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## ABSTRACT

### Interlaboratory Comparison 09/2017

Profstest SYKE carried out the interlaboratory comparison for TVOC thermodesorption measurements (ISO 16000-6) from native indoor air samples in Tenax TA thermodesorption tubes (IDA 09/17) in October-November 2017. 2EH (2-ethyl-1-hexanol), naphthalene, styrene, toluene, and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) measurements were also tested with synthetic sample. In total 10 participants took part in the intercomparison. In total 68 % of the participants reported satisfactory results, when deviation of 20–30 % from the assigned value was accepted. The calculated values were used as the assigned values for the synthetic sample for the results reported as compound specific responses. For the other measurands and samples the average of the results of the homogeneity measurements and the test results of the expert laboratory were used as the assigned value. The evaluation was based on the z scores.

Warm thanks to all the participants of this interlaboratory comparison!

**Keywords:** Interlaboratory comparison, ISO 16000-6, volatile organic compounds, TVOC, native sample, indoor air, synthetic sample

## TIIVISTELMÄ

### Laboratorioiden välinen vertailumittaus 09/2017

Profstest SYKE järjesti vertailumittauksen sisäilman VOC-määryksiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille loka-marraskuussa 2017 (IDA 09/2017). Vertailumittauksessa testattiin natiivinäytteestä kerättyjen TVOC yhdisteiden määritysten vertailtavuutta Tenax TA-termodesorptioputkista sekä synteettisen näytteen 2EH (2-etyyli-1-heksanoli), naftaleeni, styreeni, tolueneeni ja TXIB (2,2,4-trimetyyli-1,3-pentaanidioli di-isobutyraatti) määritysten vertailtavuutta. Pätevyyskokeeseen osallistui yhteensä 10 laboratoriota. Koko tulosaineistossa hyväksyttävää tuloksia oli 68 %, kun vertailuarvosta sallittiin 20–30 % poikkeama 95 % luottamusväkillä. Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella raportoiduille tuloksille. Muille testisuureille ja näytteille käytettiin homogeenisuusmääritystulosten sekä asiantuntijalaboratorion kierroskohtaisen tuloksen keskiarvoa. Osallistujien pätevyyden arviointi tehtiin z-arvon avulla.

Kiitos vertailumittauksen osallistujille!

**Avainsanat:** vertailumittaus, haihtuvat orgaaniset yhdisteet, ISO 16000-6, TVOC, natiivinäyte, synteettinen näyte, sisäilma

## SAMMANDRAG

### Interkalibrering 09/2017

Profstest SYKE genomförde i oktober-november 2017 en interkalibrering av omfattade bestämningen av Tenax TA-termodynamiska rör som används för inomhus VOC mätningar (ISO 16000-6). I kompetensprovningen testades analyserna jämförbarheten av halten TVOC-ämnen som samlats från nativa prover i Tenax TA-termodynamiska rör samt jämförbarheten av halten av 2EH (2-etyl-1-hexanol), naftalen, styren, toluen och TXIB (2,2,4-trimetyl-1,3-pentandioldiisobutytrat) som samlats från syntetiska prov. Totalt 10 deltagare deltog i interkalibreringen. Som referensvärde för de syntetiska provernas ämnesspecifika resultat användes beräkningskoncentrationerna. För övriga prov och mätstorheter användes som referensvärde medelvärden av expertlaboratoriets homogenitetsanalysresultat och testresultat. Resultaten värderades med hjälp av z värden. I kompetensprovningen var 68 % av alla resultaten acceptabla, när en total deviation på 20–30 % från referensvärdet tilläts.

Ett varmt tack till alla deltagarna i testet!

**Nyckelord:** interkalibrering, flyktiga föreningar, ISO 16000-6, TVOC, nativa prov, syntetisk prov, inomhusluft



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# 1 Introduction

Profest SYKE carried out the interlaboratory comparison (ILC) for TVOC thermodesorption measurements (ISO 16000-6 [1]) from native indoor air samples in Tenax TA thermodesorption tubes (IDA 09/17) in October-November 2017. Also 2EH (2-ethyl-1-hexanol, CAS No 104-76-7), naphthalene (CAS No 91-20-3), styrene (CAS No 100-42-5), toluene (CAS No 108-88-3), and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate, CAS No 6846-50-0) measurements were tested with the synthetic sample.

Finnish Environment Institute (SYKE) is the appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This interlaboratory comparison provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The interlaboratory comparison was carried out in accordance with the international guidelines ISO/IEC17043 [2], ISO 13528 [3] and IUPAC Technical report [4]. The Profest SYKE has been accredited by the Finnish Accreditation Service (FINAS) as a proficiency testing provider (PT01, ISO/IEC 17043, [www.finas.fi/sites/en](http://www.finas.fi/sites/en)). This interlaboratory comparison has not been carried out under the accreditation scope of the Profest SYKE.

## 2 Organizing the interlaboratory comparison

### 2.1 Responsibilities

#### **Organizer:**

Profest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre  
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Phone: +358 295 251 000  
Email: [proftest@environmenti.fi](mailto:proftest@environmenti.fi)

#### **The responsibilities in organizing the interlaboratory comparison were as follows:**

Mirja Leivuori	coordinator
Riitta Koivikko	substitute of coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

#### **The co-operation partner was:**

Finnish Institute of Occupational Health (FIOH)  
Tapani Tuomi, Product Manager,  
Analytical expert: Hanna Hovi

### **Subcontracting:**

Sample preparation and VOC measurements carried out by the Finnish Institute of Occupational Health (FIOH, accredited by FINAS T013, [www.finas.fi/sites/en](http://www.finas.fi/sites/en)).

## 2.2 Participants

In total 10 participants took part in this interlaboratory comparison. Eight of these were from Finland and two from other European countries (Appendix 1).

Nine out of ten of the participants used accredited analytical methods for at least part of the measurements. The samples were prepared and tested at the laboratory of Finnish Institute of Occupational Health and their participant code is 8 in the result tables.

## 2.3 Samples and delivery

Participants received following samples:

- Synthetic sample (IDA1Synt)
- Blank sample (IDA2Blank)
- Two native indoor air samples (IDA3TVOC) for TVOC analysis, collected from the chamber filled with building material. The results were processed as parallel results. In this intercomparison test the used chamber samples were collected from two sample batches (marked as B1 and B2).
- Blank chamber sample (IDA4Blank)

The synthetic sample was prepared gravimetrically in the laboratory of the Finnish Institute of Occupational Health. The concentrations of measurands in the synthetic sample were set taking into account the Finnish action limit presented in the decree of the Ministry of Social Affairs and Health [4]. The chamber samples (sample batch B1 and B2) were collected from emissions of building material with different coating materials. The sample preparation is described in details in the Appendix 2.

The samples were delivered on 17 October 2017 and they arrived to the participants mainly on the following day.

The samples were requested to be measured and the results to be reported latest on 25 September 2017. Two participants delivered the results one day later. The preliminary results were delivered to the participants via ProfTestWEB and email on 2 October 2017.

The results were mainly reported latest on 10 December 2017 as requested. One participant reported the results one day later due to the measurements problems. The preliminary results were delivered to the participants on 21 November 2017. The participants were requested to return the Tenax TA thermodesorption tubes to the provider latest on 24 November 2017. All participants returned the tubes to the provider within the given timetable. The provider warmly thanks all participants for the promptly returned sample tubes.

## 2.4 Homogeneity and stability

Homogeneity of the synthetic sample IDA1Synt was tested by measuring the reference compound response factors (RCRF) for 2EH, naphthalene, styrene, toluene, and TXIB from five subsamples (Appendix 3). Homogeneity of IDA3TVOC samples was tested by measuring TVOC as toluene equivalent (TE) from six samples for the batch B1 and from ten samples for the batch B2. In the calculations the samples collected from the same duct adapter were treated as parallel samples making three parallel measurements for the sample batch B1 and five parallel measurements for the sample batch B2 (Appendix 3). As the samples are known to be stable the reported test result of the expert laboratory was added to the homogeneity testing calculations as well as for the final evaluation of the homogeneity and stability of the synthetic and chamber samples. According to the homogeneity test results, all samples were considered homogenous. Furthermore, based on the data handling the samples were considered stable.

## 2.5 Feedback from the interlaboratory comparison

The feedback from the interlaboratory comparison is shown in Appendix 4. The comments from the participants mainly dealt with participants' reporting errors and comments or questions to the technical implementation of the interlaboratory comparison. The comments from the provider mainly focused on the lack of measurement uncertainties, the reported zero values for blank samples as well as on the lack of conversancy with information provided with the samples. All feedback is valuable and is exploited when improving the activities.

## 2.6 Processing the data

### 2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. Prior to the statistical results handling some outliers were rejected if the result differed from the data more than  $s_{rob} \times 5$  or 50 % from the robust mean. If the result was reported as lower than detection limit, it has not been included in calculations.

More information about the statistical handling of the data is available in the Guide for participant [6].

### 2.6.2 Assigned values

The calculated values were used as the assigned values for the measurands in the synthetic sample reported as compound responses (IDA1Synt, RCRF). The synthetic sample was prepared gravimetrically. For the other measurands and samples the average of the results of the homogeneity test and the test result of the expert laboratory was used as the assigned value. The expert laboratory integrated the TVOC area and deleted the background as described in ISO16000-6 [1].

For the calculated assigned values the expanded measurement uncertainty was estimated using standard uncertainties associated with individual operations involved in the gravimetric preparation of the sample. When the mean of the expert laboratory's results was used as the assigned value, the uncertainty was calculated using the standard deviation [3, 6].

For the calculated assigned values the standard uncertainties were between 1.2 % and 2.7 % for the results based on compound responses (RCRF) and between 1.6 % and 6.3 % for the results based on toluene equivalent (TE). For the samples using the mean value of the expert laboratory's results as the assigned value for TVOC<sub>Lab</sub> and TVOC<sub>Guide</sub>, the standard uncertainties of the assigned were lower or equal to 10 % ( $\leq 10\%$ , Appendix 5).

**After reporting the preliminary results no changes have been done for the assigned values.**

### 2.6.3 Standard deviation for proficiency assessment and z score

The standard deviation for proficiency assessment was estimated on the basis of the measurand concentration, the results of homogeneity and stability tests and the uncertainty of the assigned value. The standard deviation for the proficiency assessment ( $2 \times s_{pt}$ , at the 95 % confidence level) was set to 20–25 % for the synthetic sample and for the chamber samples to 30 %. After reporting the preliminary results **no changes have been done for the standard deviations of the proficiency assessment values.**

The reliability of the assigned value for the other test items than the synthetic sample as compounds response was tested according to the criterion  $u_{pt} / s_{pt} \leq 0.3$ , where  $u_{pt}$  is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value ( $U_{pt}$ ) divided by 2) and  $s_{pt}$  is the standard deviation for proficiency assessment [3,4]. When testing the reliability of the assigned value the criterion was fulfilled in the every case and the assigned values were considered reliable.

## 3 Results and conclusions

### 3.1 Results

The summary of the results of this interlaboratory comparison is presented in Table 1. Explanations to terms used in the result tables are presented in Appendix 6. The results and the performance of each participant are presented in Appendix 7. The reported results with their expanded uncertainties ( $k=2$ ) are presented in Appendix 8. The summaries of the z scores are shown in Appendix 9 and the z scores in the ascending order in Appendix 10.

The robust standard deviation for the results of the synthetic sample (IDA1Synt) varied from 21 to 33% and for the chamber sample (IDA3TVOC) varied from 21 to 25 % (Table 1).

Table 1. The summary of the results in the interlaboratory comparison IDA 09/2017.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	S <sub>rob</sub>	S <sub>rob</sub> %	2 x S <sub>pt</sub> %	n (all)	Acc z %
2EH <sub>R<sub>CRF</sub></sub>	IDA1Synt	ng/sample	60.0	54.9	54.9	54.0	12.6	23.0	20	9	67
	IDA2Blank	ng/sample		2.66	2.66	1.54	3.37	-	-	9	-
2EH <sub>TE</sub>	IDA1Synt	ng/sample	44.3	42.5	40.9	40.3	10.9	26.7	20	10	50
	IDA2Blank	ng/sample		1.55	1.09	-	1.89	-	-	9	-
Naphthalen <sub>R<sub>CRF</sub></sub>	IDA1Synt	ng/sample	54.1	56.0	54.6	56.3	14.5	26.6	20	9	67
	IDA2Blank	ng/sample		0.15	0.05	-	0.10	-	-	9	-
Naphthalen <sub>TE</sub>	IDA1Synt	ng/sample	79.6	82.0	81.1	79.4	17.5	21.6	20	10	60
Styrene <sub>R<sub>CRF</sub></sub>	IDA1Synt	ng/sample	270	256	256	273	57	22.5	20	9	67
	IDA2Blank	ng/sample		0.25	0.05	-	0.10	-	-	9	-
Styrene <sub>TE</sub>	IDA1Synt	ng/sample	260	265	259	260	54	20.7	20	10	70
	IDA2Blank	ng/sample		0.06	-	-	-	-	-	9	-
Toluene <sub>R<sub>CRF</sub></sub>	IDA1Synt	ng/sample	60.6	65.1	64.7	64.0	10.8	16.7	20	10	70
	IDA2Blank	ng/sample		1.20	0.31	-	0.49	-	-	10	-
TXIB <sub>R<sub>CRF</sub></sub>	IDA1Synt	ng/sample	64.9	55.4	55.4	57.1	13.2	23.9	20	9	67
	IDA2Blank	ng/sample		0.37	0.06	-	0.12	-	-	9	-
TXIB <sub>TE</sub>	IDA1Synt	ng/sample	75.7	72.8	69.8	69.6	23.0	32.9	25	10	50
	IDA2Blank	ng/sample		0.33	-	-	-	-	-	9	-
TVOC <sub>Guide</sub>	IDA3TVOC_B1	µg/m3	177	191	189	192	47	24.9	30	9	78
	IDA3TVOC_B2	µg/m3	161	139	-	139			30	2	100
	IDA4Blank	µg/m3	7.90	12.85	12.02	7.90	11.58	-	-	11	-
TVOC <sub>Guide</sub> -Chamber blank	IDA3TVOC_B1	µg/m3	168	178	176	161	43	24.5	30	9	78
	IDA3TVOC_B2	µg/m3	151	134	-	134			30	2	100
TVOC <sub>Lab</sub>	IDA3TVOC_B1	µg/m3	177	185	195	183	41	20.9	30	9	78
	IDA3TVOC_B2	µg/m3	161	139	-	139	-	-	30	2	100
	IDA4Blank	µg/m3	8.0	14.0	12.9	8.00	10.14	78.5	-	11	-
TVOC <sub>Lab</sub> -Chamber blank	IDA3TVOC_B1	µg/m3	168	160	182	160	44	24.0	30	9	67
	IDA3TVOC_B2	µg/m3	151	134	-	134	-	-	30	2	100

Rob. mean: the robust mean, s<sub>rob</sub>: the robust standard deviation, s<sub>rob</sub> %: the robust standard deviation as percent, 2×s<sub>pt</sub> %: the standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where  $|z| \leq 2$ , n(all): the total number of the participants.

## 3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the ILC. A questionnaire related to the used analytical methods was provided along the interlaboratory comparison. The summary of the answers is shown in Appendix 11. The used analytical methods and the results of the participants grouped by methods are shown in more detail in Appendix 12. The statistical comparison of the analytical methods was possible for the data where the number of the results was  $\geq 5$ . However, in this ILC there were not enough results for statistical comparison. Thus, the comparison is based on the graphical result evaluation.

### 3.2.1 Background questionnaire and identified TVOC compounds

In the background questionnaire the participants were given a list of selected VOC compounds and they were requested to report which compounds could be identified from the TVOC sample (Appendix 11). Based on the answers it could be concluded e.g. how well the highly volatile and low boiling point compounds are trapped in the cold trap, if the temperature of the cold trap is above zero or if there is some errors in the reporting of the flow rate of carrier gas, as for the GC/MS it is usually lower than 2 ml/min.

Most of the listed compounds were identified quite well, also the compounds with lower concentrations. The expert laboratory (participant 8) reported 14 identified compounds, which concentration as compounds own response (RCRF) was higher than  $> 1 \mu\text{g}/\text{m}^3$ . One participant reported all the same compounds as the expert laboratory. The other participants reported 7–11 of the compounds identified by the expert laboratory. It is noticeable that many participants reported also many other compounds from the given list (Appendix 11). However, some of the participants did not identify 1-Butanol (1 participant), 1,2-Propanediol (6 participants) or Texanol (3 participants), which can be considered to be quite common VOC compounds in indoor air samples.

### 3.2.2 Synthetic sample - methods and results as toluene equivalent and compound specific response

For measurements of the synthetic sample (IDA1Synt) mainly TD-GC-MS instruments were used. Two participants used a TD-GC-FID/MS instrument for at least part of the results. The used analytical methods of the participants and results are shown in more detail in Appendix 12. Based on the visual estimation of the results no clear differences between the used analytical methods can be concluded.

In the interlaboratory comparison the participants were requested to report the results for the synthetic sample based on the compound specific response (RCRF) and toluene equivalent (TE). Seven participants reported the first ones and eight participants the latter ones (Appendix 12). The reported results are shown in Table 2 with the calculated ratio of compound specific response results and toluene equivalent results (RCRF/TE). Based on the results variability in the ratio could be observed depending on participant and measured compounds.

Table 2. Participant results for the synthetic sample (IDA1Synt) reported as compound responses (RCRF) and toluene equivalents (TE) with the ratios of these two results (RCRF/TE).

Participant	RCRF (ng/sample)	TE (ng/sample)	Ratio RCRF/TE	Participant	RCRF (ng/sample)	TE (ng/sample)	Ratio RCRF/TE
2EH (2-ethyl-1-hexanol)				Styrene			
1	63.3	32.5	1.95	1	272.5	273.6	1.00
2	35.6	45.2	0.79	2	190.5	206.8	0.92
3	-	38.6	-	3	-	241.7	-
4	72.8	72.8	1.00	4	333	399	0.83
5	49.7	36.3	1.37	5	216	221	0.98
6	63.74	54.15	1.18	6	296.55	304.15	0.98
7	49	42	1.17	7	277	290	0.96
8	59.66	43.75	1.36	8	235.05	247.04	0.95
9	46	32.6	1.41	9	188	185	1.02
10	53.96	26.9	2.01	10	292	278.7	1.05
Naphthalene				TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate)			
1	56.3	80.1	0.70	1	62.3	72	0.87
2	35.9	90.3	0.40	2	36.8	73.6	0.50
3	-	75.9	-	3	-	94.4	-
4	89.2	116	0.77	4	73.4	51.4	1.43
5	38.8	57.5	0.67	5	42.4	54.4	0.78
6	48.72	98.8	0.49	6	48.48	134	0.36
7	64	86	0.74	7	60	86	0.70
8	56.3	75.7	0.74	8	52.06	67.1	0.78
9	50.9	60.7	0.84	9	66.4	51.3	1.29
10	64.27	78.62	0.82	10	57.07	43.53	1.31

The ratio varied between 0.79 and 2.01 for 2EH, 0.40 and 0.84 for Naphthalene, 0.83-1.05 for Styrene, and between 0.36-1.43 for TXIB (Table 2). The results varied 1.3-4 times between participants depending on the measured compound. Based on these results it seems to be highly difficult to estimate one single conversion factor to convert the result from compound response to toluene equivalent or vice versa.

### 3.2.3 Chamber samples - methods and calculation of TVOC

For the chamber samples (IDA3TVOC\_B1 and \_B2) mainly TD-GC-MS instrument was used for the measurements. Two participants used TD-GC-FID/MS instrument. The used analytical methods of the participants and results are shown in more detail in Appendix 12. Based on the visual estimation of the results no clear difference between the used analytical methods can be concluded.

The participants were requested to report TVOC results (toluene equivalents, TE) using their own method of calculation (TVOC<sub>Lab</sub>) and the method described by the organizer (TVOC<sub>Guide</sub>) (Appendix 12).

The calculations for TVOC<sub>Guide</sub> as a toluene equivalent were requested to be reported according to the following instructions based on ISO 16000-6 [1] as well as on the observed interferences from the test tubes (observed during pretesting):

#### 1. Sample IDA4Blank:

The TVOC<sub>Guide</sub> for the chamber blank had to be calculated as the sum of the concentrations of the identified and unidentified volatile organic compounds, as  $\mu\text{g}/\text{m}^3$ , between *n*-hexane (CAS

110-54-3) and *n*-hexadecane (CAS 544-76-3), including *n*-hexane and *n*-hexadecane to the sum. The results was reported in unit  $\mu\text{g}/\text{m}^3$  and calculated as toluene equivalent. As the laboratory had only a few tubes in use, the sum of potentially recognized diethyl phthalate (CAS 84-66-2) and hexamethylcyclotrisiloxane (CAS 541-05-09) within the TVOC area had to be reduced from the total area.

## 2. Sample IDA3TVOC:

The TVOC<sub>Guide</sub> for the chamber sample had to be calculated as the sum of the concentrations of the identified and unidentified volatile organic compounds, as  $\mu\text{g}/\text{m}^3$ , between *n*-hexane (CAS 110-54-3) and *n*-hexadecane (CAS 544-76-3), including *n*-hexane and *n*-hexadecane to the sum. The results was reported in unit  $\mu\text{g}/\text{m}^3$  and calculated as a toluene equivalent. As the laboratory had only a few tubes in use, the sum of potentially recognized diethyl phthalate (CAS 84-66-2) and hexamethylcyclotrisiloxane (CAS 541-05-09) within the TVOC area had to be reduced from the total area.

## 3. TVOC<sub>Guide</sub>-Chamber blank calculation:

The TVOC<sub>Guide</sub> for the chamber sample had to be calculated according to the instructions given above for the IDA3TVOC and the sum of volatile organic compounds (chamber blank) had to be reduced in the sample IDA4Blank as instructed above.

Table 3. The results for TVOC measurements based on the participants' own method (TVOC<sub>Lab</sub>) of calculation and based on the instructions of the provider (TVOC<sub>Guide</sub>) with and without the result of chamber blank.

