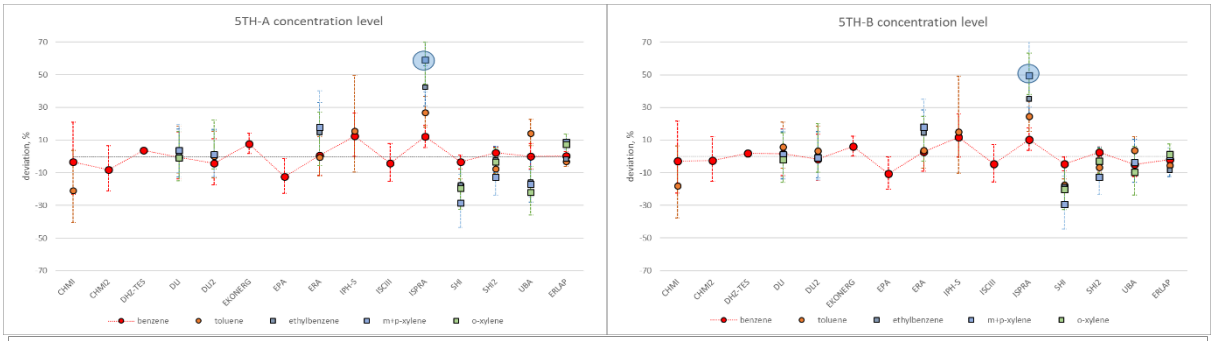
The scattering of results is represented in terms of biases with respect to the reference value or deviations of the reference value with respect to the reported laboratory value when this value is lower than the reference's one:

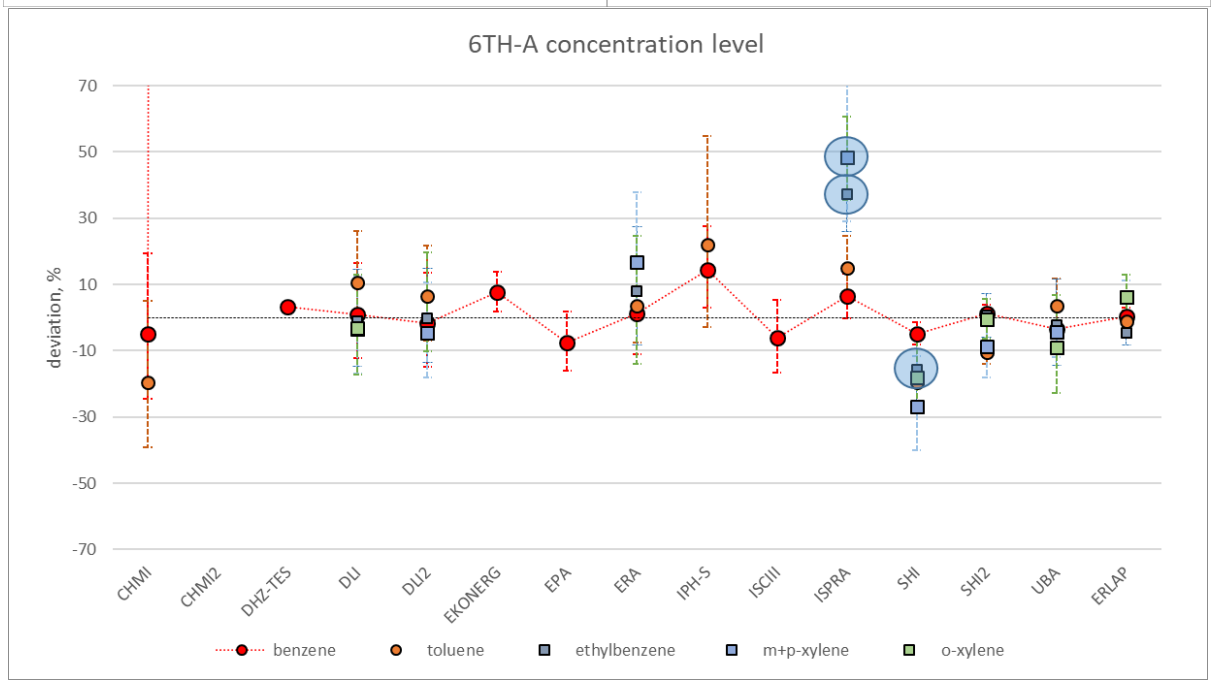
$$\text{bias}\ (\%) = \text{deviation}\ (\%), \qquad \text{if laboratory value} > \text{reference value} \qquad \text{Eq. A 19}$$

$$\text{bias}\ (\%) = \frac{\text{deviation}\ (\%)}{100+\text{deviation}\ (\%)} \cdot 100, \qquad \text{if laboratory value} < \text{reference value} \qquad \text{Eq. A 20}$$

Figure A 11. Results of the inter-laboratory comparison: Deviation (%)