Participant	Sample	Measurand	Result ( $\mu\text{g}/\text{m}^3$ )	Measurand	Result ( $\mu\text{g}/\text{m}^3$ )
1	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	178	TVOC <sub>Guide</sub>	194
		TVOC <sub>Lab</sub> -Chamber blank	178	TVOC <sub>Lab</sub>	194
2	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	600	TVOC <sub>Guide</sub>	631
		TVOC <sub>Lab</sub> -Chamber blank	600	TVOC <sub>Lab</sub>	631
3	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	213	TVOC <sub>Guide</sub>	218
		TVOC <sub>Lab</sub> -Chamber blank	224	TVOC <sub>Lab</sub>	229
4	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	155	TVOC <sub>Guide</sub>	192
		TVOC <sub>Lab</sub> -Chamber blank	155	TVOC <sub>Lab</sub>	192
5	IDA3TVOC_B2	TVOC <sub>Guide</sub> -Chamber blank	115	TVOC <sub>Guide</sub>	121
		TVOC <sub>Lab</sub> -Chamber blank	115	TVOC <sub>Lab</sub>	121
6	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	135	TVOC <sub>Guide</sub>	135
		TVOC <sub>Lab</sub> -Chamber blank	160	TVOC <sub>Lab</sub>	174
7	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	215	TVOC <sub>Guide</sub>	223
		TVOC <sub>Lab</sub> -Chamber blank	160	TVOC <sub>Lab</sub>	169
8	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	148	TVOC <sub>Guide</sub>	156
		TVOC <sub>Lab</sub> -Chamber blank	148	TVOC <sub>Lab</sub>	156
9	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	257	TVOC <sub>Guide</sub>	277
		TVOC <sub>Lab</sub> -Chamber blank	257	TVOC <sub>Lab</sub>	277
10	IDA3TVOC_B1	TVOC <sub>Guide</sub> -Chamber blank	161	TVOC <sub>Guide</sub>	167
		TVOC <sub>Lab</sub> -Chamber blank	161	TVOC <sub>Lab</sub>	167
11	IDA3TVOC_B2	TVOC <sub>Guide</sub> -Chamber blank	153	TVOC <sub>Guide</sub>	158
		TVOC <sub>Lab</sub> -Chamber blank	153	TVOC <sub>Lab</sub>	194



The calculated TVOC results, both the result by participants' own calculation method (TVOC<sub>Lab</sub>) and the result by instructed calculation method (TVOC<sub>Guide</sub>), are shown in Table 3. The results are shown with and without subtracting the result of chamber blank. The results are mostly same with both calculation methods. However, three participants have different results with their own method and with the instructed method (Table 3).

### 3.3 Uncertainties of the results

At maximum 90 % of the participants reported the expanded measurement uncertainties ( $k=2$ ) with their results for at least some of their results (Table 4, Appendix 13). For TVOC results only 60 % of the participants reported the expanded measurement uncertainties. The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used to estimate the measurement uncertainty (Appendix 13). The most used approach was based on method validation data and IQC data from both synthetic sample and routine sample replicates. One participant used modelling approach. For the estimation of uncertainties the MUKIT measurement uncertainty software is available, but it was not used in the estimations [7]. The free software is available in the webpage: [www.syke.fi/envical/en](http://www.syke.fi/envical/en). Generally, the used approach to estimate the measurement uncertainty did not make definite impact on the uncertainty estimates. However, the estimated uncertainties based on the modelling approach seemed to be underestimated (Appendix 13).

The estimated uncertainties varied for the tested measurements (Table 4). Especially, very low or high uncertainties can be considered questionable. It is evident that harmonization is still needed for the estimation of the expanded measurement uncertainties. The expanded uncertainties for TVOC measurements of the expert laboratory were under revalidation during the time of the interlaboratory comparison, thus not reported with the results. The re-estimated expanded measurement uncertainties of the expert laboratory are 50 % for the TVOC measurements.

Table 4. The range of the expanded measurement uncertainties ( $k=2$ ,  $U_i\%$ ) reported by the participants.

Measurement	IDA1Synt / IDA3TVOC_B1
2EH <sub>R</sub> CRF	8.92-38
2EH <sub>T</sub> E	2.36-38
Naphthalene <sub>R</sub> CRF	5.09-40
Naphthalene <sub>T</sub> E	2.36-50
Styrene <sub>R</sub> CRF	2.79-46
Styrene <sub>T</sub> E	2.36-50
Toluene <sub>R</sub> CRF	2.36-50
TXIB <sub>R</sub> CRF	16.7-43
TXIB <sub>T</sub> E	2.36-43
TVOC <sub>Guide</sub>	25-40
TVOC <sub>Guide</sub> -Chamber blank	25-40
TVOC <sub>Lab</sub>	25-40
TVOC <sub>Lab</sub> -Chamber blank	25-40

## 4 Evaluation of the results and recommendations

The evaluation of participants was based on the z scores, which were interpreted as follows:

Criteria	Performance
$ z  \leq 2$	Satisfactory
$2 <  z  < 3$	Questionable
$ z  \geq 3$	Unsatisfactory

In total, 68 % of the results evaluated based on z scores were satisfactory (Appendix 9) when accepted deviation from the assigned value was 20–30 % at the 95 % confidence level. About 90 % of the participants used the accredited methods in some of the measurements and 78 % of their results were satisfactory.

The summary of the performance evaluation is shown in Table 5. The percentage of the satisfactory results varied between 67 % and 100 % for the tested sample types. The overall performance for the synthetic sample (IDA1Synt) was somewhat better for the results based on the compounds own response (RCRF) than based on toluene equivalent (TE, Table 5). Overall performance was quite low (58–67 %) for the synthetic sample. For the chamber sample IDA3TVOC\_B1 the performance was slightly better (72–78 %). Noticeable is that the performance based on estimation of TVOC based on participants' calculations was lower than based on the provider's instructed calculation.

Table 5. Summary of the performance evaluation in the interlaboratory comparison IDA 09/2017.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value at 95 % confidence level (%)	Remarks
IDA1Synt, RCRF	67	20	<ul style="list-style-type: none"> <li>Difficulties in measurements for some of the participants.</li> </ul>
IDA1Synt, TE	58	20–25	<ul style="list-style-type: none"> <li>Difficulties in measurements for some of the participants.</li> </ul>
IDA3TVOC_B1 (Guide)	78	30	<ul style="list-style-type: none"> <li>Difficulties in measurements for some of the participants.</li> </ul>
IDA3TVOC_B1 (Lab)	72	30	<ul style="list-style-type: none"> <li>Difficulties in measurements for some of the participants.</li> </ul>
IDA3TVOC_B2 (Guide and Lab)	100	30	<ul style="list-style-type: none"> <li>Only two participants</li> </ul>

### Some recommendations

Based on the results of this interlaboratory comparison some recommendations for the measurements of volatile organic compounds from the indoor air samples are given:

- There were significant differences between the results expressed as toluene equivalents and the results expressed based on compounds' own responses e.g. calibration is based on pure compounds. Each compound has its own response and, therefore, the quantities are not exact if the response of another compound is used for calculations. Consequently, the limit values, or the action limits, given by the official authorities or expert organizations should, when possible, be based on analytical responses of pure compounds, and not e.g. toluene equivalents. And, vice versa, the calibrations and calculations of the laboratories should be based on pure compounds. After that the laboratory results and the limit values or the action limits are comparable and reliable.
- As recommended in the standard ISO 16000-6 [1], the TVOC value of the indoor air samples can be analyzed either by using FID or MS (EI) detection. In this test, no differences were observed between the results achieved with different detectors. Nevertheless, in this interlaboratory comparison only two participants used FID detection, other participants used MS (EI) detection.
- Also, based on ISO 16000-6 [1], it would be recommended to increase the number of pure compounds in calibrations, since some of the participants failed to identify many common indoor air compounds.

## 5 Summary

Profest SYKE carried out the interlaboratory comparison for TVOC thermodesorption measurements (ISO 16000-6) from native indoor air samples in Tenax TA thermodesorption tubes (IDA 09/17) in October-November 2017. Also 2EH (2-ethyl-1-hexanol, CAS No 104-76-7), naphthalene (CAS No 91-20-3), styrene (CAS No 100-42-5), toluene (CAS No 108-88-3), and TXIB (2, 2, 4-trimethyl-1,3-pentanediol diisobutyrate, CAS No 6846-50-0) measurements were tested in the synthetic sample. In total 10 participants took part in the intercomparison.

The calculated value was used as the assigned value for the measurands of the synthetic sample reported as compound specific responses. For the other measurands and samples the average of the results of the homogeneity measurements and the test results of the expert laboratory were used as assigned value. For synthetic sample the standard uncertainties of the assigned values were between 1.2 % and 2.7 % for results based on compound specific responses (RCRF) and between 1.6 % and 6.3 % for results based on toluene equivalent (TE). For the chamber samples using the mean value of the expert laboratory's result as the assigned value for  $TVOC_{Lab}$  and  $TVOC_{Guide}$ , the standard uncertainties of the assigned were lower or equal to 10 %.

The evaluation of the performance was based on the z scores. In this interlaboratory comparison 68 % of the data was regarded to be satisfactory when the result was accepted to

deviate from the assigned value from 20 to 30 % at 95 % confidence level. About 90 % of the participants used accredited methods and 78 % of their results were satisfactory. In the interlaboratory comparison the participants were requested to report the results for the synthetic sample based on the compound specific response and toluene equivalent. Based on these results it seems to be highly difficult to estimate one single conversion factor to convert the result from compound response to toluene equivalent or vice versa.

## 6 Summary in Finnish

Profest SYKE järjesti vertailumittauksen sisäilman VOC-määrittäjiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille loka-marraskuussa 2017 (IDA 09/2017). Vertailumittauksessa testattiin natiivinäytteestä kerättyjen TVOC yhdisteiden määrittästen vertailtavuutta Tenax TA-termodesorptioputkista sekä synteettisen näytteen 2EH (2-etyyli-1-heksanoli, CAS No 104-76-7), naftaleeni (CAS No 91-20-3), styreeni (CAS No 100-42-5), tolueni (CAS No 108-88-3) ja TXIB (2,2,4-trimetyyli-1,3-pentaanidioli di-isobutyyraatti, CAS No 6846-50-0) määrittästen vertailtavuutta. Vertailumittaukseen osallistui yhteensä 10 laboratoriota.

Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella raportoiduille tuloksille. Muille testisuureille ja näytteille käytettiin asiantuntijalaboratorion homogeenisuusmäärittästulosten sekä kierroskohtaisen tuloksen keskiarvoa.

Synteettisen näytteen vertailuarvon standardimittausepävarmuus vaihteli välillä 1,2–2,7 % omalla vasteella (RCRF) raportoiduille tuloksille sekä välillä 1,6–6,3 % tolueniekvivalenttina (TE) raportoiduille tuloksille. Kammionäytteiden  $TVOC_{Lab}$  ja  $TVOC_{Guide}$ , vertailuarvojen standardiepävarmuus oli pienempi tai yhtä suuri kuin 10 %.

Osallistujien pätevyuden arviointi tehtiin z-arvon avulla. Koko tulosaineistossa hyväksyttävää tuloksia oli 68 %, kun vertailuarvosta sallittiin 20–30 % poikkeama 95 % luottamusvälillä. Noin 90 % osallistujista käytti akkreditoituja määrittäsmenetelmiä ja näistä tuloksista oli hyväksyttävää 78 %. Vertailumittauksessa pyydettiin osallistujia raportoimaan synteettisen näytteen tulokset yhdisteen omalla vasteella sekä tolueniekvivalenttina. Vertailumittauksen tulosten mukaan on vaikea arvioida yhtä ainoaa muuntokerrointa tuloksen muuntamiseksi yhdisteen omasta vasteesta toluenin ekvivalentiksi tai päinvastoin.

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## APPENDIX 1: Participants in the interlaboratory comparison

Country	Institute
Denmark	Eurofins Product Testing
Finland	Eurofins Environment Testing Finland Oy, Lahti Finnish Institute of Occupational Health Kiwa Inspecta Oy, KiwaLab, Oulu Metropolilab Oy Mikrobioni Oy Ositum Oy WSP Finland Oy, Sisäilmalaboratorio VTT Expert Services Oy
Portugal	INEGI - Institute of Science and Innovation in Mechanical and Industrial Engineering, Laboratory for Indoor Air Quality

## APPENDIX 2: Preparation of the samples

The preparation of the samples was carried out in the laboratory of Finnish Institute of Occupational Health (FIOH). The used chemicals and preparation of the synthetic sample are shown in Tables 1 and 2.

Table 1. The used chemicals for the synthetic sample IDA1Synt.

Measurand/Solvent	Name, Producer, Product code, Purity
2-ethyl-1-hexanol, 2EH	Sigma Aldrich 538051, ≥99.6 %, LOT MKBH0228V
Methanol	Merck 20864.292 GPR Rectapur, 100 %, LOT 12L220518
Naphthalene	Merck 8.20846.0100 for synthesis, ≥99%, LOT S687746416
Styrene	Merck 8.07689.0100 for Synthesis, ≥99 %, LOT S7213279706
Toluene	Merck 1.00849.1000 MS Suprasolv, ≥99.8 %, LOT 17464349
2,2,4-trimethyl-1,3-pentanediol diisobutyrate, TXIB	Acros 42200050, 98 % LOT A0149330

Table 2. Weighing results for the preparation of synthetic sample IDA1Synt.

Measurand/ Solvent	Mass (g)	Concentration (ng/ml) (V <sub>tot</sub> = 20 ml)	Addition of 2 µl to each thermodesorption tube, (ng/sample)	Assigned value RCRF
2EH	0.00577	28.85	57.7	60.0
Methanol	15.74746			
Naphthalene	0.00524	26.2	52.4	54.1
Styrene	0.02584	129.2	258.4	270
Toluene	0.00583	29.15	58.3	60.6
TXIB	0.00629	31.45	62.9	64.9

### Preparation of the Chamber samples

The native samples were prepared using a chamber at the laboratory of FIOH. Air flow, temperature and humidity are controlled in the chamber (Fig 1). The chamber has twelve sampling ports and parallel samples could be collected from each port enabling collection of total 24 samples (Fig 2). Calibrated air pumps provided by FIOH were used for sample collection (Fig 2). The used TA-Tenax thermodesorption tubes were produced by Markes and the dimensions were as industry-standard 89 mm (3½-inch) long × 6.4 mm (¼-inch) outer diameter.

Prior to the sample preparation the chamber was cleaned and the collection tubes were changed. Temperature was adjusted to 23°C ± 1°C and humidity to 50 RH% ± 5.

The collection of the samples started on 24<sup>th</sup> August, 2017 and the samples were collected to Tenax TA tubes. First the blank samples (IDA4Blank) were collected and selected tubes were tested before the native samples (IDA3TVOC) were prepared. The second blank sampling started two hours after the first one.





Figure 1. The used chamber for the native samples in the laboratory of Finnish Institute of Occupational Health.

After the collection of the blank samples the selected building materials with different coatings were placed into the chamber and the chamber was closed. Native sample (IDA3TVOC) collection (first batch) started 24 hours after the chamber was closed, on 25<sup>th</sup> August, 2017. Second sample batch was collected two hours after the first batch. After sampling building materials were removed from the chamber, and the chamber was cleaned.

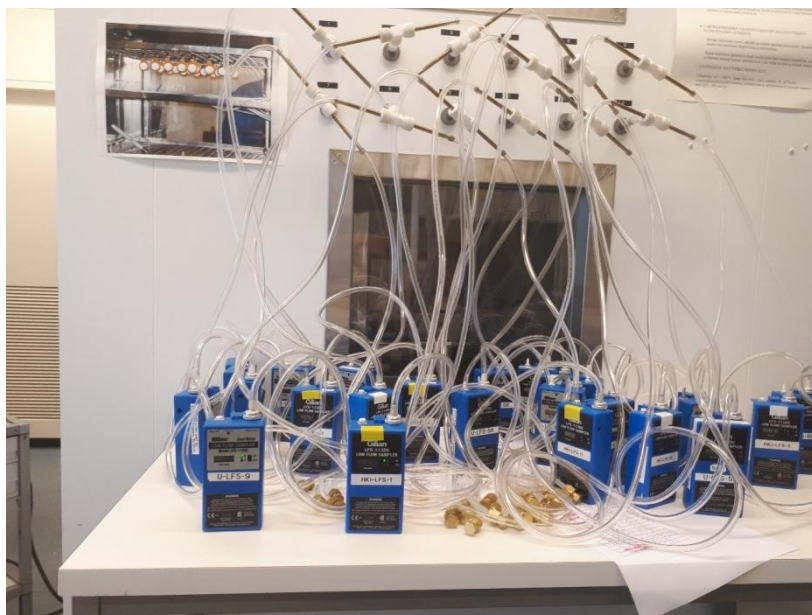


Figure 2. The sampling ports and the used calibrated air pumps in the preparation of the native samples in the laboratory of Finnish Institute of Occupational Health.



## APPENDIX 3: Homogeneity of the samples

Homogeneity of the synthetic sample IDA1Synt was tested by measuring 2EH, naphthalene, styrene, toluene and TXIB (as compound specific response (RCRF, Reference Compound Response Factor)) from five subsamples. The samples collected from the chamber (IDA3TVOC) were tested as toluene equivalents (TE) measuring TVOC from six samples for the batch B1 and from ten samples for the batch B2. In the calculations the samples collected from the same duct adapter were handled as parallel samples making three parallel measurements for the sample batch B1 and five parallel measurements for the sample batch B2.

### Criteria for homogeneity:

$$s_{\text{anal}}/s_{\text{pt}} < 0.5 \text{ and } s_{\text{sam}}^2 < c, \text{ where}$$

$s_{\text{anal}}$  = analytical deviation, standard deviation of the results within sub samples

$s_{\text{pt}}\%$  = standard deviation for proficiency assessment

$s_{\text{sam}}$  = between-sample deviation, standard deviation of the results between sub samples

$$c = F1 \times s_{\text{all}}^2 + F2 \times s_{\text{anal}}^2, \text{ where}$$

$$s_{\text{all}}^2 = (0.3 \times s_{\text{pt}})^2,$$

F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Table 1. Results from the homogeneity testing.

Measurand/Sample	Concentration [TE, $\mu\text{g}/\text{m}^3$ ]	n	Spt %	Spt	$s_{\text{anal}}$	$s_{\text{anal}}/s_{\text{pt}}$	$s_{\text{anal}}/s_{\text{pt}} < 0.5?$	$s_{\text{sam}}^2$	c	$s_{\text{sam}}^2 < c?$
TVOC <sub>Lab</sub> -Chamber Blank /IDA3TVOC_B1	168	4	15	25.1	8.8	0.35	Yes	243	365	Yes
TVOC <sub>Lab</sub> -Chamber Blank /IDA3TVOC_B2	151	4	15	22.7	19.1	0.84	No*	11.4	1091	Yes

\*Taking account the expanded measurement uncertainty of the expert laboratory, the criteria can be considered as passed.

### Criterion for homogeneity without parallel results:

$$s_{\text{sam}}/s_{\text{pt}} < 0.5, \text{ where}$$

$s_{\text{pt}}$  = standard deviation for proficiency assessment

$s_{\text{sam}}$  = between-sample deviation, standard deviation of results between sub samples

Measurand/Sample	Concentration [RCRF, ng/sample]	n	Spt %	Spt	$s_{\text{sam}}$	$s_{\text{sam}}/s_{\text{pt}}$	$s_{\text{sam}}/s_{\text{pt}} < 0.5?$
2EH/IDA1Synt	54.6	6	10	5.46	0.96	0.18	Yes
Naphthalene/IDA1Synt	56.6	6	10	5.66	0.84	0.15	Yes
Styrene/IDA1Synt	243	6	10	24.3	5.3	0.22	Yes
TXIB/IDA1Synt	56.9	6	10	5.69	2.68	0.47	Yes
Toluene/IDA1Synt	55.1	6	10	3.86	1.11	0.20	Yes

**Conclusion:** Mainly, the criteria were fulfilled. Thus, all the samples could be regarded as homogenous.

## APPENDIX 4: Feedback from the interlaboratory comparison

## FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Profest
	The used transport service mixed the parcels of the samples for two participants. The participants received different samples than expected. (Because of the confidentiality of the customers, the participant's codes are not informed.)	The provider has clarified the incident with the transport service and agreed on the procedures in the future interlaboratory comparisons, to avoid similar occurrences in future. The participants measured the delivered samples.
1	The participant informed that their sample IDA4Blank was leaking and was not measurable.	The provider delivered a new sample to the participant. The leaked tubes will be checked by the expert laboratory. For the next round more samples will be prepared to take into account the possibility of the leaking of the tubes. Participants should contact the provider in such cases for delivery of new samples.
3	The participant thanks from the fast delivery of the preliminary results, the very well organized interlaboratory comparison, and wished a continuation for similar test.	The provider would like to thank the participant for the positive feedback. The next intercomparison will be organized during 2018 ( <a href="http://www.syke.fi/proftest/en">www.syke.fi/proftest/en</a> > Annual schemes).
4	The participant wished longer time for returning the testing tubes.	All the participants returned the testing tubes within the requested time. If more testing tubes are needed for a method validation after the interlaboratory comparison, the participants can request them from the provider. This was informed also in the information and sample letters of the test.
	The participant informed that the concentration of styrene was too high. However, they found out some analytical problems in their styrene measurement.	In this test the concentrations of measurands in the synthetic sample were set taking into account the Finnish action limit presented in the decree of the Ministry of Social Affairs and Health [5].
7	The participant informed that they need more measuring time due to different sample tube dimension used in the test samples, thus the total measuring time was longer than usual.	The provider extended the reporting deadline until Monday 13 November, 2017. The participants are advised to take into account the given timeframe and adjust their measurements accordingly.
	The participant reported within the replies of the background information that one of their chamber sample IDA3TVOC was leaking and was not measurable.	The provider evaluated the reported one result for the chamber sample. The provider recommends to be report the problems with the samples directly to the provider, who considers if a new sample is needed.

Participant	Comments to the results	Action / Profest
3	<p>The participant pointed out that in the ISO 16000-6 [1] there is no exact guide how to calculate TVOC, especially, if many intensive peaks are present in the area of measurement.</p> <p>The participant wished for better pre-information about the need to report the identified substances in the background questionnaire, as they had not allocated enough time for reporting such information.</p>	<p>TVOC calculation is very challenging, and thus it needs proper training for the analytical personnel in the laboratory. In cases when automatic integration is used, the integration should be checked and, if needed, correct manually.</p> <p>The provider informed this reporting task in the covering letter of the samples: <i>"Additionally, there is an electronic questionnaire (Webropol) about the used analytical methods and recognized compounds"</i>. If similar questionnaire will be used in the forthcoming interlaboratory comparisons, the provider will describe the task more clearly.</p> <p>Also, the reporting of the identified substances will focus on specific height of the peak or specific concentration in forthcoming tests.</p>
7	<p>The participants asked more detail information of measurement of GC-MSD for TVOC as toluene equivalent (integration option, number of calibration solutions, integration mode).</p> <p>The participant pointed out that there are also other sources (e.g. instrument) or substances, which might disturb the measurement than compounds mentioned in the covering letter of samples.</p> <p>The participant wished to mention by which analytical technique (FID/MSD) the VOC measurements were done in the final report.</p>	<p>This information was not asked from the participants in the background questionnaire. If the provider will get more feedback from the participants that such information should be collected, more detailed questions will be asked in forthcoming tests.</p> <p>There might be other sources or substances of disturbance than what was mentioned in the cover letter of samples. The substances from the used thermodesorption tubes, which during pretesting were noticed to be possibly disturbing the measurements, were mentioned in the letter. If there is disturbance from e.g. the instrument, the participant should take that into account in their blank value. The provider will consider the need of more detailed instructions for sources and substances of disturbance in forthcoming test.</p> <p>In the final reports of Profest SYKE the used measurement techniques are mainly discussed. If there is enough data the possible differences between different methods are statistically tested. In cases with low number of results, as in this interlaboratory comparison, this is done visually from the graphics of results.</p>
1	<p>Participant reported results for the second synthetic sample IDA1Synt (ng/sample):  <math>2EH_{RCRF}</math>: 63.2; <math>2EH_{TE}</math>: 32.6  <math>Napthalene_{RCRF}</math>: 55.4; <math>Napthalene_{TE}</math>: 79.3  <math>Styrene_{RCRF}</math>: 256.6; <math>Styrene_{TE}</math>: 261.4  <math>Toluene_{RCRF}</math>: 59.4  <math>TXIB_{RCRF}</math>: 62.7; <math>TXIB_{TE}</math>: 72.3</p>	<p>All the second results were satisfactory with the exception of questionable <math>2EH_{TE}</math> result. The participant can recalculate the z scores according to the Guide for participants [5].</p>
10	<p>Participant asked to check the calculation of their zeta values.</p>	<p>The provider asked an example of participant's calculation. The used formula by the participant needed some corrections. More detailed information of used statistical formulas is available from the Guide for participants [6].</p>

**FEEDBACK TO THE PARTICIPANTS**

Participant	Comments
5	During the results reporting the provider noticed very high result for the chamber blank sample. The provider contacted the participant and got information that they recognized a high concentration of dipropylene glycolmethylether in the blank sample. They subtracted this value and got the blank level as known from the background information. The reason for the original value will be discussed further with the analytical expert.
7	The participant informed in the answers of the background information that one of their chamber sample IDA3TVOC was leaking and was not measurable. The provider recommends to reporting any problems with the samples for considering to delivering new samples.
8, 9, 10	The participants did not report the expanded measurement uncertainties for TVOC measurements. Participants 8 and 10 are accredited laboratories, whom should report uncertainties with their results. Participant 8 informed that their uncertainties were under re-validation during the test and informed their uncertainties afterwards.
1, 3, 4, 6, 7,8, 10	The participants reported zero results for some blank samples. This caused difficulties in the statistical treatment of results, and thus not all mean values of measurands were representative in blank samples. In this test zero values were not deleted from the database, however they will be eliminated in forthcoming tests. In the analytical measurements there is always a detection limit for specific substance. Thus, the correct way to inform these low values is to report result as lower or equal to detection limit. The provider strongly recommends participants to update the reporting procedure for to low concentration results.
1	The participant wished to report results for both ordered synthetic samples. They informed this when they reported their results. It is possible to order multiple samples and to report multiple results but should be informed to the provider during registration the samples are ordered. The provider recommends participants inform this kind of need within their registration.

## APPENDIX 5: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	$U_{pt}$	$U_{pt}, \%$	Evaluation method of assigned value	$u_{pt}/s_{pt}$
2EH <sub>RCRF</sub>	IDA1Synt	ng/sample	60.0	1.4	2.4	Calculated value	0.12
	IDA2Blank	ng/sample					
2EH <sub>TE</sub>	IDA1Synt	ng/sample	44.3	0.7	1.6	Expert	0.08
	IDA2Blank	ng/sample					
Naphthalene <sub>RCRF</sub>	IDA1Synt	ng/sample	54.1	1.4	2.6	Calculated value	0.13
	IDA2Blank	ng/sample					
Naphthalene <sub>TE</sub>	IDA1Synt	ng/sample	79.6	1.9	2.4	Expert	0.12
Styrene <sub>RCRF</sub>	IDA1Synt	ng/sample	270	3	1.2	Calculated value	0.06
	IDA2Blank	ng/sample					
Styrene <sub>TE</sub>	IDA1Synt	ng/sample	260	7	2.5	Expert	0.13
	IDA2Blank	ng/sample					
Toluene <sub>RCRF</sub>	IDA1Synt	ng/sample	60.6	1.5	2.4	Calculated value	0.12
	IDA2Blank	ng/sample					
TVOC <sub>Guide</sub>	IDA3TVOC_B1	µg/m <sup>3</sup>	177	13	7.4	Expert	0.25
	IDA3TVOC_B2	µg/m <sup>3</sup>	161	15	9.3	Expert	0.31
	IDA4Blank	µg/m <sup>3</sup>	7.90			Median	
TVOC <sub>Guide</sub> -Chamber blank	IDA3TVOC_B1	µg/m <sup>3</sup>	168	12	7.1	Expert	0.24
	IDA3TVOC_B2	µg/m <sup>3</sup>	151	16	10.4	Expert	0.35
TVOC <sub>Lab</sub>	IDA3TVOC_B1	µg/m <sup>3</sup>	177	13	7.4	Expert	0.25
	IDA3TVOC_B2	µg/m <sup>3</sup>	161	15	9.3	Expert	0.31
	IDA4Blank	µg/m <sup>3</sup>	8.00			Median	
TVOC <sub>Lab</sub> -Chamber blank	IDA3TVOC_B1	µg/m <sup>3</sup>	168	12	7.1	Expert	0.24
	IDA3TVOC_B2	µg/m <sup>3</sup>	151	16	10.4	Expert	0.35
TXIB <sub>RCRF</sub>	IDA1Synt	ng/sample	64.9	1.8	2.7	Calculated value	0.14
	IDA2Blank	ng/sample					
TXIB <sub>TE</sub>	IDA1Synt	ng/sample	75.7	4.8	6.3	Expert	0.25
	IDA2Blank	ng/sample					

$U_{pt}$  = Expanded uncertainty of the assigned value

Criterion for reliability of the assigned value  $u_{pt}/s_{pt} \leq 0.3$ , where

$s_{pt}$  = target value of the standard deviation for proficiency assessment

$u_{pt}$  = standard uncertainty of the assigned value

If  $u_{pt}/s_{pt} \leq 0.3$ , the assigned value is reliable and the z scores are qualified.

## APPENDIX 6: Terms in the results tables

**Results of each participant**

<b>Measurand</b>	The tested parameter
<b>Sample</b>	The code of the sample
<b>z score</b>	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$ , where $x_i$ = the result of the individual participant $x_{pt}$ = the assigned value $s_{pt}$ = the standard deviation for proficiency assessment
<b>Assigned value</b>	The value attributed to a particular property of a proficiency test item
<b><math>2 \times s_{pt}</math> %</b>	The standard deviation for proficiency assessment ( $s_{pt}$ ) at the 95 % confidence level
<b>Participants's result</b>	The result reported by the participant (the mean value of the replicates)
<b>Md</b>	Median
<b>SD</b>	Standard deviation
<b>SD%</b>	Standard deviation, %
<b>n (stat)</b>	Number of results in statistical processing

**Summary on the z scores**

S – satisfactory ( $-2 \leq z \leq 2$ )

Q – questionable ( $2 < z < 3$ ), positive error, the result deviates more than  $2 \times s_{pt}$  from the assigned value

q – questionable ( $-3 < z < -2$ ), negative error, the result deviates more than  $2 \times s_{pt}$  from the assigned value

U – unsatisfactory ( $z \geq 3$ ), positive error, the result deviates more than  $3 \times s_{pt}$  from the assigned value

u – unsatisfactory ( $z \leq -3$ ), negative error, the result deviates more than  $3 \times s_{pt}$  from the assigned value

**Robust analysis**

The items of data are sorted into increasing order,  $x_1, x_2, x_i, \dots, x_p$ .

Initial values for  $x^*$  and  $s^*$  are calculated as:

$$x^* = \text{median of } x_i \text{ (} i = 1, 2, \dots, p \text{)}$$

$$s^* = 1.483 \times \text{median of } |x_i - x^*| \text{ (} i = 1, 2, \dots, p \text{)}$$

The mean  $x^*$  and  $s^*$  are updated as follows:

Calculate  $\varphi = 1.5 \times s^*$ . A new value is then calculated for each result  $x_i$  ( $i = 1, 2 \dots p$ ):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of  $x^*$  and  $s^*$  are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134 \sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates  $x^*$  and  $s^*$  can be derived by an iterative calculation, i.e. by updating the values of  $x^*$  and  $s^*$  several times, until the process convergences [2].

## APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pl</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)
2EH <sub>R</sub> CRF	ng/sample	IDA1Synt		0.55	60.0	20	63.3	54.0	54.9	11.2	20.4	9
	ng/sample	IDA2Blank					5.00	1.54	2.66	2.97	111.8	7
2EH <sub>T</sub> E	ng/sample	IDA1Synt		-2.66	44.3	20	32.5	40.3	42.5	13.2	31.0	10
	ng/sample	IDA2Blank					0.70	0.00	1.55	2.69	173.8	7
Naphthalene <sub>R</sub> CRF	ng/sample	IDA1Synt		0.41	54.1	20	56.3	56.3	56.0	15.9	28.3	9
	ng/sample	IDA2Blank					0.90	0.00	0.15	0.34	221.5	7
Naphthalene <sub>T</sub> E	ng/sample	IDA1Synt		0.06	79.6	20	80.1	79.4	82.0	17.2	21.0	10
	ng/sample	IDA2Blank					0.0					
Styrene <sub>R</sub> CRF	ng/sample	IDA1Synt		0.09	270	20	273	273	256	51	19.8	9
	ng/sample	IDA2Blank					1.60	0.00	0.25	0.60	239.2	7
Styrene <sub>T</sub> E	ng/sample	IDA1Synt		0.52	260	20	274	260	265	61	22.9	10
	ng/sample	IDA2Blank					0.40	0.00	0.06	0.15	264.6	7
Toluene <sub>R</sub> CRF	ng/sample	IDA1Synt		0.31	60.6	20	62.5	64.0	65.1	11.3	17.4	10
	ng/sample	IDA2Blank					0.70	0.00	1.20	2.84	237.0	8
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		0.64	177	30	194	192	191	47	24.4	8
	µg/m <sup>3</sup>	IDA4Blank			7.90		16.20	7.90	12.85	11.93	92.8	11
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		0.39	168	30	178	161	178	43	24.1	8
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		0.64	177	30	194	183	185	26	14.1	7
	µg/m <sup>3</sup>	IDA4Blank			8.00		16.20	8.00	13.97	11.12	79.6	11
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		0.39	168	30	178	160	160	11	6.9	6
TXIB <sub>R</sub> CRF	ng/sample	IDA1Synt		-0.40	64.9	20	62.3	57.1	55.4	11.7	21.1	9
	ng/sample	IDA2Blank					2.40	0.00	0.37	0.90	242.7	7
TXIB <sub>T</sub> E	ng/sample	IDA1Synt		-0.39	75.7	25	72.0	69.6	72.8	26.9	37.0	10
	ng/sample	IDA2Blank					2.30	0.00	0.33	0.87	264.6	7

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pl</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)
2EH <sub>R</sub> CRF	ng/sample	IDA1Synt		-4.07	60.0	20	35.6	54.0	54.9	11.2	20.4	9
	ng/sample	IDA2Blank					1.54	1.54	2.66	2.97	111.8	7
2EH <sub>T</sub> E	ng/sample	IDA1Synt		0.20	44.3	20	45.2	40.3	42.5	13.2	31.0	10
	ng/sample	IDA2Blank										
Naphthalene <sub>R</sub> CRF	ng/sample	IDA1Synt		-3.36	54.1	20	35.9	56.3	56.0	15.9	28.3	9
	ng/sample	IDA2Blank					0.16	0.00	0.15	0.34	221.5	7
Naphthalene <sub>T</sub> E	ng/sample	IDA1Synt		1.34	79.6	20	90.3	79.4	82.0	17.2	21.0	10
	ng/sample	IDA2Blank										
Styrene <sub>R</sub> CRF	ng/sample	IDA1Synt		-2.94	270	20	191	273	256	51	19.8	9
	ng/sample	IDA2Blank					0.15	0.00	0.25	0.60	239.2	7
Styrene <sub>T</sub> E	ng/sample	IDA1Synt		-2.05	260	20	207	260	265	61	22.9	10
	ng/sample	IDA2Blank										
Toluene <sub>R</sub> CRF	ng/sample	IDA1Synt		-2.48	60.6	20	45.6	64.0	65.1	11.3	17.4	10
	ng/sample	IDA2Blank					0.70	0.00	1.20	2.84	237.0	8
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		17.08	177	30	631	192	191	47	24.4	8
	µg/m <sup>3</sup>	IDA4Blank			7.90		30.20	7.90	12.85	11.93	92.8	11
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		17.15	168	30	600	161	178	43	24.1	8
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		17.08	177	30	631	183	185	26	14.1	7
	µg/m <sup>3</sup>	IDA4Blank			8.00		30.20	8.00	13.97	11.12	79.6	11
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		17.15	168	30	600	160	160	11	6.9	6

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Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)
TXIB <sub>R</sub> CRF	ng/sample	IDA1Synt		-4.33	64.9	20	36.8	57.1	55.4	11.7	21.1	9
	ng/sample	IDA2Blank					0.19	0.00	0.37	0.90	242.7	7
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		-0.22	75.7	25	73.6	69.6	72.8	26.9	37.0	10

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)
2EH <sub>TE</sub>	ng/sample	IDA1Synt		-1.29	44.3	20	38.6	40.3	42.5	13.2	31.0	10
	ng/sample	IDA2Blank					0.00	0.00	1.55	2.69	173.8	7
Naphthalen <sub>E</sub> TE	ng/sample	IDA1Synt		-0.46	79.6	20	75.9	79.4	82.0	17.2	21.0	10
	ng/sample	IDA2Blank					0.0					
Styrene <sub>TE</sub>	ng/sample	IDA1Synt		-0.70	260	20	242	260	265	61	22.9	10
	ng/sample	IDA2Blank					0.00	0.00	0.06	0.15	264.6	7
Toluene <sub>R</sub> CRF	ng/sample	IDA1Synt		0.78	60.6	20	65.3	64.0	65.1	11.3	17.4	10
	ng/sample	IDA2Blank					0.00	0.00	1.20	2.84	237.0	8
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		1.53	177	30	218	192	191	47	24.4	8
	µg/m <sup>3</sup>	IDA4Blank			7.90		4.80	7.90	12.85	11.93	92.8	11
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		1.78	168	30	213	161	178	43	24.1	8
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		1.97	177	30	229	183	185	26	14.1	7
	µg/m <sup>3</sup>	IDA4Blank			8.00		5.20	8.00	13.97	11.12	79.6	11
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		2.22	168	30	224	160	160	11	6.9	6
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		1.98	75.7	25	94.4	69.6	72.8	26.9	37.0	10
	ng/sample	IDA2Blank					0.00	0.00	0.33	0.87	264.6	7

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)
2EH <sub>R</sub> CRF	ng/sample	IDA1Synt		2.13	60.0	20	72.8	54.0	54.9	11.2	20.4	9
	ng/sample	IDA2Blank					7.10	1.54	2.66	2.97	111.8	7
2EH <sub>TE</sub>	ng/sample	IDA1Synt		6.43	44.3	20	72.8	40.3	42.5	13.2	31.0	10
	ng/sample	IDA2Blank					7.10	0.00	1.55	2.69	173.8	7
Naphthalen <sub>E</sub> R <sub>R</sub> CRF	ng/sample	IDA1Synt		6.49	54.1	20	89.2	56.3	56.0	15.9	28.3	9
	ng/sample	IDA2Blank					0.00	0.00	0.15	0.34	221.5	7
Naphthalen <sub>E</sub> TE	ng/sample	IDA1Synt		4.57	79.6	20	116.0	79.4	82.0	17.2	21.0	10
	ng/sample	IDA2Blank					0.0					
Styrene <sub>R</sub> CRF	ng/sample	IDA1Synt		2.33	270	20	333	273	256	51	19.8	9
	ng/sample	IDA2Blank					0.00	0.00	0.25	0.60	239.2	7
Styrene <sub>TE</sub>	ng/sample	IDA1Synt		5.35	260	20	399	260	265	61	22.9	10
	ng/sample	IDA2Blank					0.00	0.00	0.06	0.15	264.6	7
Toluene <sub>R</sub> CRF	ng/sample	IDA1Synt		4.37	60.6	20	87.1	64.0	65.1	11.3	17.4	10
	ng/sample	IDA2Blank					0.00	0.00	1.20	2.84	237.0	8
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		0.56	177	30	192	192	191	47	24.4	8
	µg/m <sup>3</sup>	IDA4Blank			7.90		37.70	7.90	12.85	11.93	92.8	11
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.52	168	30	155	161	178	43	24.1	8
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		0.56	177	30	192	183	185	26	14.1	7
	µg/m <sup>3</sup>	IDA4Blank			8.00		37.70	8.00	13.97	11.12	79.6	11
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.52	168	30	155	160	160	11	6.9	6
TXIB <sub>R</sub> CRF	ng/sample	IDA1Synt		1.31	64.9	20	73.4	57.1	55.4	11.7	21.1	9
	ng/sample	IDA2Blank					0.00	0.00	0.37	0.90	242.7	7



Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×Spt %	Participant's result	Md	Mean	sd	sd %	n (stat)
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		-2.57	75.7	25	51.4	69.6	72.8	26.9	37.0	10
	ng/sample	IDA2Blank					0.00	0.00	0.33	0.87	264.6	7

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×Spt %	Participant's result	Md	Mean	sd	sd %	n (stat)
2EH <sub>RCRF</sub>	ng/sample	IDA1Synt		-1.72	60.0	20	49.7	54.0	54.9	11.2	20.4	9
	ng/sample	IDA2Blank					<5	1.54	2.66	2.97	111.8	7
2EH <sub>TE</sub>	ng/sample	IDA1Synt		-1.81	44.3	20	36.3	40.3	42.5	13.2	31.0	10
	ng/sample	IDA2Blank					<5	0.00	1.55	2.69	173.8	7
Naphthalen <sub>RRCRF</sub>	ng/sample	IDA1Synt		-2.83	54.1	20	38.8	56.3	56.0	15.9	28.3	9
	ng/sample	IDA2Blank					<5	0.00	0.15	0.34	221.5	7
Naphthalen <sub>TE</sub>	ng/sample	IDA1Synt		-2.78	79.6	20	57.5	79.4	82.0	17.2	21.0	10
	ng/sample	IDA2Blank					<5					
Styren <sub>RRCRF</sub>	ng/sample	IDA1Synt		-2.00	270	20	216	273	256	51	19.8	9
	ng/sample	IDA2Blank					<5	0.00	0.25	0.60	239.2	7
Styren <sub>TE</sub>	ng/sample	IDA1Synt		-1.50	260	20	221	260	265	61	22.9	10
	ng/sample	IDA2Blank					<5	0.00	0.06	0.15	264.6	7
Toluen <sub>RRCRF</sub>	ng/sample	IDA1Synt		-0.74	60.6	20	56.1	64.0	65.1	11.3	17.4	10
	ng/sample	IDA2Blank					<5	0.00	1.20	2.84	237.0	8
TVOC <sub>Guide</sub>	µg/m3	IDA3TVOC_B2		-1.68	161	30	121	139	139	26	18.9	2
	µg/m3	IDA4Blank			7.90		6.16	7.90	12.85	11.93	92.8	11
TVOC <sub>Guide</sub> -Chamber blank	µg/m3	IDA3TVOC_B2		-1.61	151	30	115	134	134	27	20.5	2
TVOC <sub>Lab</sub>	µg/m3	IDA3TVOC_B2		-1.68	161	30	121	139	139	26	18.9	2
	µg/m3	IDA4Blank			8.00		6.16	8.00	13.97	11.12	79.6	11
TVOC <sub>Lab</sub> -Chamber blank	µg/m3	IDA3TVOC_B2		-1.61	151	30	115	134	134	27	20.5	2
TXIB <sub>RRCRF</sub>	ng/sample	IDA1Synt		-3.47	64.9	20	42.4	57.1	55.4	11.7	21.1	9
	ng/sample	IDA2Blank					<5	0.00	0.37	0.90	242.7	7
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		-2.25	75.7	25	54.4	69.6	72.8	26.9	37.0	10
	ng/sample	IDA2Blank					<5	0.00	0.33	0.87	264.6	7

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×Spt %	Participant's result	Md	Mean	sd	sd %	n (stat)
2EH <sub>RRCRF</sub>	ng/sample	IDA1Synt		0.62	60.0	20	63.7	54.0	54.9	11.2	20.4	9
	ng/sample	IDA2Blank					0.00	1.54	2.66	2.97	111.8	7
2EH <sub>TE</sub>	ng/sample	IDA1Synt		2.22	44.3	20	54.2	40.3	42.5	13.2	31.0	10
	ng/sample	IDA2Blank					0.00	0.00	1.55	2.69	173.8	7
Naphthalen <sub>RRCRF</sub>	ng/sample	IDA1Synt		-0.99	54.1	20	48.7	56.3	56.0	15.9	28.3	9
	ng/sample	IDA2Blank					0.00	0.00	0.15	0.34	221.5	7
Naphthalen <sub>TE</sub>	ng/sample	IDA1Synt		2.41	79.6	20	98.8	79.4	82.0	17.2	21.0	10
	ng/sample	IDA2Blank					0.0					
Styren <sub>RRCRF</sub>	ng/sample	IDA1Synt		0.98	270	20	297	273	256	51	19.8	9
	ng/sample	IDA2Blank					0.00	0.00	0.25	0.60	239.2	7
Styren <sub>TE</sub>	ng/sample	IDA1Synt		1.70	260	20	304	260	265	61	22.9	10
	ng/sample	IDA2Blank					0.00	0.00	0.06	0.15	264.6	7
Toluen <sub>RRCRF</sub>	ng/sample	IDA1Synt		0.34	60.6	20	62.7	64.0	65.1	11.3	17.4	10
	ng/sample	IDA2Blank					0.00	0.00	1.20	2.84	237.0	8
TVOC <sub>Guide</sub>	µg/m3	IDA3TVOC_B1		-1.58	177	30	135	192	191	47	24.4	8
	µg/m3	IDA4Blank			7.90		0.00	7.90	12.85	11.93	92.8	11