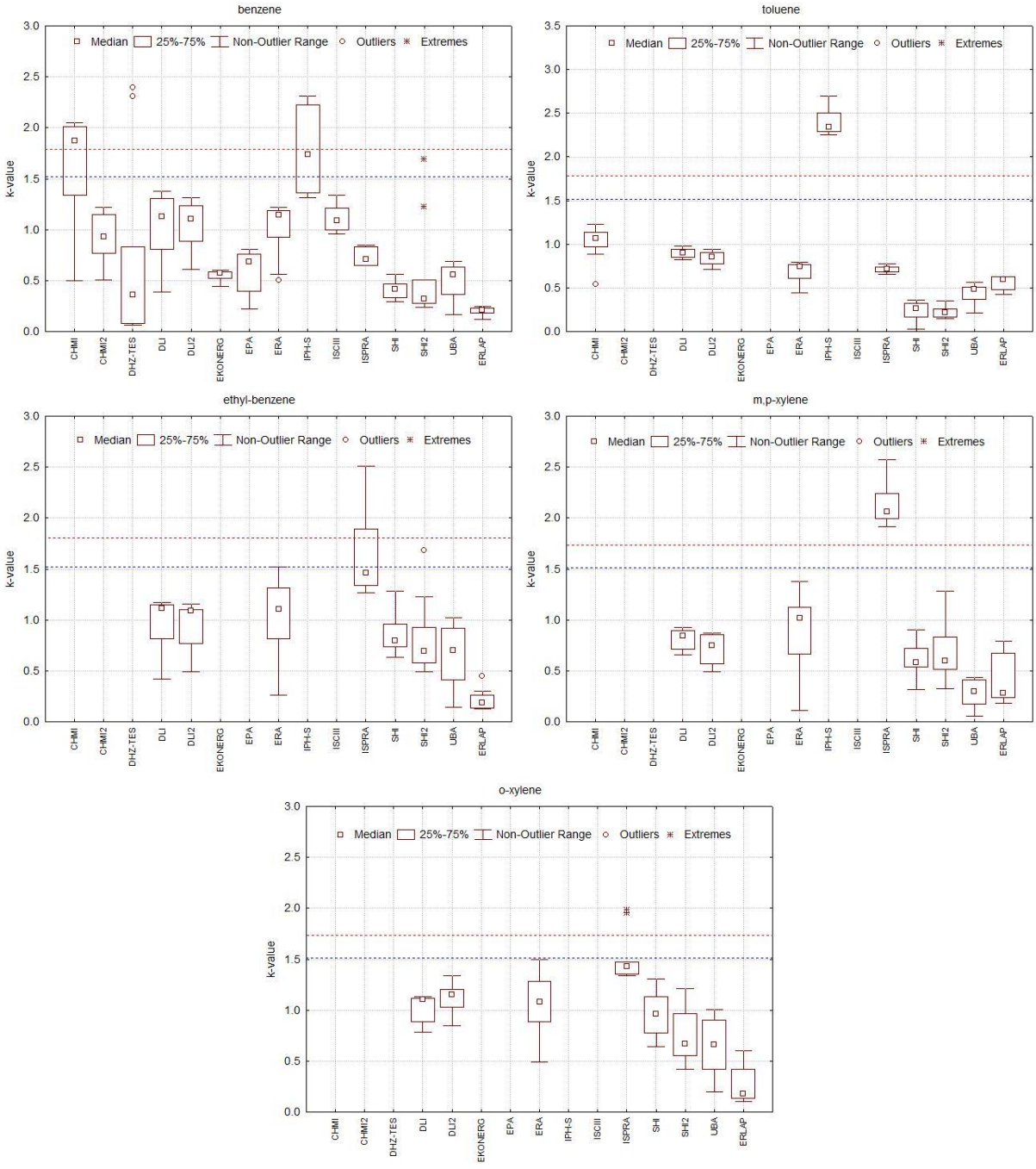


|--------| Expanded uncertainty E_n outliers

Source: JRC, 2023

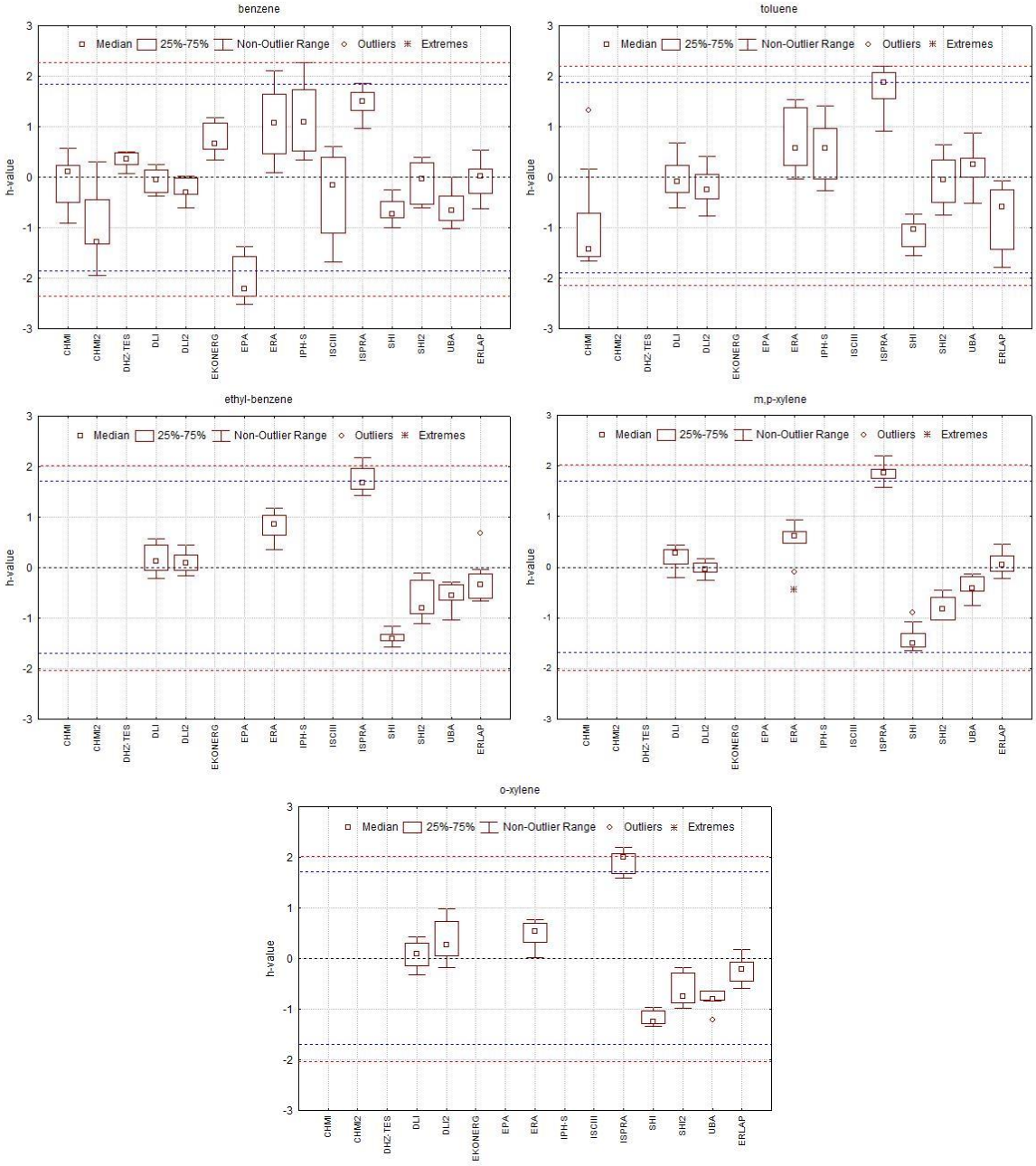
Annex 7. h and k statistic results of the inter-laboratory comparison

Figure A 12. Initial k-values for the inter-laboratory comparison exercise



Source: JRC, 2023

Figure A 13. Initial h-values for the inter-laboratory comparison exercise

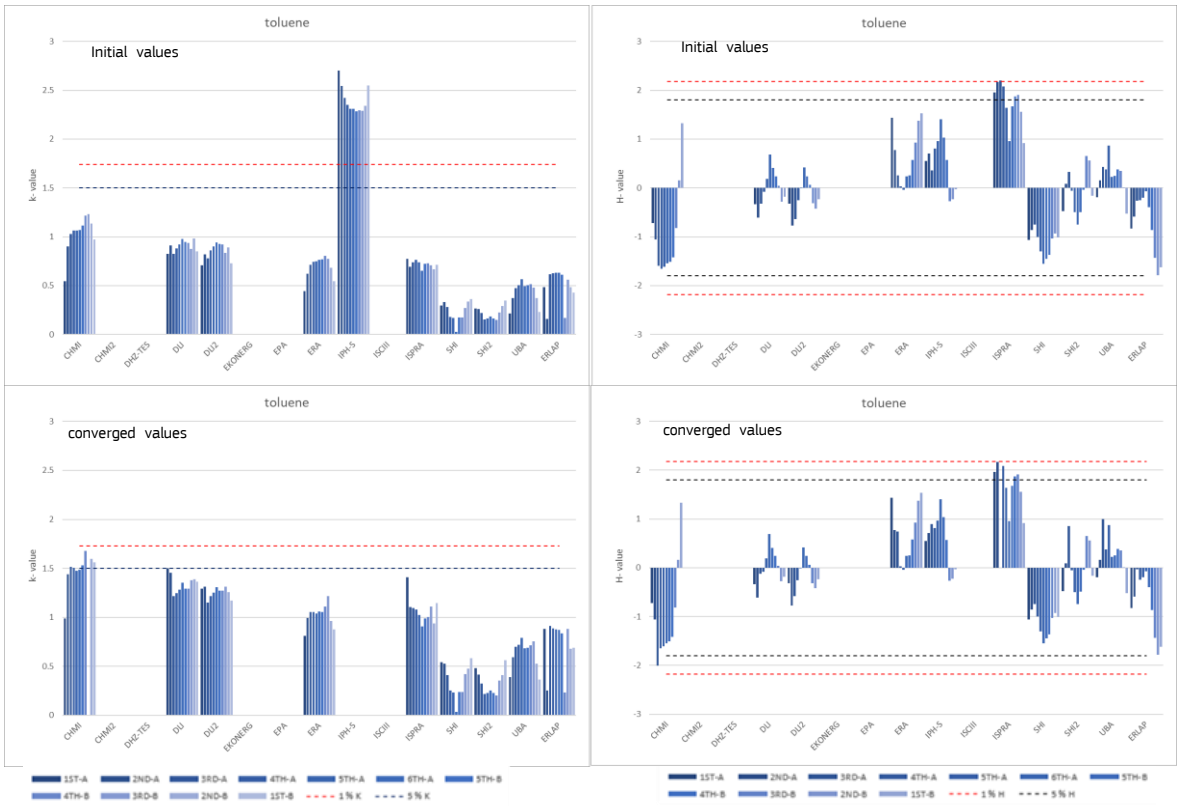


Source: JRC, 2023

Figure A 14. Benzene: initial and converged h and k statistics