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Participant 6													
Measurand	Unit	Sample		z score	Assigned value	2×S <sub>pl</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-1.31	168	30	135	161	178	43	24.1	8	
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.13	177	30	174	183	185	26	14.1	7	
	µg/m <sup>3</sup>	IDA4Blank		8.00	8.00		12.00	8.00	13.97	11.12	79.6	11	
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.34	168	30	160	160	160	11	6.9	6	
TXIB <sub>RCRF</sub>	ng/sample	IDA1Synt		-2.53	64.9	20	48.5	57.1	55.4	11.7	21.1	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.37	0.90	242.7	7	
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		6.16	75.7	25	134.0	69.6	72.8	26.9	37.0	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.33	0.87	264.6	7	

Participant 7													
Measurand	Unit	Sample		z score	Assigned value	2×S <sub>pl</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
2EH <sub>RCRF</sub>	ng/sample	IDA1Synt		-1.83	60.0	20	49.0	54.0	54.9	11.2	20.4	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	1.54	2.66	2.97	111.8	7	
2EH <sub>TE</sub>	ng/sample	IDA1Synt		-0.52	44.3	20	42.0	40.3	42.5	13.2	31.0	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	1.55	2.69	173.8	7	
Naphthalen <sub>RCRF</sub>	ng/sample	IDA1Synt		1.83	54.1	20	64.0	56.3	56.0	15.9	28.3	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.15	0.34	221.5	7	
Naphthalen <sub>TE</sub>	ng/sample	IDA1Synt		0.80	79.6	20	86.0	79.4	82.0	17.2	21.0	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.06	0.15	264.6	7	
Styrene <sub>RCRF</sub>	ng/sample	IDA1Synt		0.26	270	20	277	273	256	51	19.8	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.25	0.60	239.2	7	
Styrene <sub>TE</sub>	ng/sample	IDA1Synt		1.15	260	20	290	260	265	61	22.9	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.06	0.15	264.6	7	
Toluen <sub>RCRF</sub>	ng/sample	IDA1Synt		2.05	60.6	20	73.0	64.0	65.1	11.3	17.4	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	1.20	2.84	237.0	8	
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		1.73	177	30	223	192	191	47	24.4	8	
	µg/m <sup>3</sup>	IDA4Blank		7.90	8.00		8.00	7.90	12.85	11.93	92.8	11	
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		1.87	168	30	215	161	178	43	24.1	8	
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.30	177	30	169	183	185	26	14.1	7	
	µg/m <sup>3</sup>	IDA4Blank		8.00	8.00		8.00	8.00	13.97	11.12	79.6	11	
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.32	168	30	160	160	160	11	6.9	6	
TXIB <sub>RCRF</sub>	ng/sample	IDA1Synt		-0.76	64.9	20	60.0	57.1	55.4	11.7	21.1	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.37	0.90	242.7	7	
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		1.09	75.7	25	86.0	69.6	72.8	26.9	37.0	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.33	0.87	264.6	7	

Participant 8													
Measurand	Unit	Sample		z score	Assigned value	2×S <sub>pl</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
2EH <sub>RCRF</sub>	ng/sample	IDA1Synt		-0.06	60.0	20	59.7	54.0	54.9	11.2	20.4	9	
	ng/sample	IDA2Blank		4.96	4.96		4.96	1.54	2.66	2.97	111.8	7	
2EH <sub>TE</sub>	ng/sample	IDA1Synt		-0.12	44.3	20	43.8	40.3	42.5	13.2	31.0	10	
	ng/sample	IDA2Blank		3.02	3.02		3.02	0.00	1.55	2.69	173.8	7	
Naphthalen <sub>RCRF</sub>	ng/sample	IDA1Synt		0.41	54.1	20	56.3	56.3	56.0	15.9	28.3	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.15	0.34	221.5	7	
Naphthalen <sub>TE</sub>	ng/sample	IDA1Synt		-0.49	79.6	20	75.7	79.4	82.0	17.2	21.0	10	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.06	0.15	264.6	7	
Styrene <sub>RCRF</sub>	ng/sample	IDA1Synt		-1.29	270	20	235	273	256	51	19.8	9	
	ng/sample	IDA2Blank		0.00	0.00		0.00	0.00	0.25	0.60	239.2	7	

Participant 8													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
Styrene <sub>TE</sub>	ng/sample	IDA1Synt		-0.50	260	20	247	260	265	61	22.9	10	
	ng/sample	IDA2Blank		0.00			0.00	0.00	0.06	0.15	264.6	7	
Toluene <sub>RCRF</sub>	ng/sample	IDA1Synt		-0.65	60.6	20	56.7	64.0	65.1	11.3	17.4	10	
	ng/sample	IDA2Blank		0.00			0.00	0.00	1.20	2.84	237.0	8	
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.80	177	30	156	192	191	47	24.4	8	
	µg/m <sup>3</sup>	IDA4Blank		0.00	7.90		7.90	7.90	12.85	11.93	92.8	11	
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.80	168	30	148	161	178	43	24.1	8	
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.80	177	30	156	183	185	26	14.1	7	
	µg/m <sup>3</sup>	IDA4Blank		0.00	8.00		7.90	8.00	13.97	11.12	79.6	11	
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.80	168	30	148	160	160	11	6.9	6	
TXIB <sub>RCRF</sub>	ng/sample	IDA1Synt		-1.98	64.9	20	52.1	57.1	55.4	11.7	21.1	9	
	ng/sample	IDA2Blank		0.00			0.00	0.00	0.37	0.90	242.7	7	
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		-0.91	75.7	25	67.1	69.6	72.8	26.9	37.0	10	
	ng/sample	IDA2Blank		0.00			0.00	0.00	0.33	0.87	264.6	7	

Participant 9													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×S <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
2EH <sub>RCRF</sub>	ng/sample	IDA1Synt		-2.33	60.0	20	46.0	54.0	54.9	11.2	20.4	9	
	ng/sample	IDA2Blank		<5,0			<5,0	1.54	2.66	2.97	111.8	7	
2EH <sub>TE</sub>	ng/sample	IDA1Synt		-2.64	44.3	20	32.6	40.3	42.5	13.2	31.0	10	
	ng/sample	IDA2Blank		<3,5			<3,5	0.00	1.55	2.69	173.8	7	
Naphthalene <sub>RCRF</sub>	ng/sample	IDA1Synt		-0.59	54.1	20	50.9	56.3	56.0	15.9	28.3	9	
	ng/sample	IDA2Blank		<3,1			<3,1	0.00	0.15	0.34	221.5	7	
Naphthalene <sub>TE</sub>	ng/sample	IDA1Synt		-2.37	79.6	20	60.7	79.4	82.0	17.2	21.0	10	
	ng/sample	IDA2Blank		<3,7			<3,7						
Styrene <sub>RCRF</sub>	ng/sample	IDA1Synt		-3.04	270	20	188	273	256	51	19.8	9	
	ng/sample	IDA2Blank		<2,1			<2,1	0.00	0.25	0.60	239.2	7	
Styrene <sub>TE</sub>	ng/sample	IDA1Synt		-2.88	260	20	185	260	265	61	22.9	10	
	ng/sample	IDA2Blank		<2,1			<2,1	0.00	0.06	0.15	264.6	7	
Toluene <sub>RCRF</sub>	ng/sample	IDA1Synt		1.65	60.6	20	70.6	64.0	65.1	11.3	17.4	10	
	ng/sample	IDA2Blank		<3,4			<3,4	0.00	1.20	2.84	237.0	8	
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		3.77	177	30	277	192	191	47	24.4	8	
	µg/m <sup>3</sup>	IDA4Blank		0.00	7.90		20.00	7.90	12.85	11.93	92.8	11	
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		3.53	168	30	257	161	178	43	24.1	8	
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		3.77	177	30	277	183	185	26	14.1	7	
	µg/m <sup>3</sup>	IDA4Blank		0.00	8.00		20.00	8.00	13.97	11.12	79.6	11	
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		3.53	168	30	257	160	160	11	6.9	6	
TXIB <sub>RCRF</sub>	ng/sample	IDA1Synt		0.23	64.9	20	66.4	57.1	55.4	11.7	21.1	9	
	ng/sample	IDA2Blank		<5,0			<5,0	0.00	0.37	0.90	242.7	7	
TXIB <sub>TE</sub>	ng/sample	IDA1Synt		-2.58	75.7	25	51.3	69.6	72.8	26.9	37.0	10	
	ng/sample	IDA2Blank		<3,9			<3,9	0.00	0.33	0.87	264.6	7	

APPENDIX 7 (6/6)

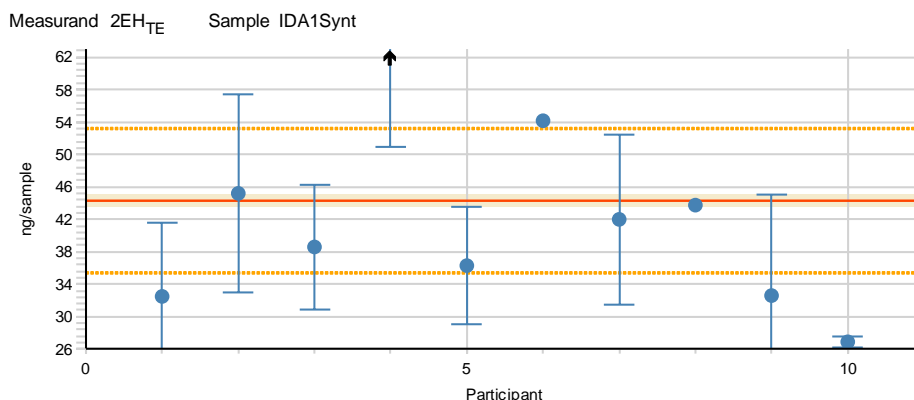
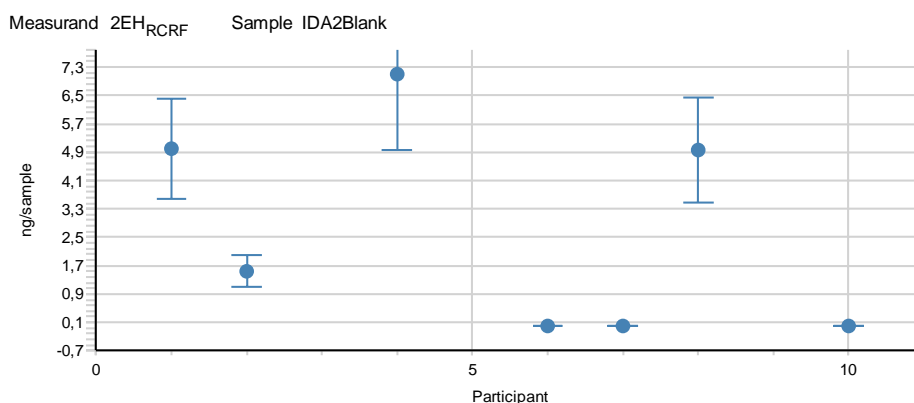
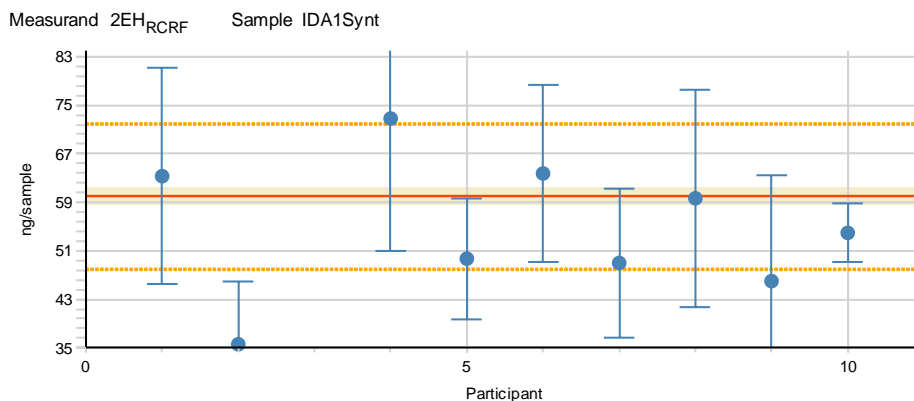
Participant 10													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
2EH <sub>R</sub> CRF	ng/sample	IDA1Synt		-1.01	60.0	20	54.0	54.0	54.9	11.2	20.4	9	
	ng/sample	IDA2Blank					0.00	1.54	2.66	2.97	111.8	7	
2EH <sub>T</sub> E	ng/sample	IDA1Synt		-3.93	44.3	20	26.9	40.3	42.5	13.2	31.0	10	
	ng/sample	IDA2Blank					0.00	0.00	1.55	2.69	173.8	7	
Naphthalene <sub>R</sub> CRF	ng/sample	IDA1Synt		1.88	54.1	20	64.3	56.3	56.0	15.9	28.3	9	
	ng/sample	IDA2Blank					0.00	0.00	0.15	0.34	221.5	7	
Naphthalene <sub>T</sub> E	ng/sample	IDA1Synt		-0.12	79.6	20	78.6	79.4	82.0	17.2	21.0	10	
	ng/sample	IDA2Blank					0.0						
Styrene <sub>R</sub> CRF	ng/sample	IDA1Synt		0.81	270	20	292	273	256	51	19.8	9	
	ng/sample	IDA2Blank					0.00	0.00	0.25	0.60	239.2	7	
Styrene <sub>T</sub> E	ng/sample	IDA1Synt		0.72	260	20	279	260	265	61	22.9	10	
	ng/sample	IDA2Blank					0.00	0.00	0.06	0.15	264.6	7	
Toluene <sub>R</sub> CRF	ng/sample	IDA1Synt		1.71	60.6	20	71.0	64.0	65.1	11.3	17.4	10	
	ng/sample	IDA2Blank					8.17	0.00	1.20	2.84	237.0	8	
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.39	177	30	167	192	191	47	24.4	8	
	µg/m <sup>3</sup>	IDA4Blank			7.90		5.86	7.90	12.85	11.93	92.8	11	
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.28	168	30	161	161	178	43	24.1	8	
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.39	177	30	167	183	185	26	14.1	7	
	µg/m <sup>3</sup>	IDA4Blank			8.00		5.86	8.00	13.97	11.12	79.6	11	
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B1		-0.28	168	30	161	160	160	11	6.9	6	
TXIB <sub>R</sub> CRF	ng/sample	IDA1Synt		-1.21	64.9	20	57.1	57.1	55.4	11.7	21.1	9	
	ng/sample	IDA2Blank					0.00	0.00	0.37	0.90	242.7	7	
TXIB <sub>T</sub> E	ng/sample	IDA1Synt		-3.40	75.7	25	43.5	69.6	72.8	26.9	37.0	10	
	ng/sample	IDA2Blank					0.00	0.00	0.33	0.87	264.6	7	

Participant 11													
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s <sub>pt</sub> %	Participant's result	Md	Mean	sd	sd %	n (stat)	
TVOC <sub>Guide</sub>	µg/m <sup>3</sup>	IDA3TVOC_B2		-0.13	161	30	158	139	139	26	18.9	2	
	µg/m <sup>3</sup>	IDA4Blank			7.90		4.50	7.90	12.85	11.93	92.8	11	
TVOC <sub>Guide</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B2		0.10	151	30	153	134	134	27	20.5	2	
TVOC <sub>Lab</sub>	µg/m <sup>3</sup>	IDA3TVOC_B2		-0.13	161	30	158	139	139	26	18.9	2	
	µg/m <sup>3</sup>	IDA4Blank			8.00		4.50	8.00	13.97	11.12	79.6	11	
TVOC <sub>Lab</sub> -Chamber blank	µg/m <sup>3</sup>	IDA3TVOC_B2		0.10	151	30	153	134	134	27	20.5	2	

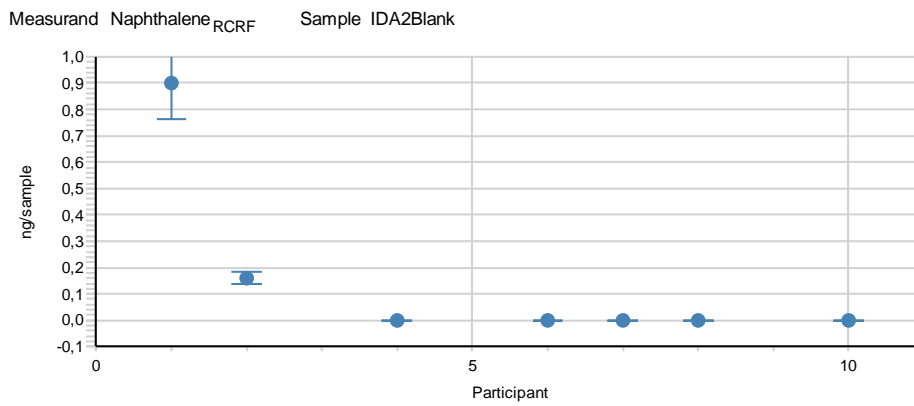
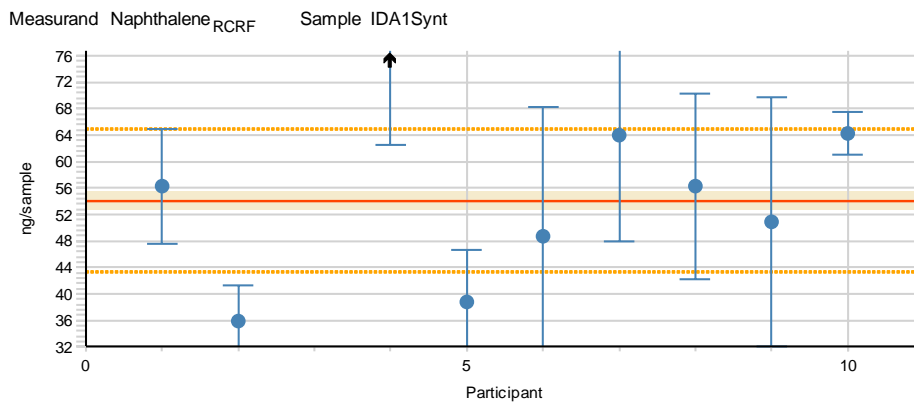
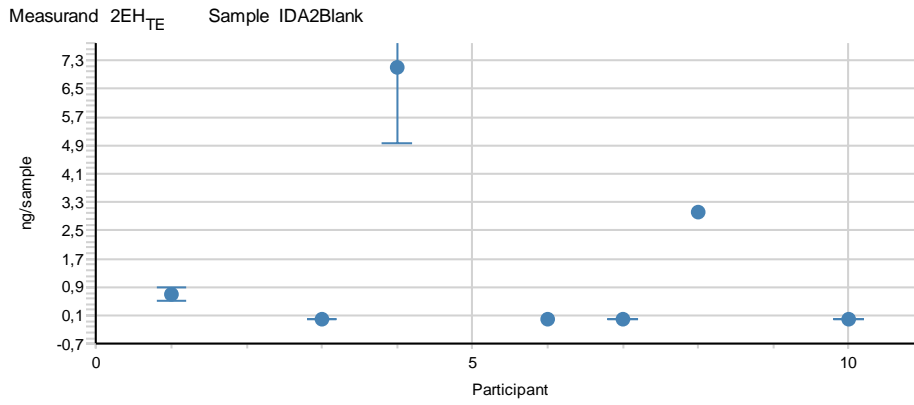
## APPENDIX 8: Results of participants and their uncertainties

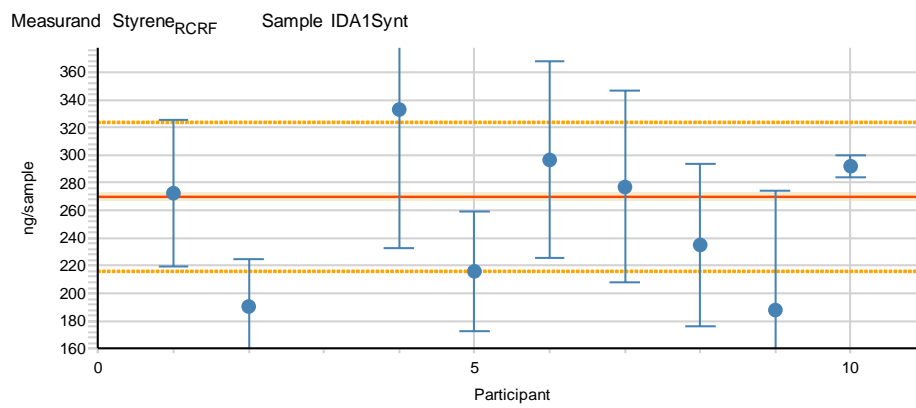
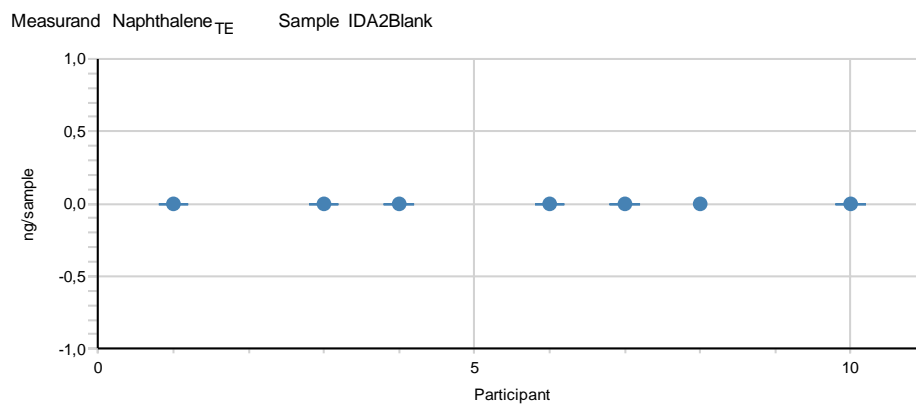
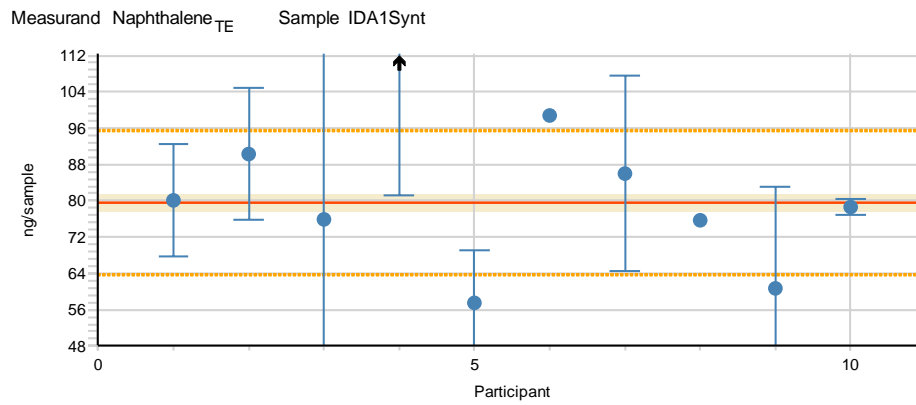
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.