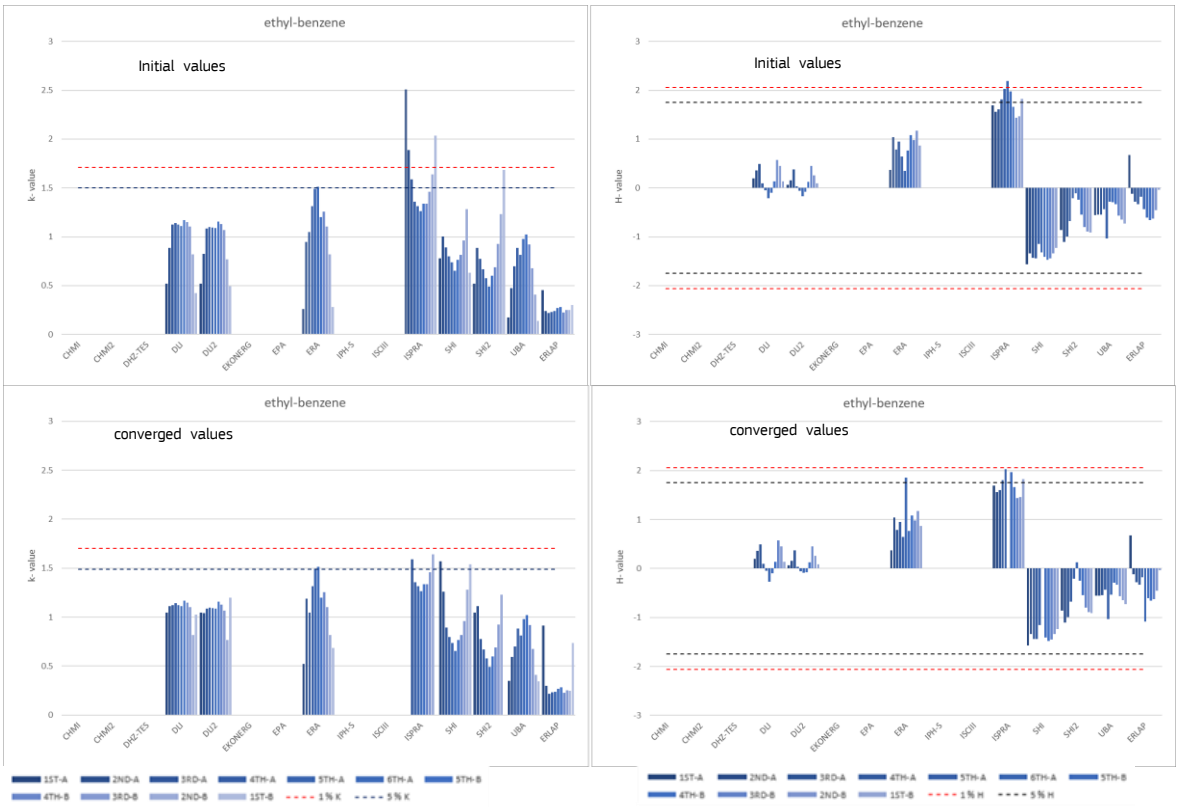
Source: JRC, 2023

Figure A 15. Toluene: initial and converged h and k statistics



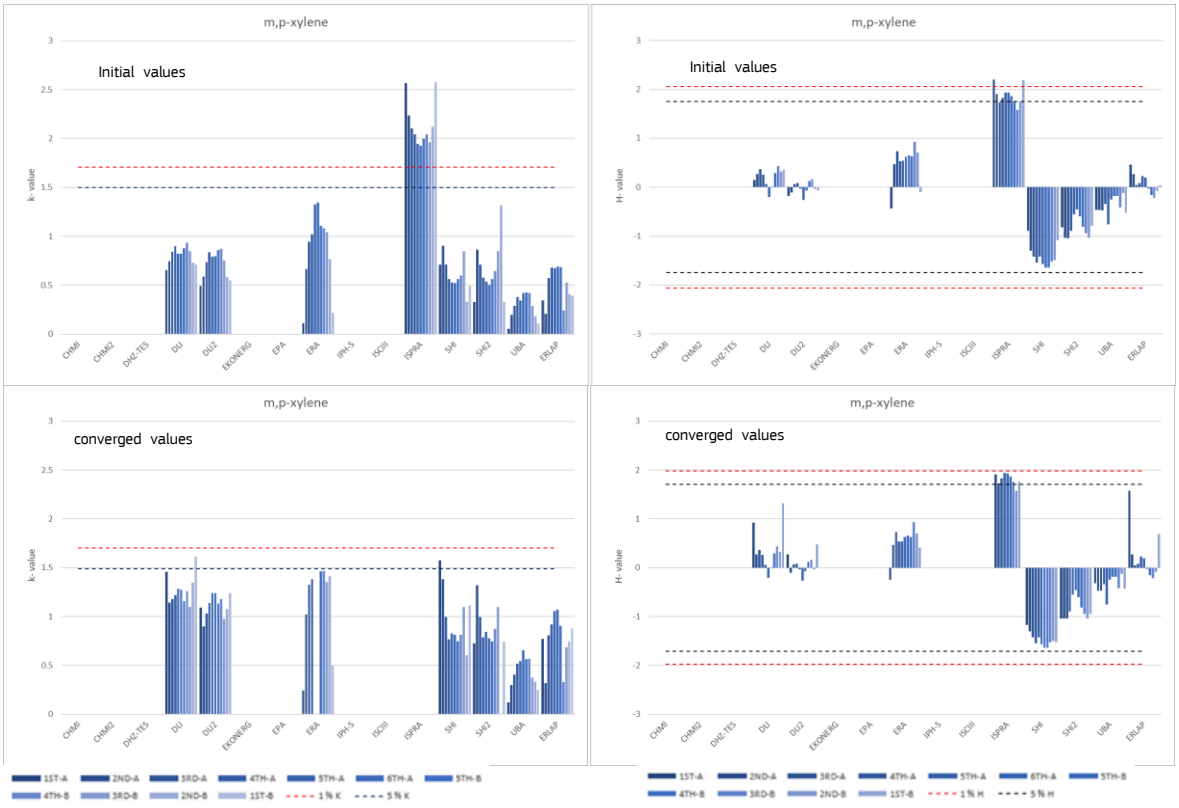
Source: JRC, 2023

Figure A 16. Ethyl-benzene: initial and converged h and k statistics



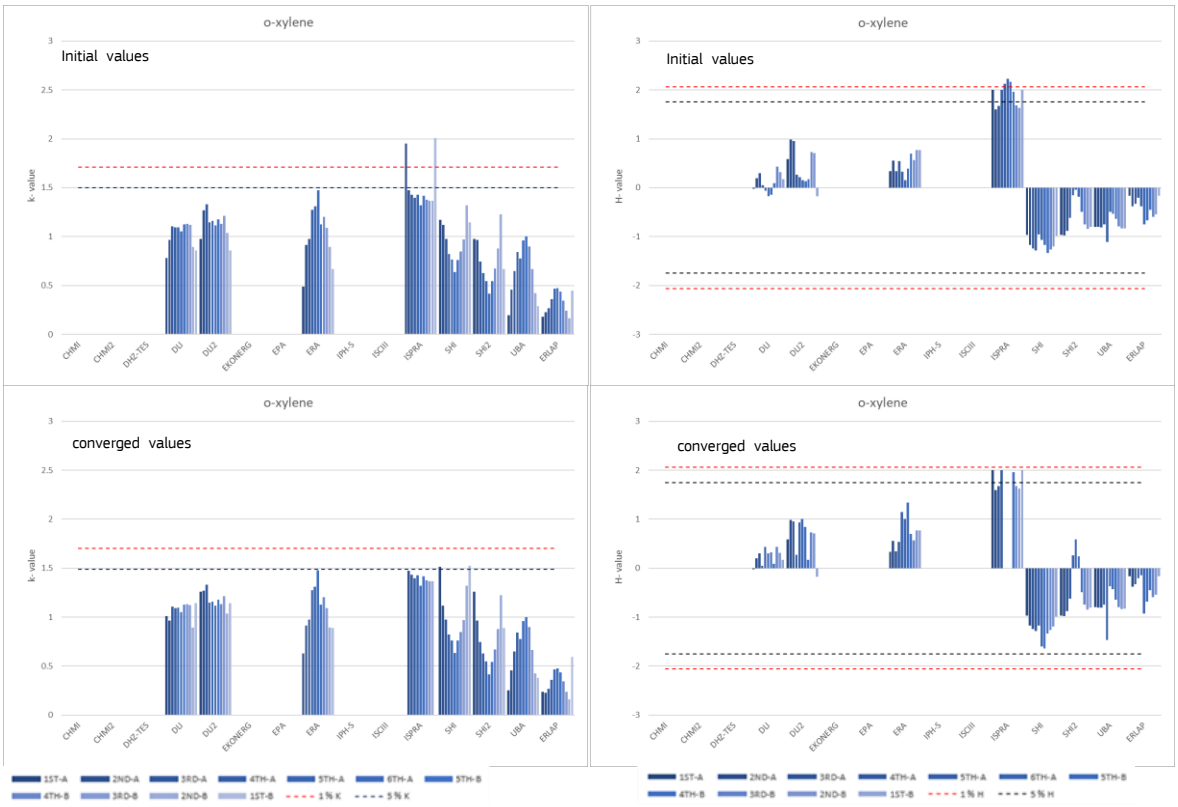
Source: JRC, 2023

Figure A 17. m,p-Xylene: initial and converged h and k statistics



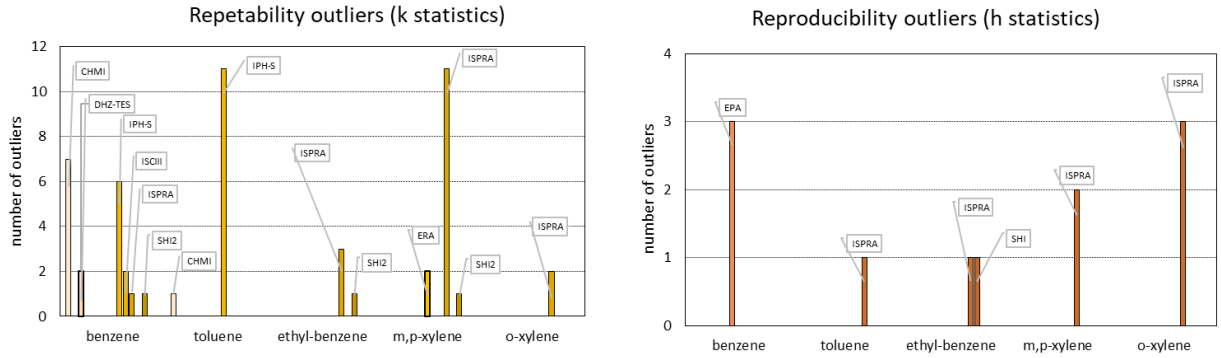
Source: JRC, 2023

Figure A 18. o-Xylene: initial and converged h and k statistics



Source: JRC, 2023

Figure A 19. Number of outliers identified by laboratory and compound after convergence