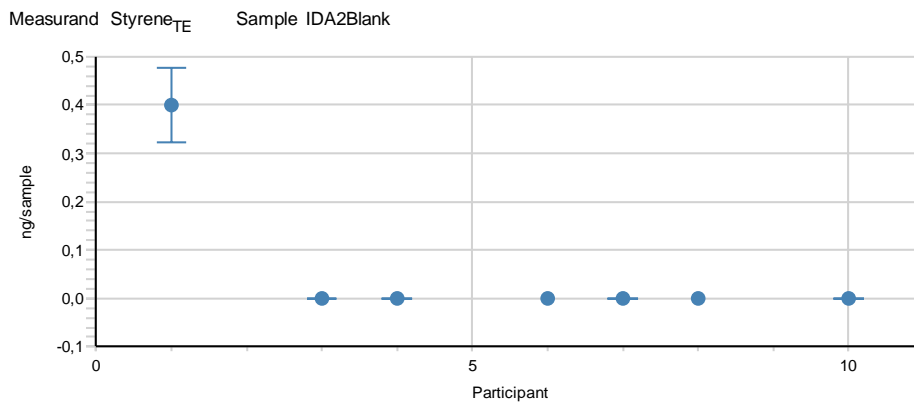
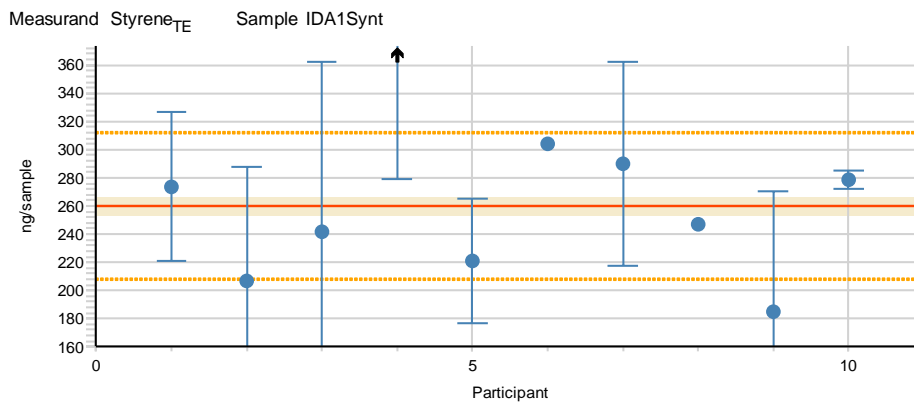
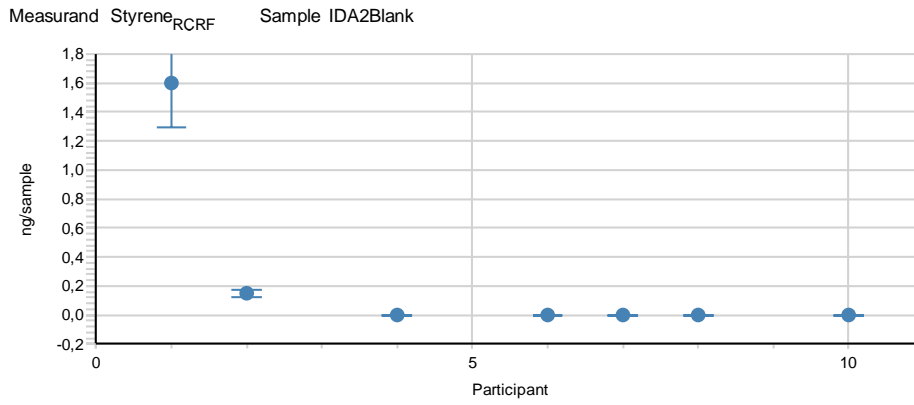


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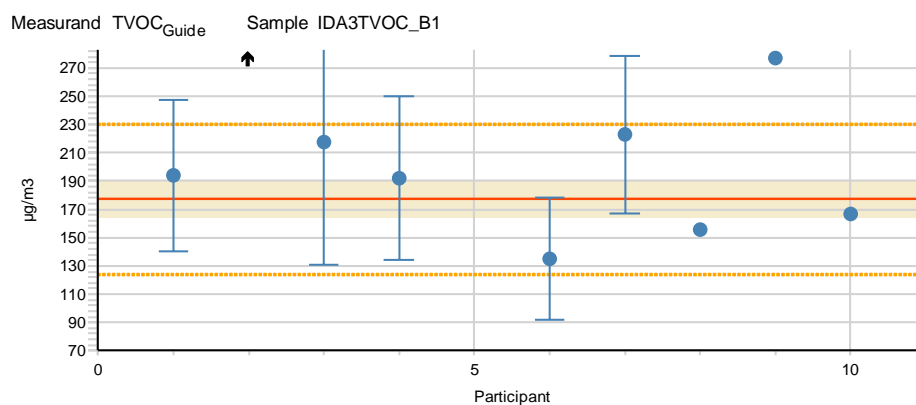
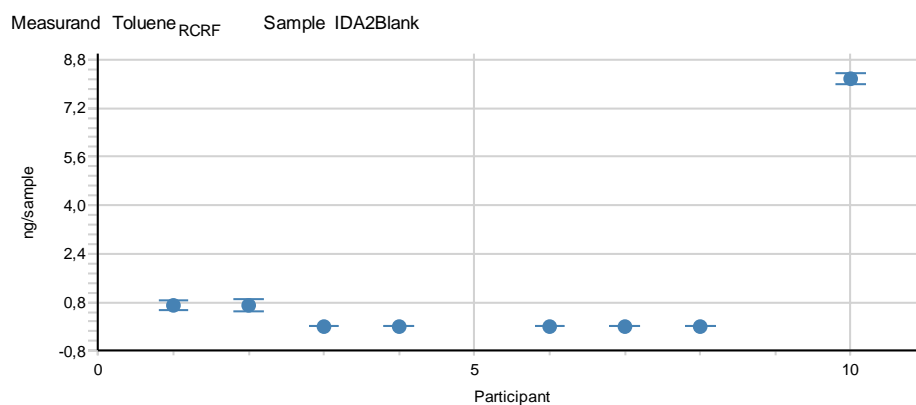
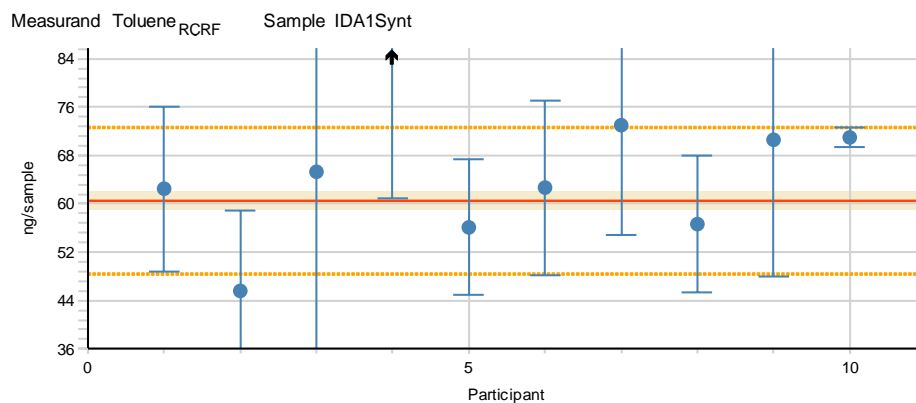




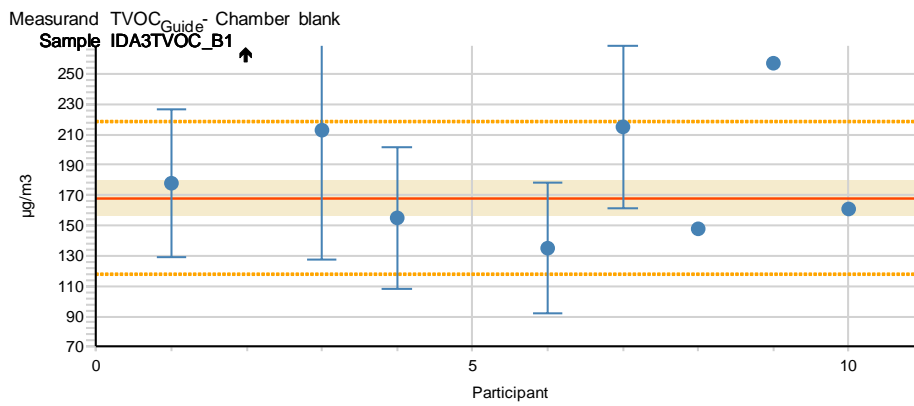
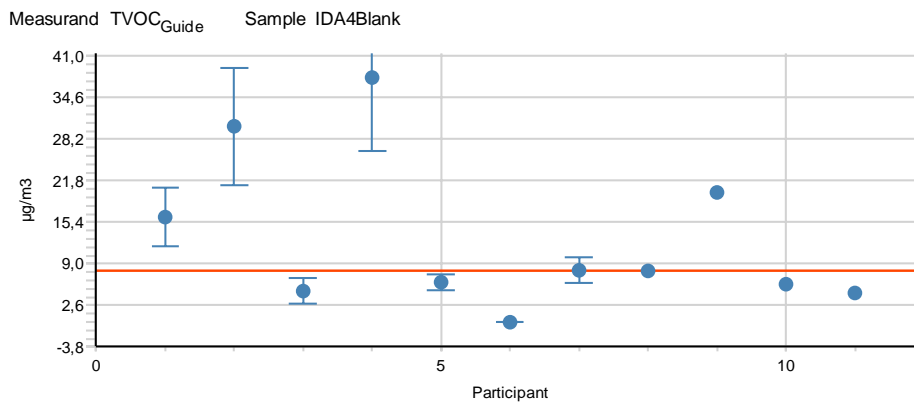
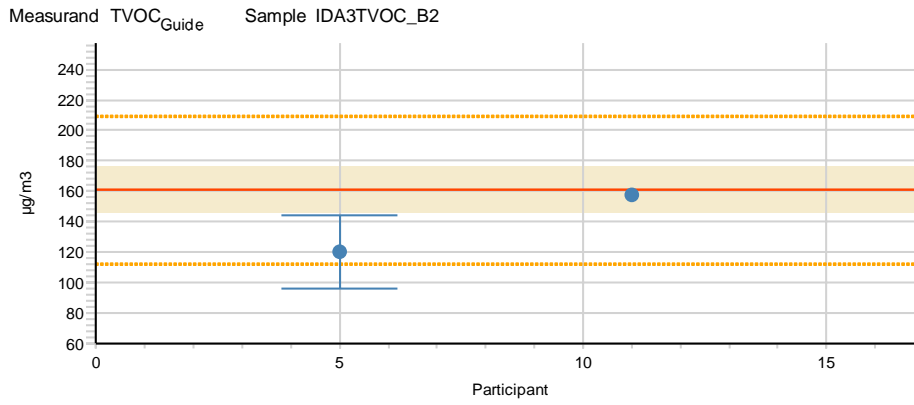
APPENDIX 8 (4/10)

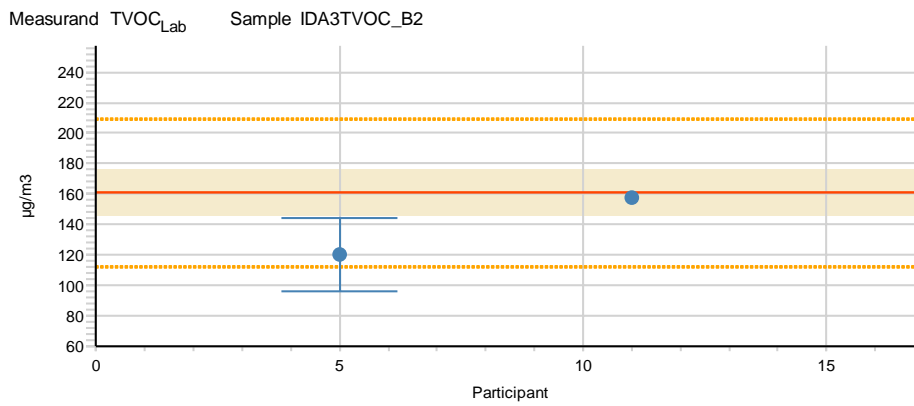
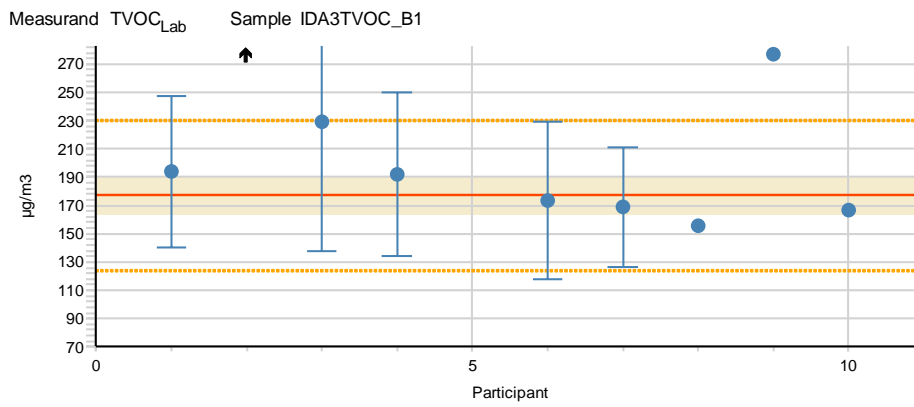
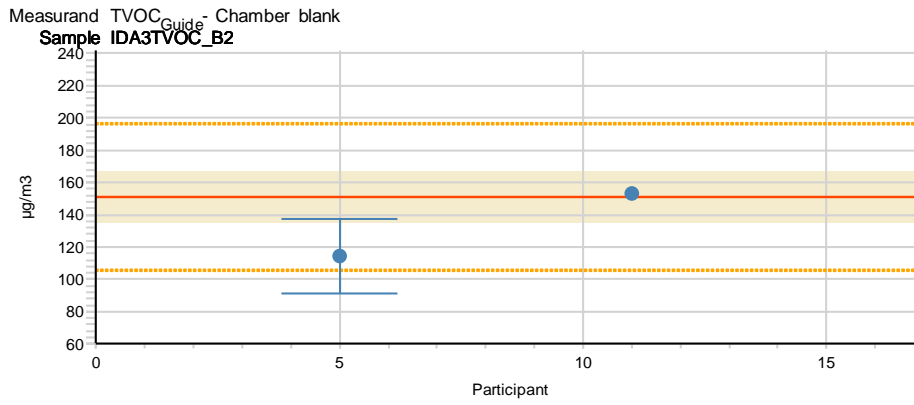




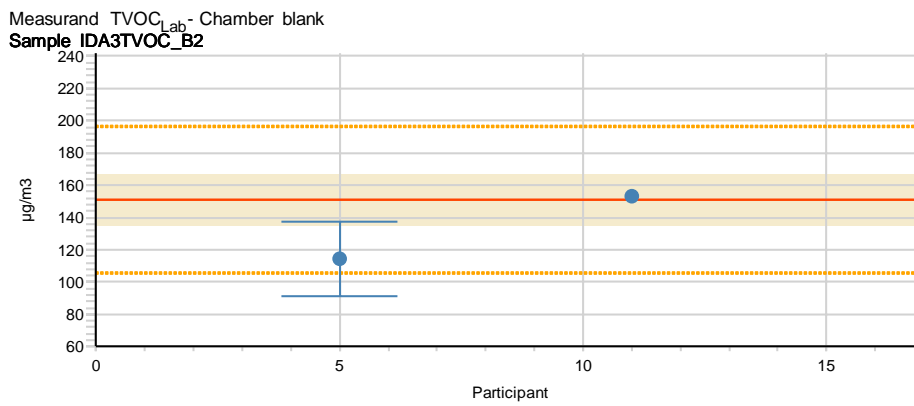
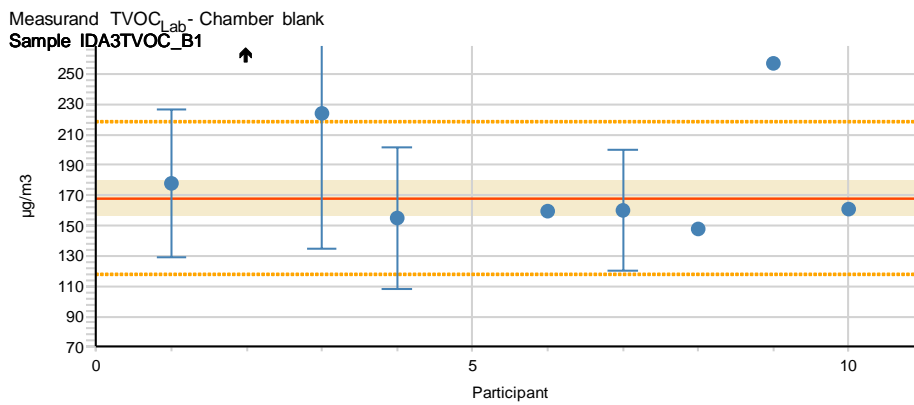
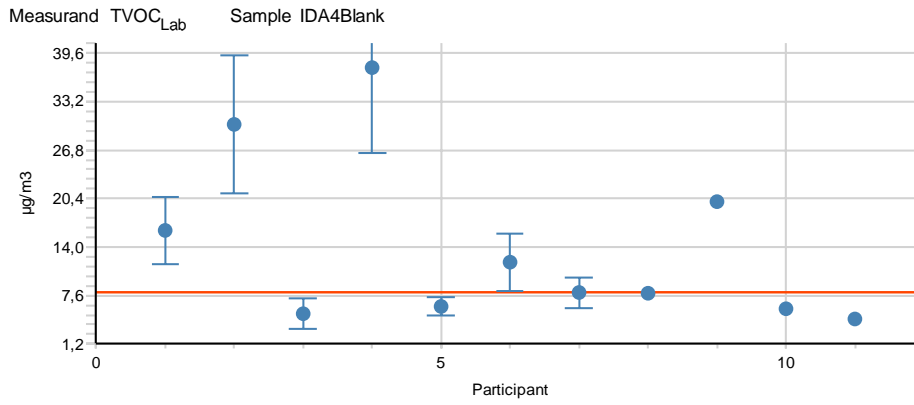


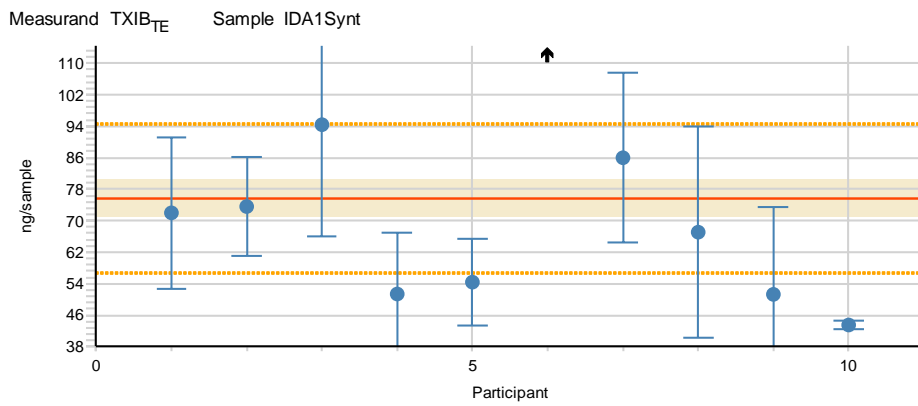
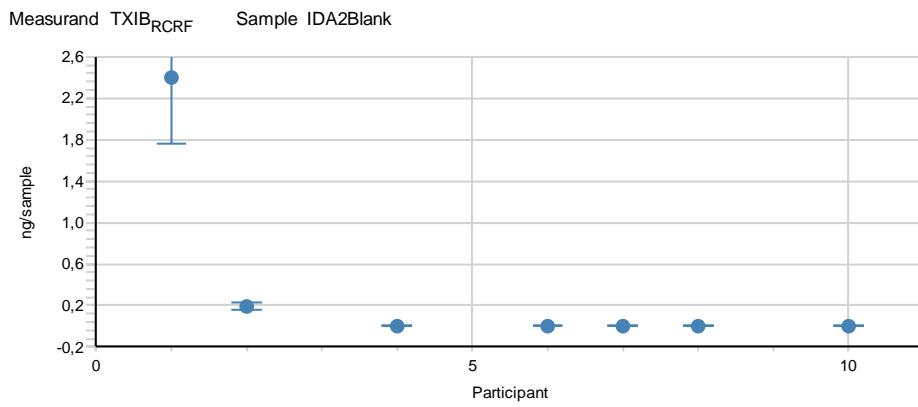
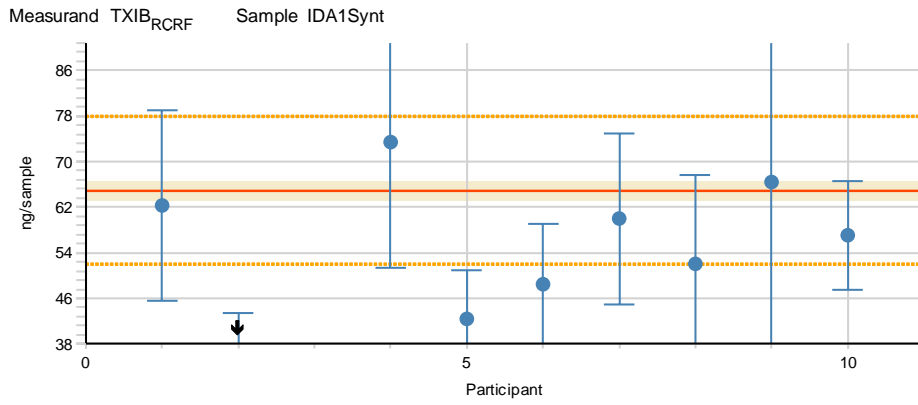
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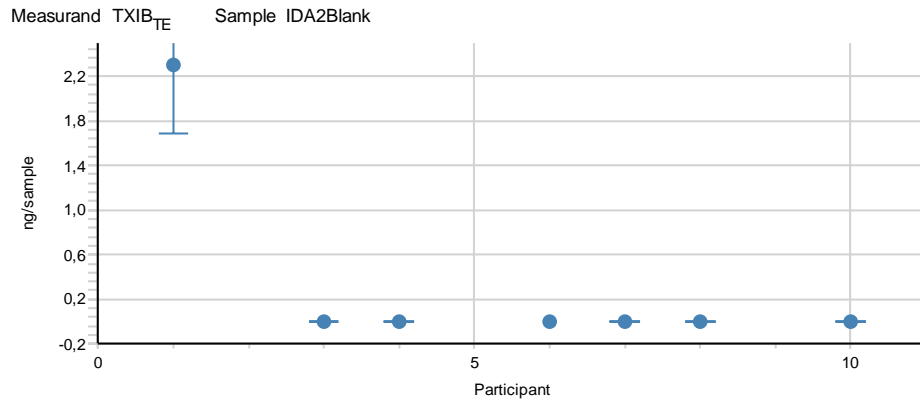