Source: JRC, 2023

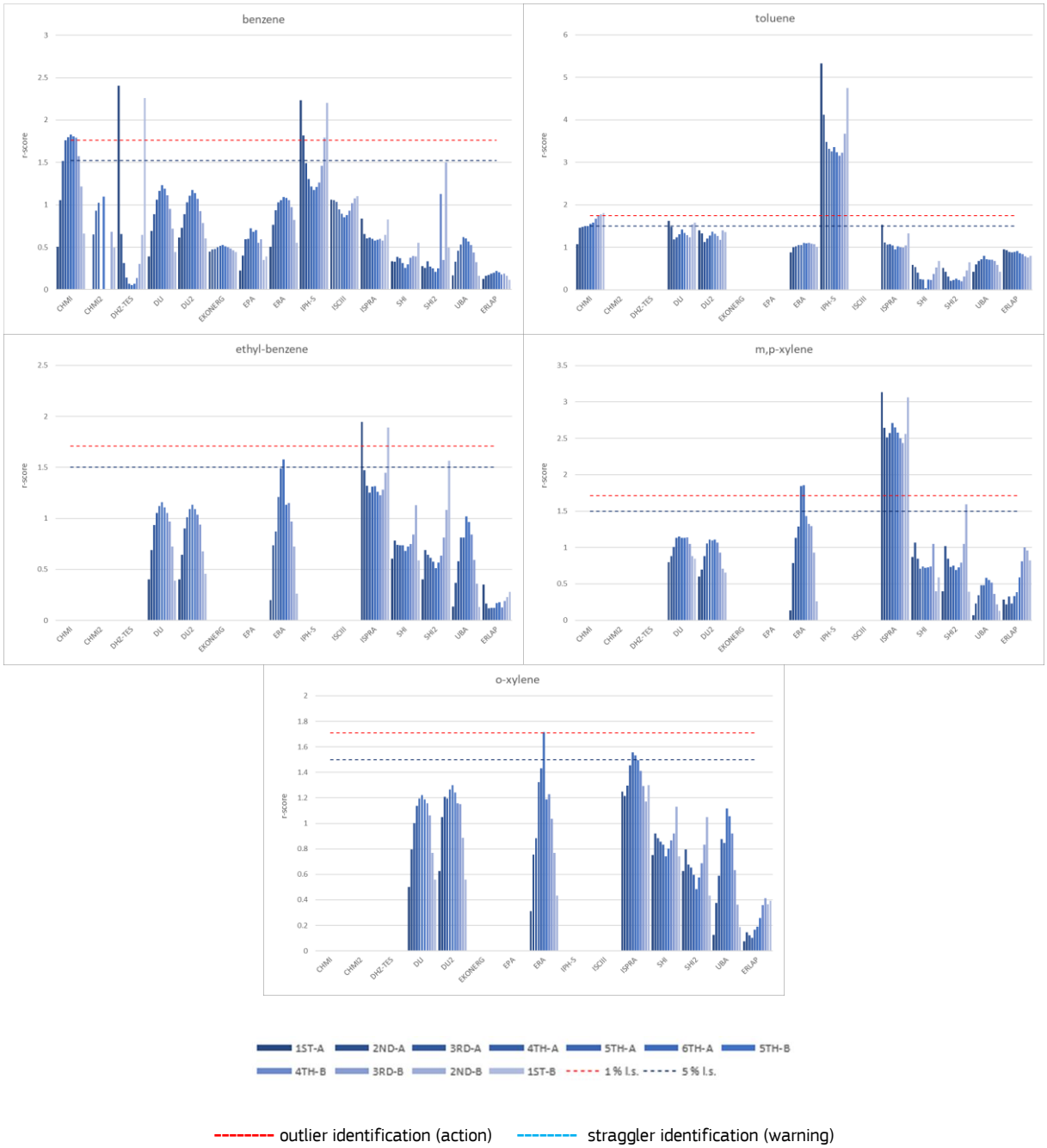
Table A 20. Removed outliers for the estimation of the repeatability and the reproducibility of the comparison exercise

	benzene		toluene		ethyl-benzene		m,p-xylene		o-xylene	
LEVEL	k-value	h-value	k-value	h-value	k-value	h-value	k-value	h-value	k-value	h-value
1st A	DHZ-TES, IPHS, ISCIII, ISPRA		IPHS		ISPRA		ISPRA	ISPRA	ISPRA	
2nd A	IPHS, ISCIII, SHI2	EPA	IPHS		ISPRA		ISPRA			
3rd A	CHMI, IPHS		IPHS	ISPRA			ISPRA			
4th A	CHM		IPHS				ISPRA			
5th A	CHM		IPHS				ISPRA, ERA			ISPRA
6th A	CHM		IPHS			ISPRA, SHI	ISPRA, ERA			ISPRA
5th B	CHM		IPHS				ISPRA			ISPRA
4th B	CHM	EPA	IPHS				ISPRA			
3rd B	CHM, IPHS	EPA	CHMI, IPHS				ISPRA			
2nd B	IPHS		IPHS				ISPRA,SHI2			
1st B	DHZ-TES, IPHS, ISPRA		IPHS		ISPRA,SHI2		ISPRA	ISPRA	ISPRA	

Source: JRC, 2023

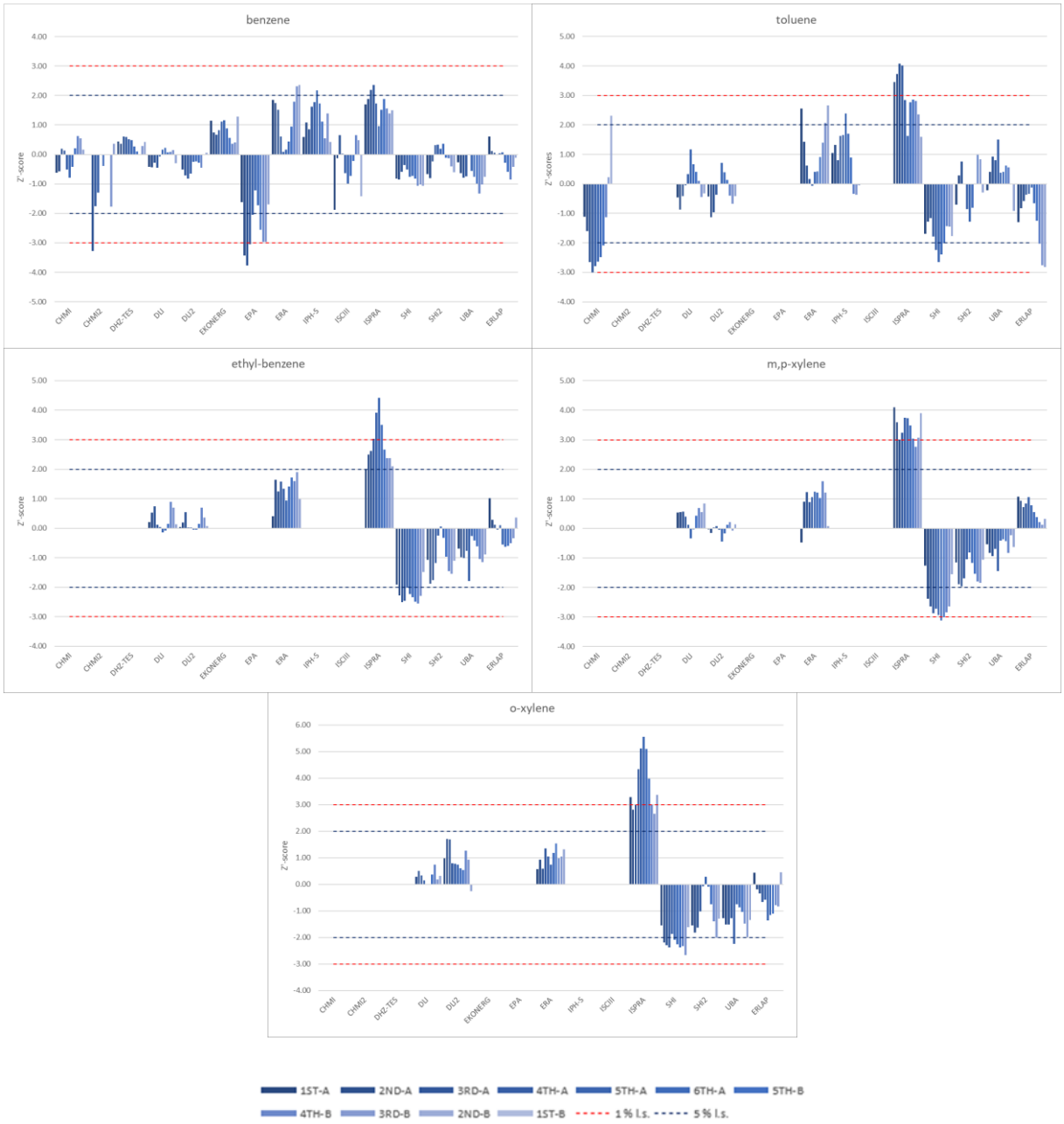
Annex 8. r score, Z' score and E_n score of the inter-laboratory comparison

Figure A 20. Repeatability score (r score) for the inter-laboratory comparison exercise