APPENDIX 8 (8/10)





APPENDIX 8 (10/10)



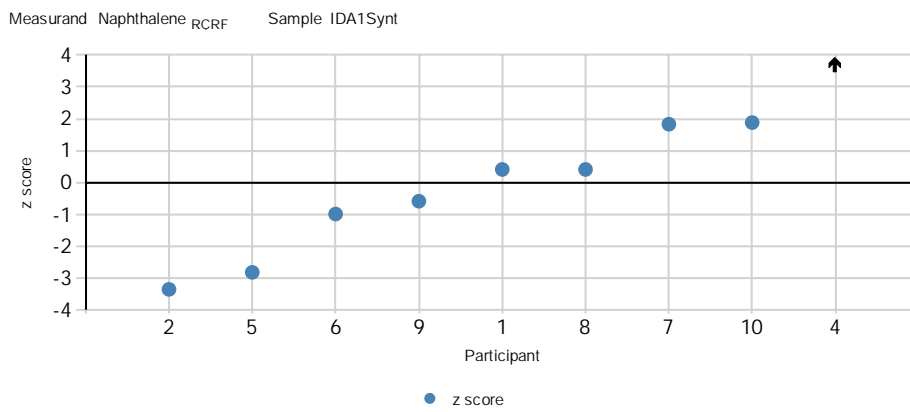
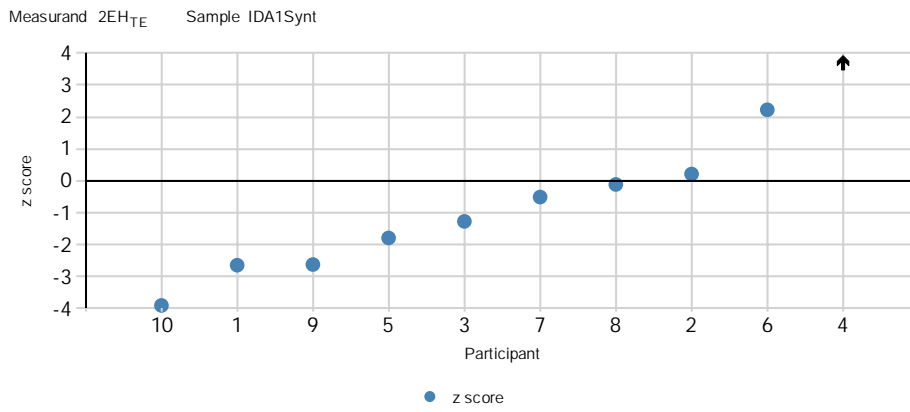
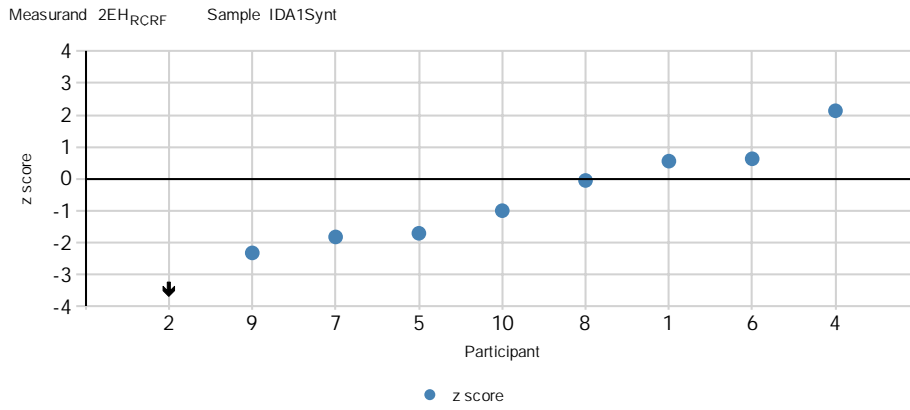
## APPENDIX 9: Summary of the z scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%	
2EH <sub>R</sub> CRF	IDA1Synt	S	<i>u</i>	.	Q	S	S	S	S	<i>q</i>	S	.	.	.	.	.	.	.	.	.	.	.	.	.	66.7	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
2EH <sub>TE</sub>	IDA1Synt	<i>q</i>	S	S	U	S	Q	S	S	<i>q</i>	<i>u</i>	.	.	.	.	.	.	.	.	.	.	.	.	.	50.0	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Naphthalene <sub>R</sub> CRF	IDA1Synt	S	<i>u</i>	.	U	<i>q</i>	S	S	S	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	66.7	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Naphthalene <sub>TE</sub>	IDA1Synt	S	S	S	U	<i>q</i>	Q	S	S	<i>q</i>	S	.	.	.	.	.	.	.	.	.	.	.	.	.	60.0	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Styrene <sub>R</sub> CRF	IDA1Synt	S	<i>q</i>	.	Q	S	S	S	S	<i>u</i>	S	.	.	.	.	.	.	.	.	.	.	.	.	.	66.7	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Styrene <sub>TE</sub>	IDA1Synt	S	<i>q</i>	S	U	S	S	S	S	<i>q</i>	S	.	.	.	.	.	.	.	.	.	.	.	.	.	70.0	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Toluene <sub>R</sub> CRF	IDA1Synt	S	<i>q</i>	S	U	S	S	Q	S	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	70.0	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TVOC <sub>Guide</sub>	IDA3TVOC_B1	S	U	S	S	.	S	S	S	U	S	.	.	.	.	.	.	.	.	.	.	.	.	.	77.8	
	IDA3TVOC_B2	.	.	.	.	S	.	.	.	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	100	
	IDA4Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TVOC <sub>Guide</sub> -Chamber blank	IDA3TVOC_B1	S	U	S	S	.	S	S	S	U	S	.	.	.	.	.	.	.	.	.	.	.	.	.	77.8	
	IDA3TVOC_B2	.	.	.	.	S	.	.	.	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	100	
TVOC <sub>Lab</sub>	IDA3TVOC_B1	S	U	S	S	.	S	S	S	U	S	.	.	.	.	.	.	.	.	.	.	.	.	.	77.8	
	IDA3TVOC_B2	.	.	.	.	S	.	.	.	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	100	
	IDA4Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TVOC <sub>Lab</sub> -Chamber blank	IDA3TVOC_B1	S	U	Q	S	.	S	S	S	U	S	.	.	.	.	.	.	.	.	.	.	.	.	.	66.7	
	IDA3TVOC_B2	.	.	.	.	S	.	.	.	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	100	
TXIB <sub>R</sub> CRF	IDA1Synt	S	<i>u</i>	.	S	<i>u</i>	<i>q</i>	S	S	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	66.7	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
TXIB <sub>TE</sub>	IDA1Synt	S	S	S	<i>q</i>	<i>q</i>	U	S	S	<i>q</i>	<i>u</i>	.	.	.	.	.	.	.	.	.	.	.	.	.	50.0	
	IDA2Blank	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
%		92	23	89	38	69	69	92	100	23	85	100														
accredited		13	13	9	13	4	13	13	13	13		3														

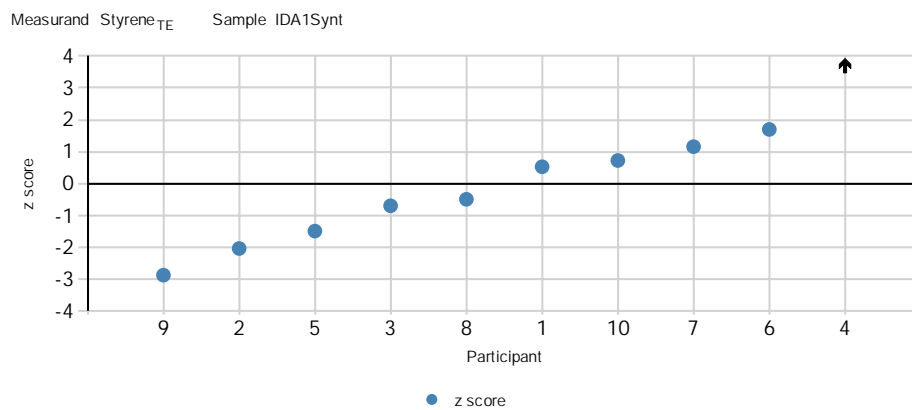
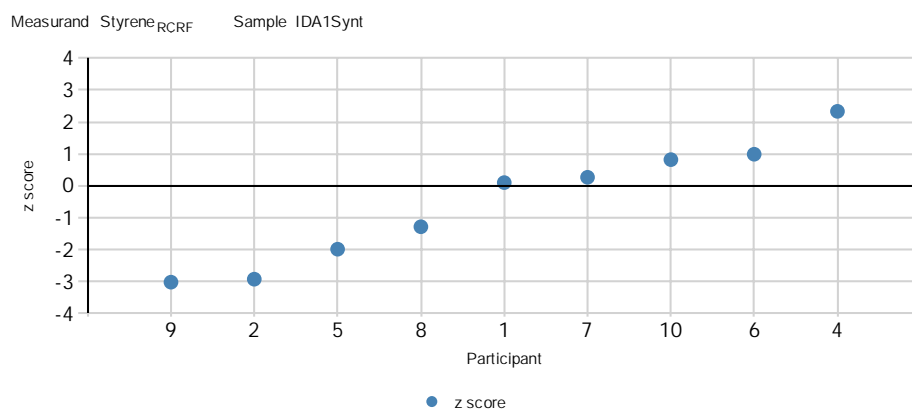
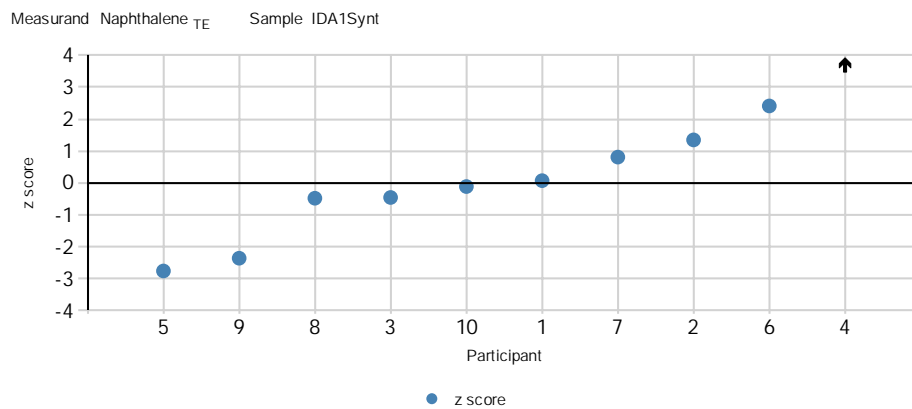
**S** - satisfactory ( $-2 \leq z \leq 2$ ), **Q** - questionable ( $2 < z < 3$ ), **q** - questionable ( $-3 < z < -2$ ),  
**U** - unsatisfactory ( $z \geq 3$ ), and **u** - unsatisfactory ( $z \leq -3$ ), respectively  
**bold** - accredited, **italics** - non-accredited, normal - other  
% - percentage of satisfactory results

Totally satisfactory, % in all: 68      % in accredited: 66      % in non-accredited: 78

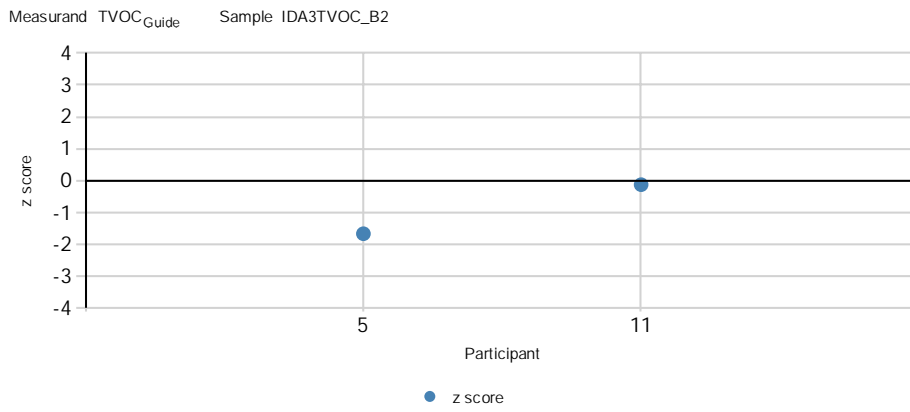
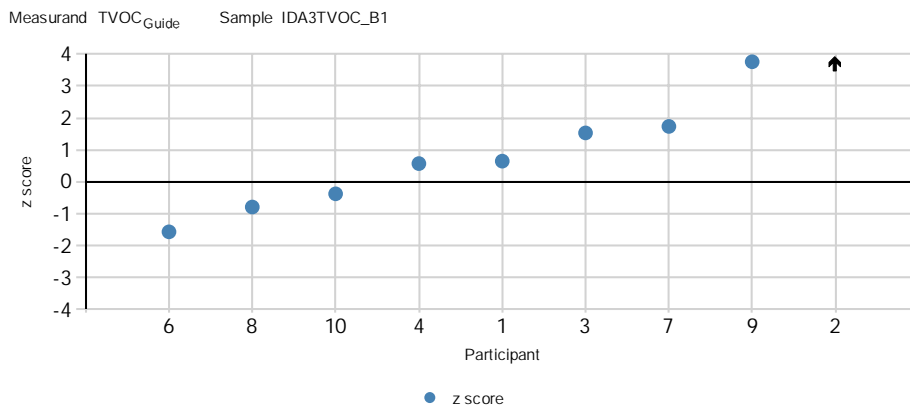
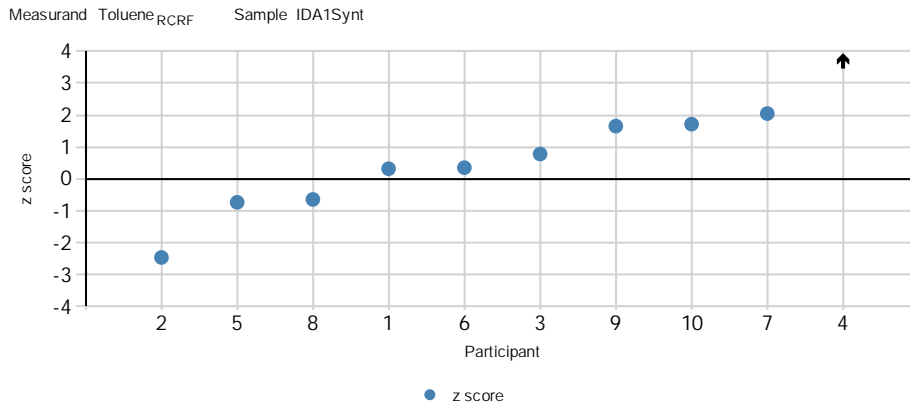
APPENDIX 10: z scores in ascending order

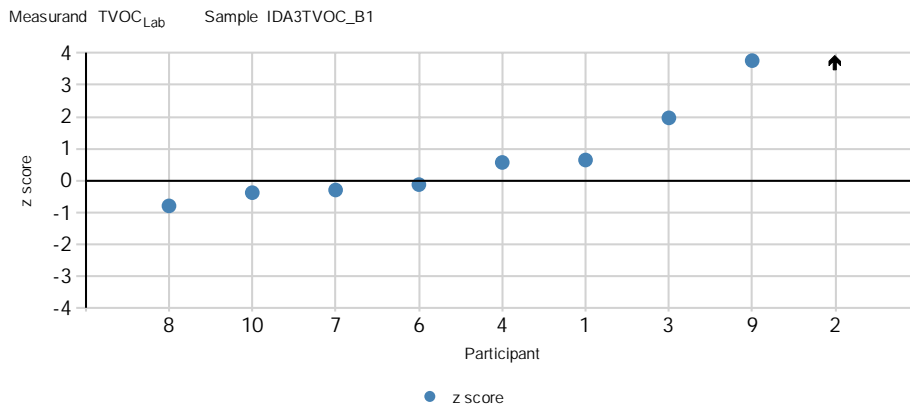
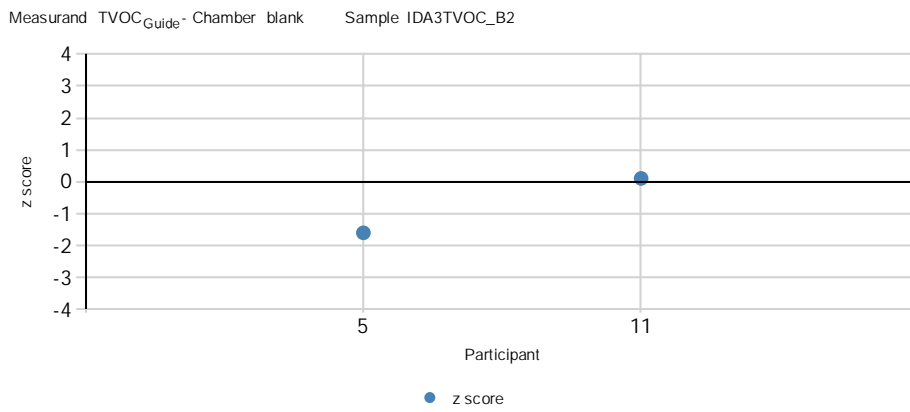
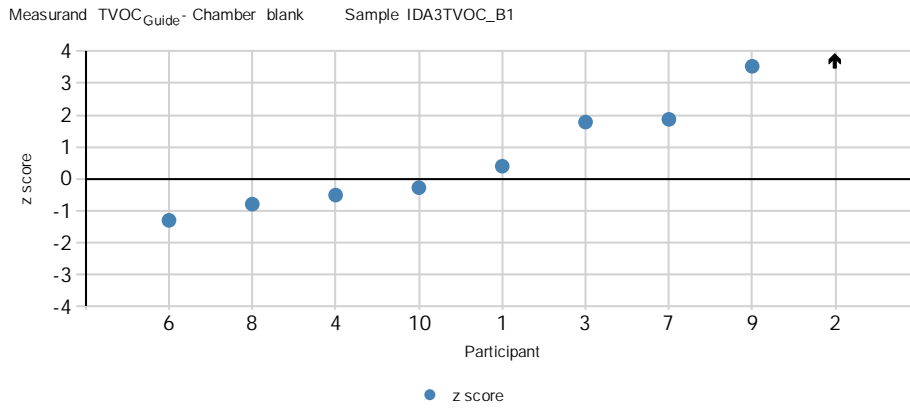




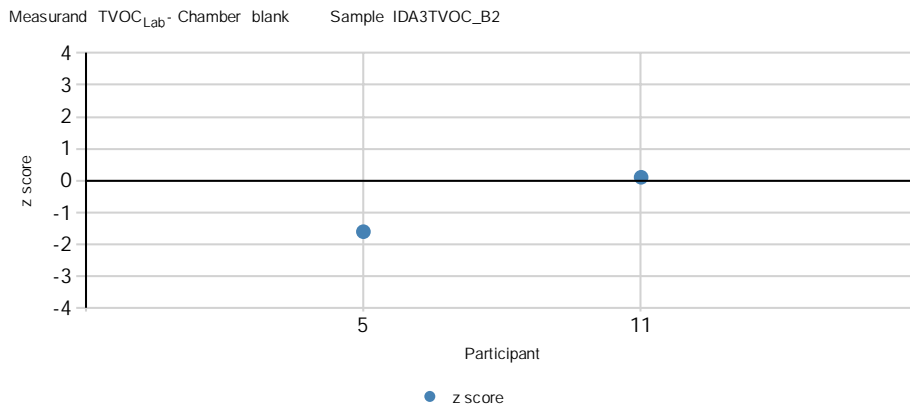
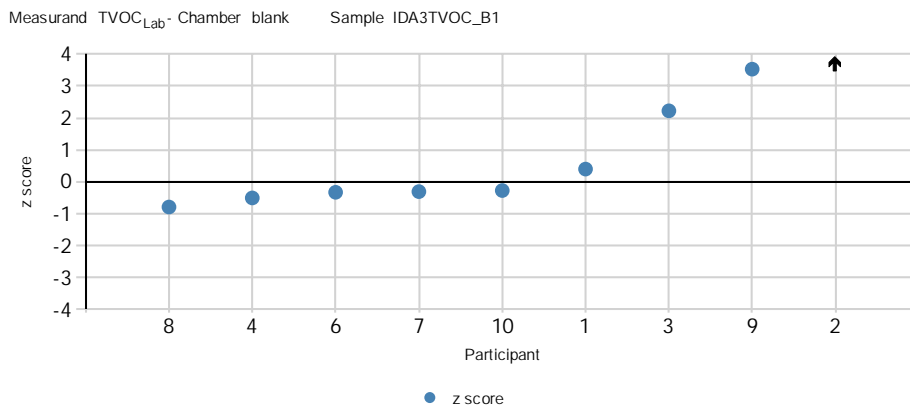
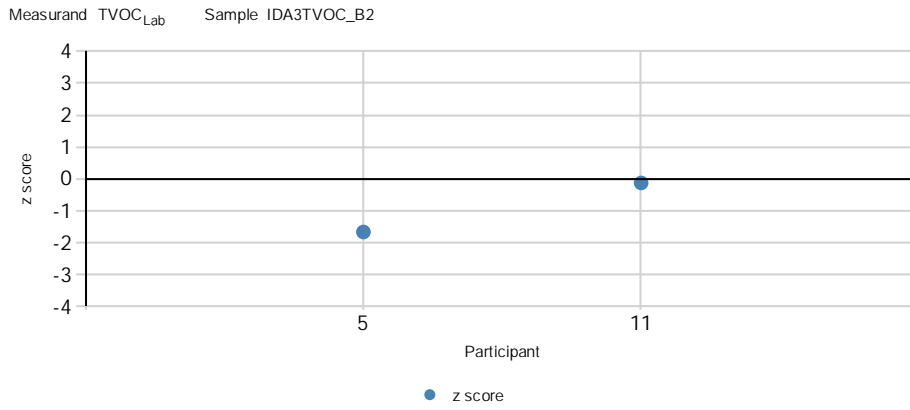