Source: JRC, 2023

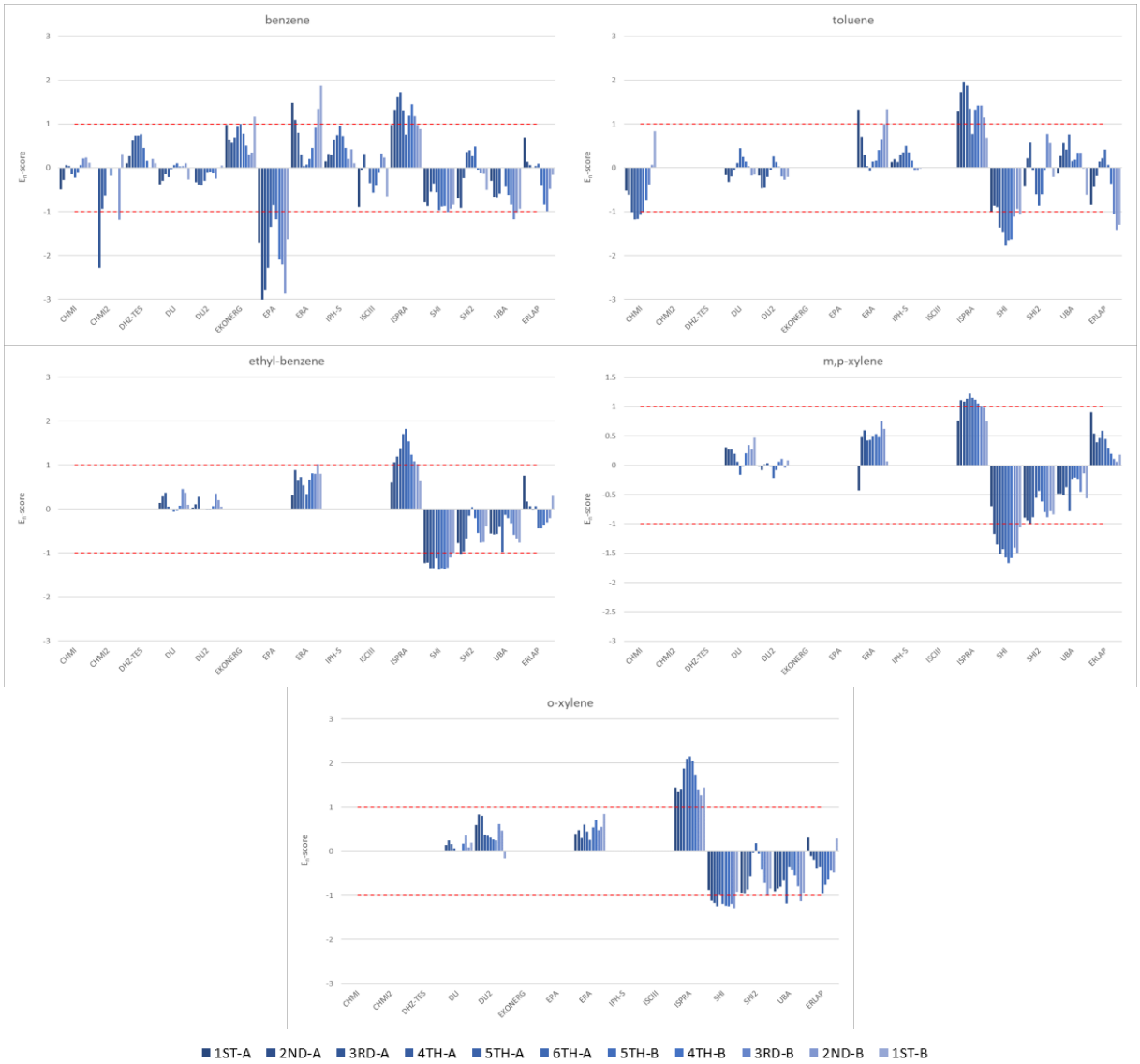
Figure A 21. Z' score for the inter-laboratory comparison exercise



outlier identification (action) straggler identification (warning)

Source: JRC. 2023

Figure A 22. E_n score for the inter-laboratory comparison exercise



Source: JRC, 2023

Annex 9. Analysers and method description: example of reporting sheet

Figure A 23. Reporting sheet

Participating Laboratory	Star Trek Enterprise Organic Laboratory				
Acronym	STEOL				
Person(s) responsible	Spock				
Contact e-mails:	SPOCK@ENTREPRISE.STARTREK				
Telephone contact:	.+5557722				
Characteristic of your BTEX analyser					
Trademark	SPECTRA				
Model:	GC -007				
Version:	ALFA				
Year of manufacture:	3016				
	Helium	Nitrogen	Hydrogen	Carbon dioxide	Air
Carrier gas:	---	YES	---	---	---
Other gases used:	---	---	---	---	YES
Operating system:	MICROSOLVE DOORS 3000				
	SECOND EDITION				
Cycle time, min:	15 min				
Adsorbent material:	TENAX GR 35-60 mesh (Length 8 cm)				
Sampling control	Piston - pump				
Sampling temperature, °C	Ambient temperature				
Sample volume, ml	100 mL				
Number of adsorbent tubes	1				
Desorption temperature, `					
Desorption time, sec					
Desorption flow, ml/min					
Cryo-trap detail	KRIPTONITE GR 35-60 mesh (Length 8 cm)				
Trapping temperature, °C	Ambient temperature				
Desorption temperature, °C	180 °C	Desorption time, sec	40 s		
Desorption flow, ml/min	1,5 mL/min	split flow, ml/min			
Stripper column	TTREK 555: 94% dimethylpolysiloxane- 6% cyanopropylphenyl ID 0,32 mm; Film 1,8				
Analytical column	Capillary column STAR TREK 624				
phase:	94% dimethylpolysiloxane - 6% cyanopropylphenyl				
length, m:	13 m				
diameter (ID) mm:	0,32 mm				
thickness (µm):	1,8 mm				
analytical conditions:	0 min-3 min at 50 °C; 3 min-6 min ramp at 20/3 °C/min; 6 min-11 min at 70 °C; 11 min-14 min ramp at 20/3 °C/min; 14 min-15 min at 50 °C				
Traceability of your calibration Standard					
Certified reference material (CRM):	Earth & Mars Institute (EMI)				
Certified by	Earth & Mars Institute (EMI)				
Certified number:	555 999				
Compound	Concentration, ppb (mol/mol)	Expanded Uncertainty, ±ppb(mol/mol)			
Benzene	500 x 10-9 mol/mol	± 15 x 10-9 mol/mol			
Toluene	487 x 10-9 mol/mol	± 15 x 10-9 mol/mol			
Ethyl-benzene	254 x 10-9 mol/mol	± 7 x 10-9 mol/mol			
m-Xylene	128 x 10-9 mol/mol	± 4 x 10-9 mol/mol			
p-Xylene	124 x 10-9 mol/mol	± 4 x 10-9 mol/mol			
o-Xylene	243 x 10-9 mol/mol	± 7 x 10-9 mol/mol			
Other methods					
Dilution of CRM	CALIBRATOR SPOCK MODEL 3000. RANGE 0 nmol/mol - 15 nmol/mol				
Static Injection					
Permeation					
Additional comments					

Source: Pérez Ballesta et al. EUR 30239 EN, 2020

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