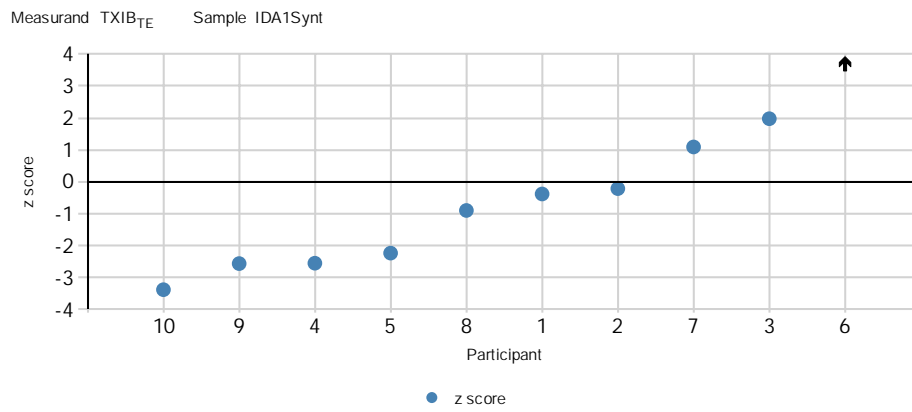
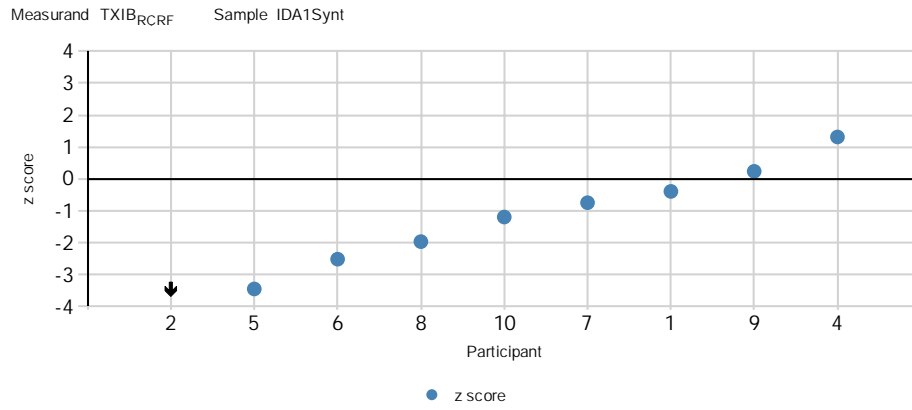
APPENDIX 10 (3/6)





APPENDIX 10 (5/6)





## APPENDIX 11: Analytical methods and recognized compounds

Participant	8	1	2	3	4	5	6	7	9	10
What kind of thermodesorption system/instrument was used?	Markes TD100	Markes TD-100 with MFCs	SHIMADZU	Markes TD100 - Agilent GC-MS (6890-5973)	Markes TD100	Markes TD-100	Markes Unity 2 TD /Agilent GC-MSD (7890A /5975C)	Markes TD100	Perkin Elmer Turbomatrix 650 ATD, Turbomass XL GC and Turbomass Gold MS	STD DANI, model TD Master
What desorption temperature was used, in (°C)?	280	320	280	280	300	300	270	260	300	260°C
What desorption flow was the used, in ml/min?	50 ml/min	50	50	50	20	40	30	50	50	34 ml/min
How long was desorption time, in minutes?	10	Primary desorption was 8 mins and secondary 5 mins	5	5	8	7	10	6	15	10 min
What was the temperature of the cryo cold trap and the heating temperature, in °C?	-30 300	+15	-20, 280	0	-10 and 310	10 - 300	-10, 300	20/ 280	-30 and 300	-35°C and 300°C
What was flow rate of carrier gas, in ml/min?	1 ml/min	At the beging it was 1 ml/min but we are using the constant pressure mode (30 psi)	50	20	1	50	2	1	1,2	0.44 ml/min

Participant	8	1	2	3	4	5	6	7	9	10
Which type of analytical column was used?	HP-5	HP-5 ms (50 m x 0,200 mm x 0,33 µm)	ZB-5MSPlus	HP-5MS	HP5-MSUI 30x0,25x0,25	HP-5 30m, diameter 0,25mm, film thickness 0,25µm	HP 5	HP MS5	DB-1701	HP-5MS (50 m X 200 um x 0.33 um)
What kind of detector(s) was used?	MSD	Agilent 5977 A MS with inert ion source	single quadrupole MS	MSD (Agilent 5973)	MSD and FID	MS	MSD	MS, FID (double column system)	MS	MSD
Did your results include the recovery rate?	no	no		No	No	No	no	no	No, but results are usually corrected with internal standard	Yes.
Other comments?				Ca. 50 compounds were analyzed in TVOC-are, not all compounds! We were not aware of this "extra" task so we ran out of time in analyzing the compounds.	No			leak test failed for 358879 (several attempts), tube not analysed		
Do you have suggestions for substances for the next intercomparison?		More analytes from this list: <a href="https://www.ttl.fi/wp-content/uploads/2016/09/sisaympariston-viitearvoja.pdf">https://www.ttl.fi/wp-content/uploads/2016/09/sisaympariston-viitearvoja.pdf</a>		More exact information what should be done in time!	No					yes, tetrachloroethylene and benzene

APPENDIX 11 (3/4)

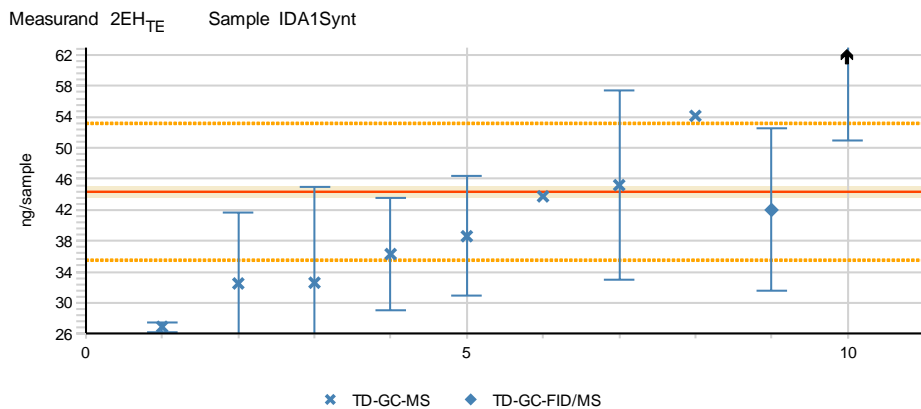
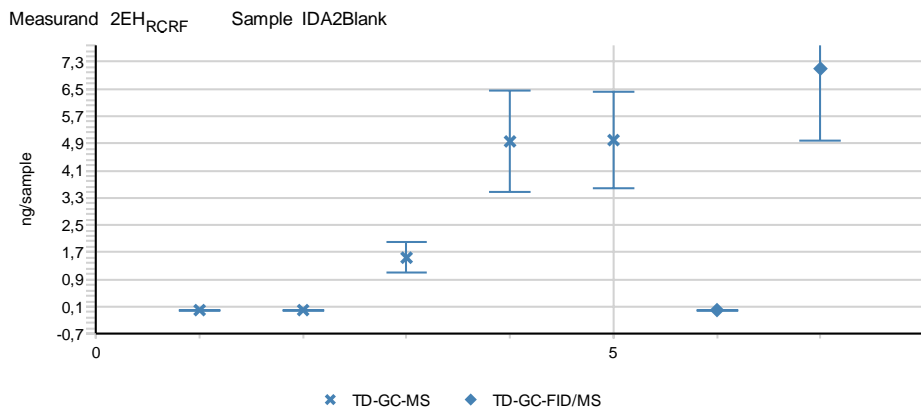
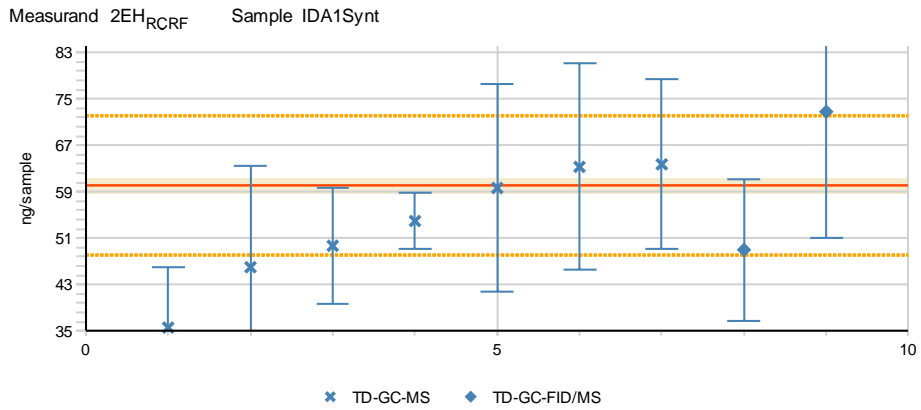
Participant	8	1	2	3	4	5	6	7	9	10
Recognized compounds from the expected 14 (> 1 µg/m³ RCRF)	14	14	11	7	8	7	11	8	9	12
Which VOC compounds were recognized from the chamber samples? Please, select below (1/6).	Borneol, 464-45-9, 1-Butanol, 71-36-3	1-Butanol, 71-36-3, Borneol, 464-45-9, Benzaldehyde, 100-52-7, Acetic acid glacial, 64-19-7	Acetic acid glacial, 64-19-7, Benzaldehyde, 100-52-7, Borneol, 464-45-9, 1-Butanol, 71-36-3	Borneol, 464-45-9	Benzaldehyde, 100-52-7, Benzene, 71-43-2, Borneol, 464-45-9, 1-Butanol, 71-36-3, 2-(2-Butoxyethoxy)ethanol, 112-34-5	1-Butanol, 71-36-3	Borneol, 464-45-9, 1-Butanol, 71-36-3	Acetic acid glacial, 64-19-7, Benzene, 71-43-2, 1-Butanol, 71-36-3	1-Butanol, 71-36-3, Borneol, 464-45-9	Acetic acid glacial, 64-19-7, Benzaldehyde, 100-52-7, Borneol, 464-45-9, 1-Butanol, 71-36-3
Which one VOC compounds were recognized from the chamber samples? Please, select below (2/6).	Camphor, 76-22-2, 1,8-Cineole, 470-82-6, Decanal, 112-31-2, Di(propylene glycol)monobutylether, 29911-28-2	Di(propyleneglycol)monobutylether, 29911-28-2, Decanal, 112-31-2, Decamethylcyclotrasiloxane, 541-02-6, 1,8-Cineole, 470-82-6, Camphor, 76-22-2	Camphor, 76-22-2, 1,8-Cineole, 470-82-6, Decanal, 112-31-2, Di(propyleneglycol)monobutylether, 29911-28-2	Decanal, 112-31-2, Decamethylcyclopentasiloxane, 541-02-6, 1,8-Cineole, 470-82-6, 3-Carene, 13466-78-9, Camphor, 76-22-2	Camphor, 76-22-2, 3-Carene, 13466-78-9, Decamethylcyclopentasiloxane, 541-02-6, Decanal, 112-31-2, Dodecane, 112-40-3	1,8-Cineole, 470-82-6, Di(propylene glycol)monobutylether, 29911-28-2	Camphor, 76-22-2, Di(propylene glycol)monobutylether, 29911-28-2, Decanal, 112-31-2	Di(propyleneglycol)monobutylether, 29911-28-2, Decanal, 112-31-2	Camphor, 76-22-2	Camphor, 76-22-2, 3-Carene, 13466-78-9, 1,8-Cineole, 470-82-6, Decamethylcyclopentasiloxane, 541-02-6, Di(propyleneglycol)monobutylether, 29911-28-2
Which one VOC compounds were recognized from the chamber samples? Please, select below (3/6).	2-Ethyl-1-hexanol, 104-76-7, Fenchyl alcohol, 1632-73-1	Fenchyl alcohol, 1632-73-1, n-Hexadecane, 544-76-3, Hexanal, 66-25-1, 2-Ethyl-1-hexanol, 104-76-7	2-Ethyl-1-hexanol, 104-76-7, Fenchyl alcohol, 1632-73-1	Fenchyl alcohol, 1632-73-1	2-Ethyl-1-hexanol, 104-76-7	2-Ethyl-1-hexanol, 104-76-7	Fenchyl alcohol, 1632-73-1, 2-Ethyl-1-hexanol, 104-76-7	2-Ethyl-1-hexanol, 104-76-7	Fenchyl alcohol, 1632-73-1, 2-Ethyl-1-hexanol, 104-76-7	2-Ethyl-1-hexanol, 104-76-7, Fenchyl alcohol, 1632-73-1

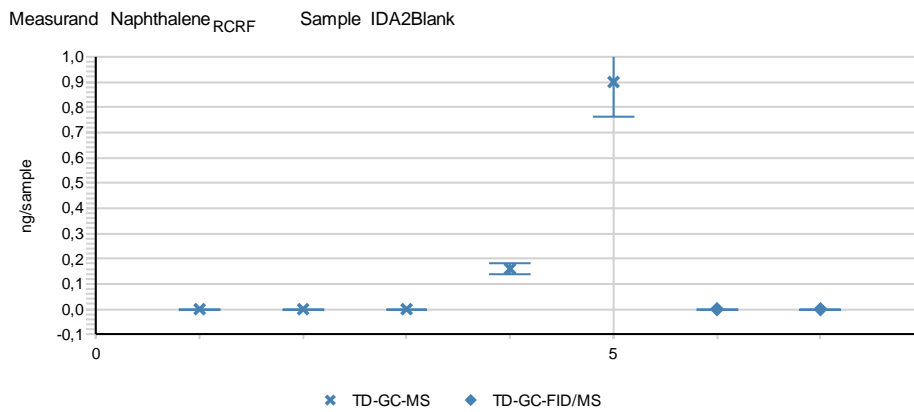
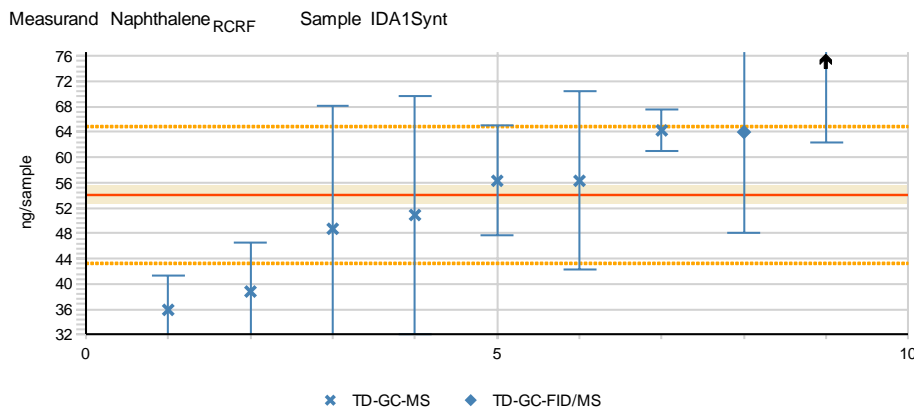
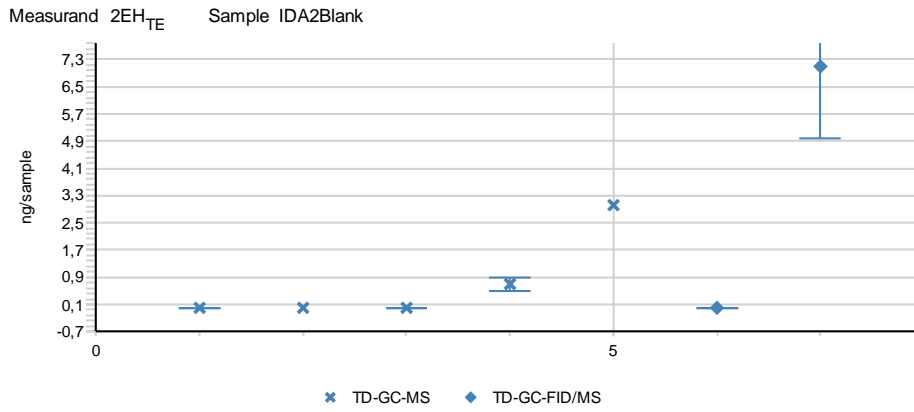


Participant	8	1	2	3	4	5	6	7	9	10
Which one VOC compounds were recognized from the chamber samples? Please, select below (4/6).	Limonene, 5989-27-5, 1-Methyl-4-isopropylbenzene, 99-87-6, 1-Methyl-4-isopropylenebenzene, 1195-32-0	Limonene, 5989-27-5, 1-Methyl-4-isopropylbenzene, 99-87-6, 1-Methyl-4-isopropylenebenzene, 1195-32-0	Limonene, 5989-27-5, 1-Methyl-4-isopropylbenzene, 99-87-6	Limonene, 5989-27-5	Limonene, 5989-27-5, 1-Methyl-4-isopropylenebenzene, 1195-32-0, 1-Methoxy-2-propanol, 107-98-2, Naphthalene, 91-20-3, Pentadecane, 629-62-9	1-Methyl-4-isopropylenebenzene, 1195-32-0	1-Methyl-4-isopropylenebenzene, 1195-32-0, 1-Methyl-4-isopropylbenzene, 99-87-6, Limonene, 5989-27-5	Limonene, 5989-27-5	1-Methyl-4-isopropylenebenzene, 1195-32-0, 1-Methyl-4-isopropylbenzene, 99-87-6, Limonene, 5989-27-5	Limonene, 5989-27-5, 1-Methyl-4-isopropylbenzene, 99-87-6, 1-Methyl-4-isopropylenebenzene, 1195-32-0
Which one VOC compounds were recognized from chamber the samples? Please, select below (5/6).	1,2-Propanediol, 57-55-6, alpha-Terpinolene, 586-62-9	Phenol, 108-95-2, alpha-Pinene, 80-56-8, 1,2-Propanediol, 57-55-6, alpha-Terpinolene, 586-62-9, Toluene, 108-88-3	Phenol, 108-95-2, alpha-Pinene, 80-56-8, 1,2-Propanediol, 57-55-6	Toluene, 108-88-3, alpha-Terpinolene, 586-62-9, alpha-Pinene, 80-56-8	Phenol, 108-95-2, alpha-Pinene, 80-56-8, Styrene, 100-42-5, Toluene, 108-88-3	alpha-Terpinolene, 586-62-9	Phenol, 108-95-2	Toluene, 108-88-3, alpha-Terpinolene, 586-62-9, 1,2-Propanediol, 57-55-6, alpha-Pinene, 80-56-8, Phenol, 108-95-2	beta-Pinene, 127-91-3, alpha-Terpinolene, 586-62-9, alpha-Pinene, 80-56-8	Phenol, 108-95-2, alpha-Pinene, 80-56-8, Toluene, 108-88-3
Which one VOC compounds were recognized from the chamber samples? Please, select below (6/6).	2,2,4-Trimethyl-1,3-pentanediolmono(2-methylpropanoate), Texanol, 25265-77-4	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, 6846-50-0, 2,2,4-Trimethyl-1,3-pentanediolmono(2-methylpropanoate), Texanol, 25265-77-4	n-Tridecane, 629-50-5		n-Tridecane, 629-50-5, 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, 6846-50-0, 2,2,4-Trimethyl-1,3-pentanediolmono(2-methylpropanoate), Texanol, 25265-77-4, m-Xylene, 108-38-3, o-Xylene, 95-47-6, p-Xylene, 106-42-3	2,2,4-Trimethyl-1,3-pentanediol mono(2-methylpropanoate), Texanol, 25265-77-4	2,2,4-Trimethyl-1,3-pentanediolmono(2-methylpropanoate), Texanol, 25265-77-4	2,2,4-Trimethyl-1,3-pentanediolmono(2-methylpropanoate), Texanol, 25265-77-4	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, 6846-50-0	2,2,4-Trimethyl-1,3-pentanediolmono(2-methylpropanoate), Texanol, 25265-77-4, m-Xylene, 108-38-3, p-Xylene, 106-42-3

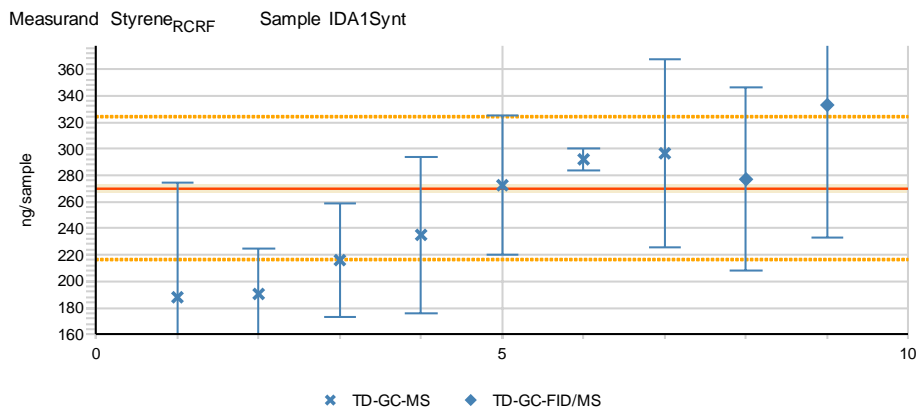
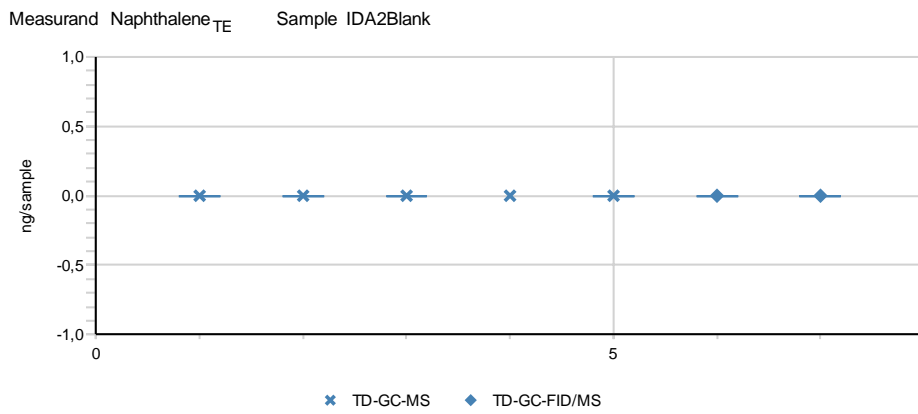
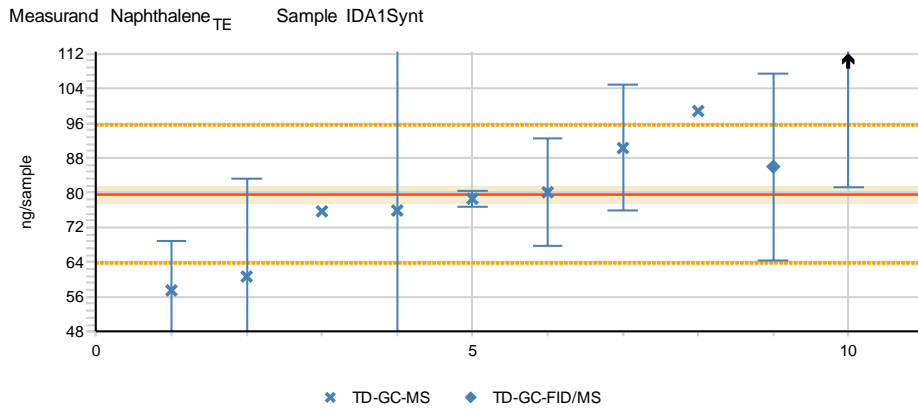
## APPENDIX 12: Results grouped according to the methods

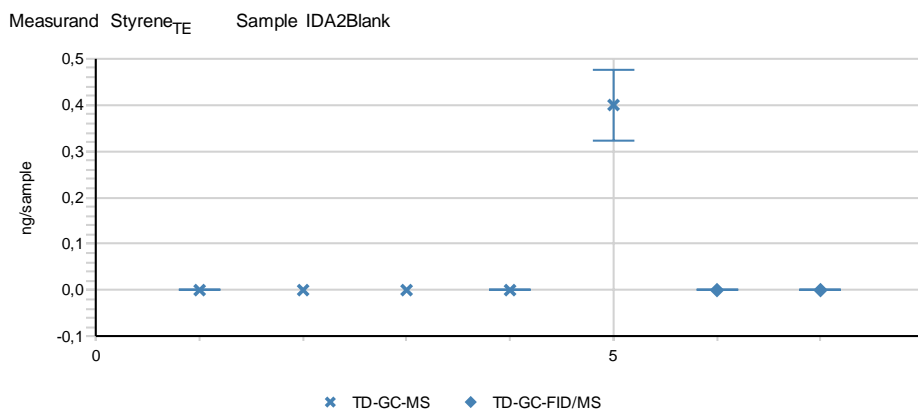
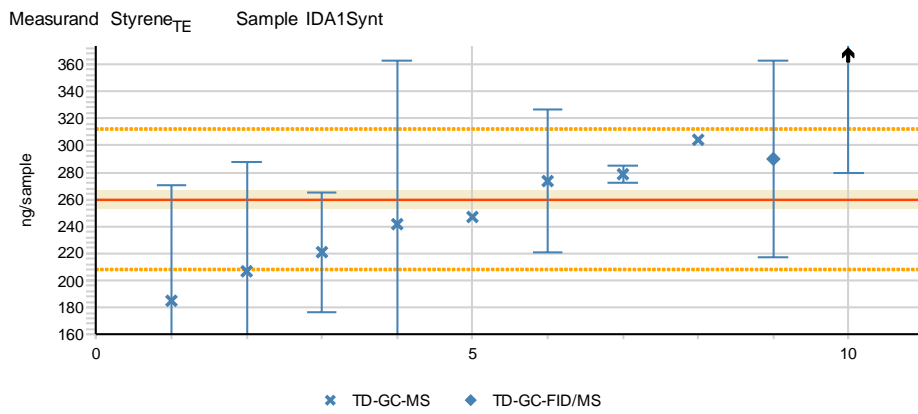
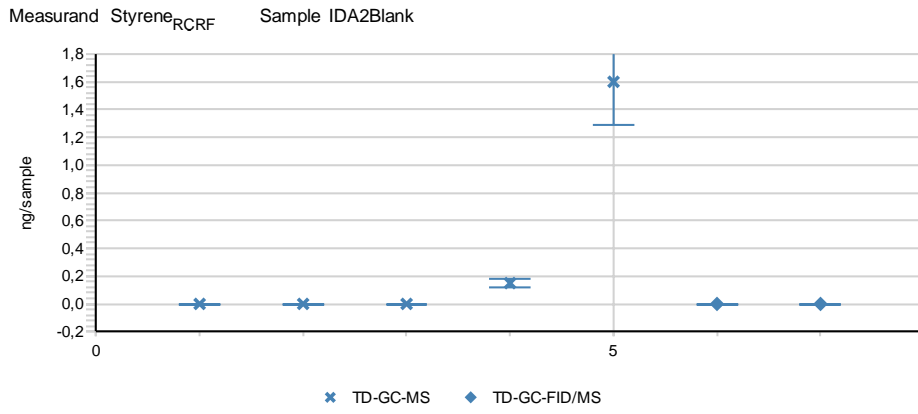
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



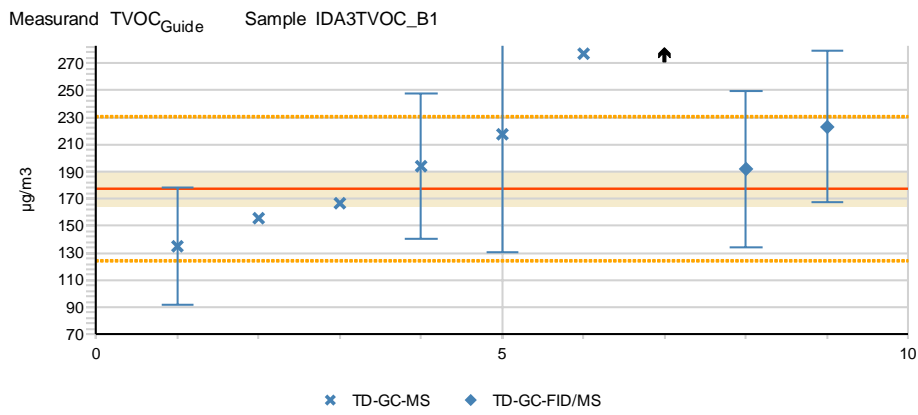
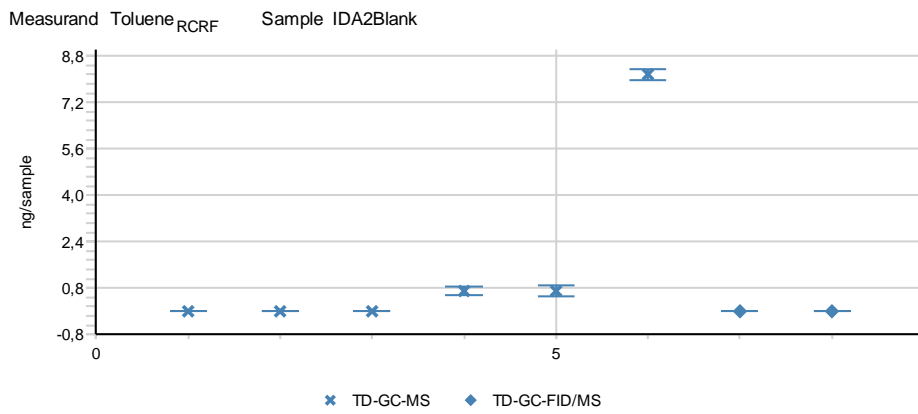
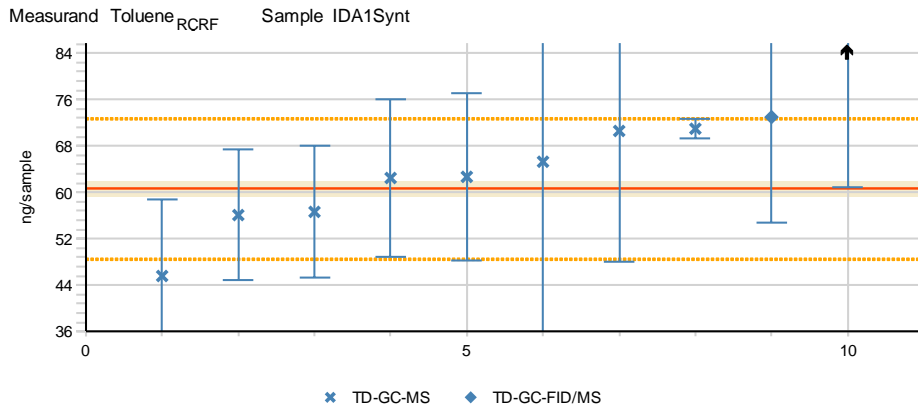


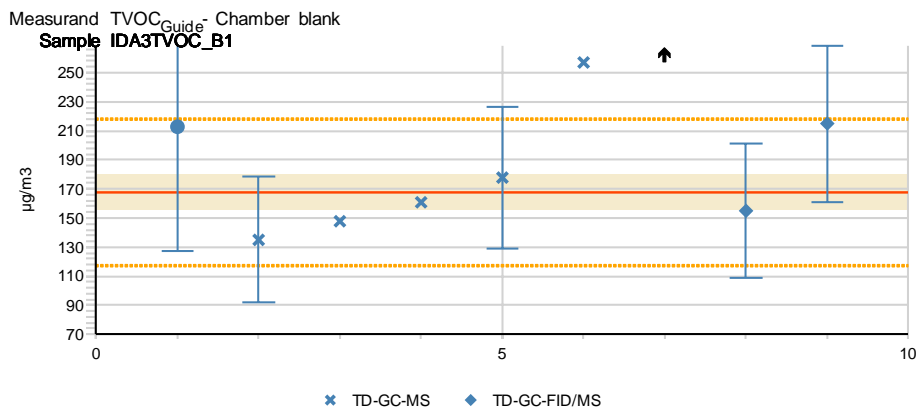
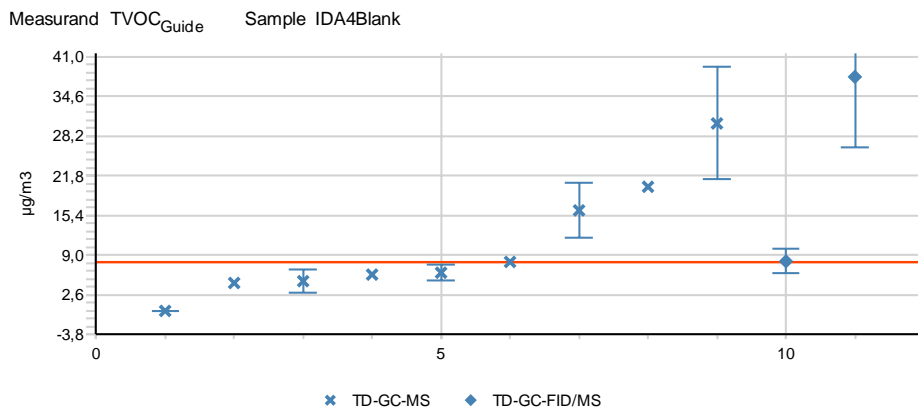
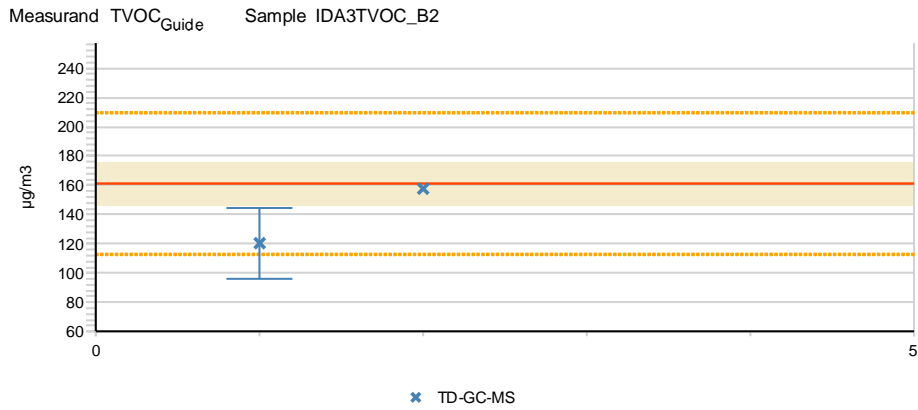
APPENDIX 12 (3/10)



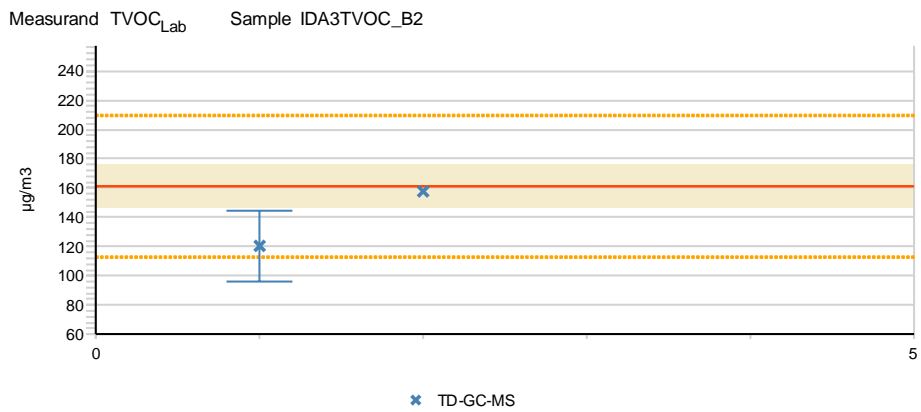
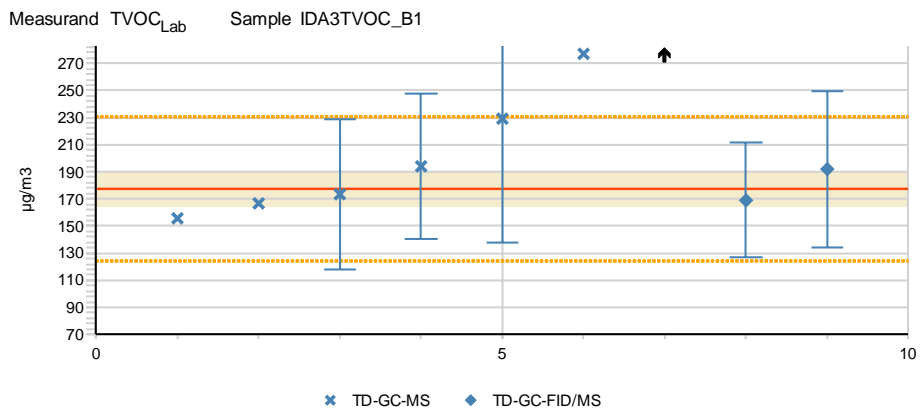
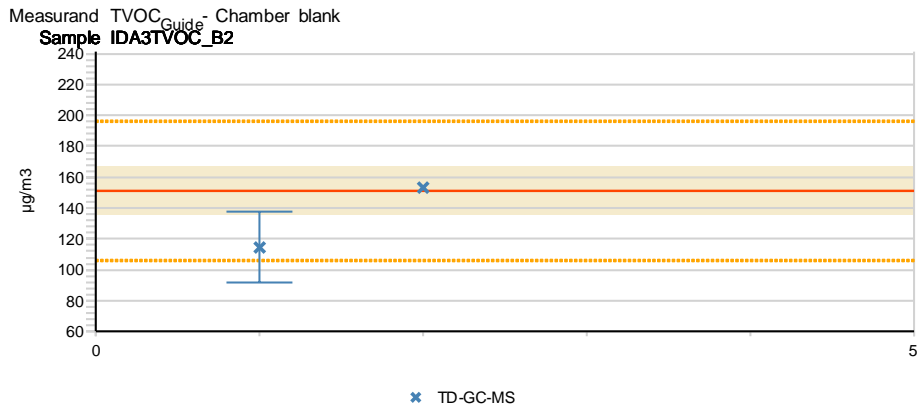


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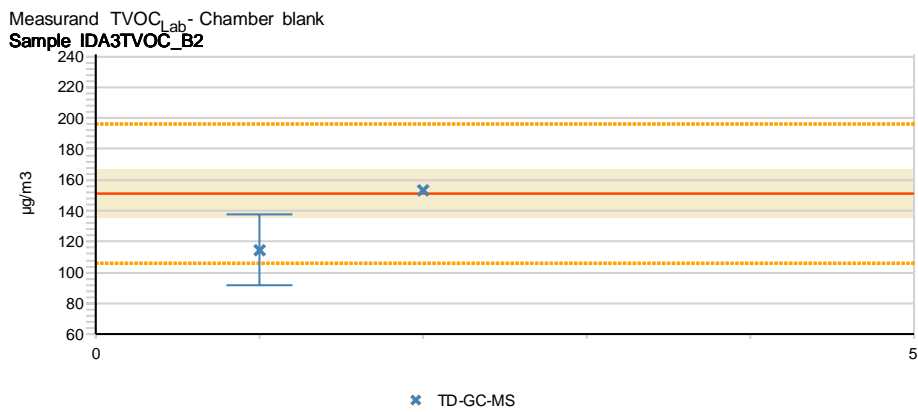
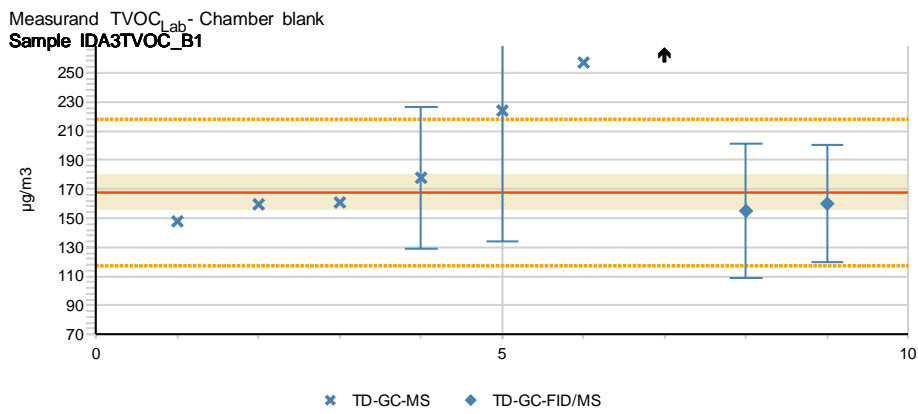
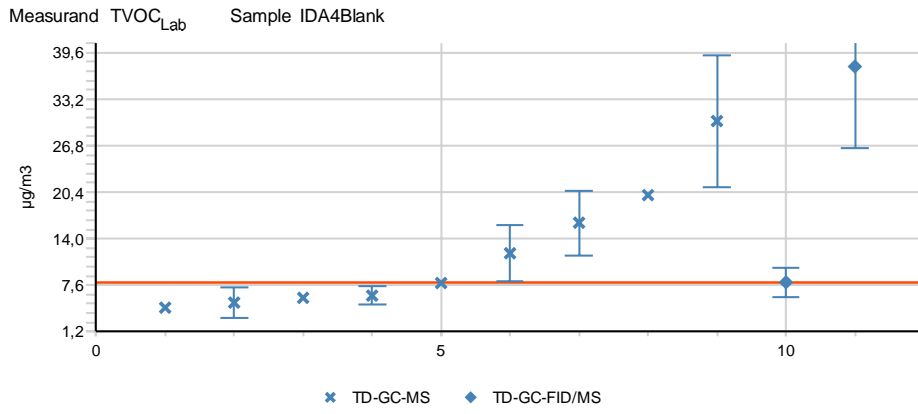




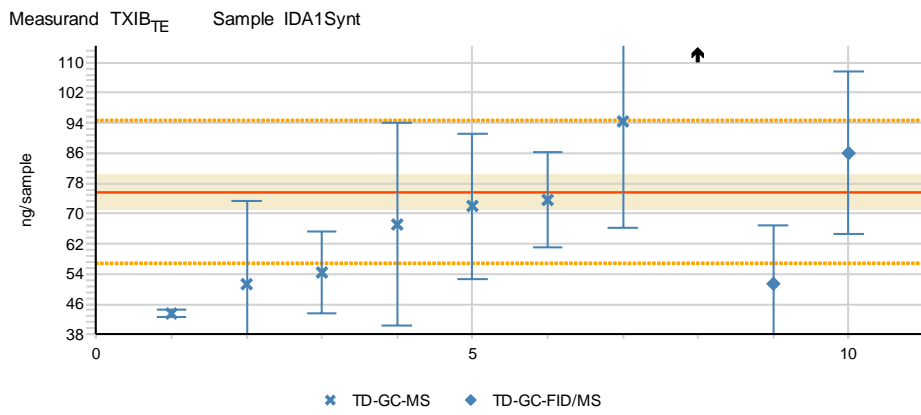
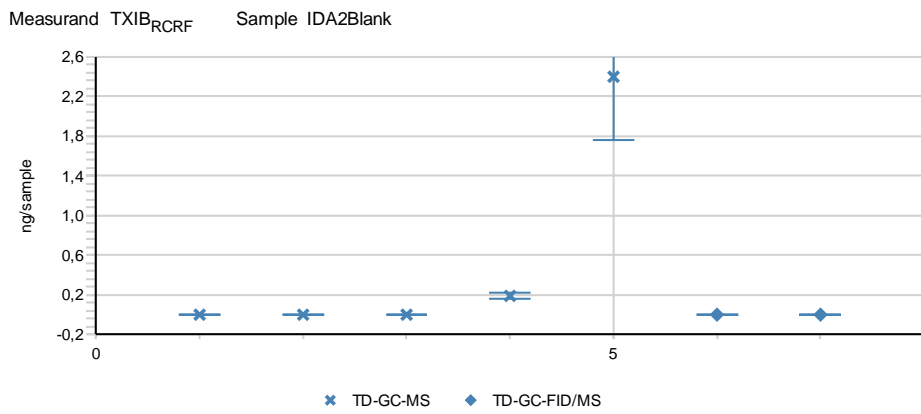
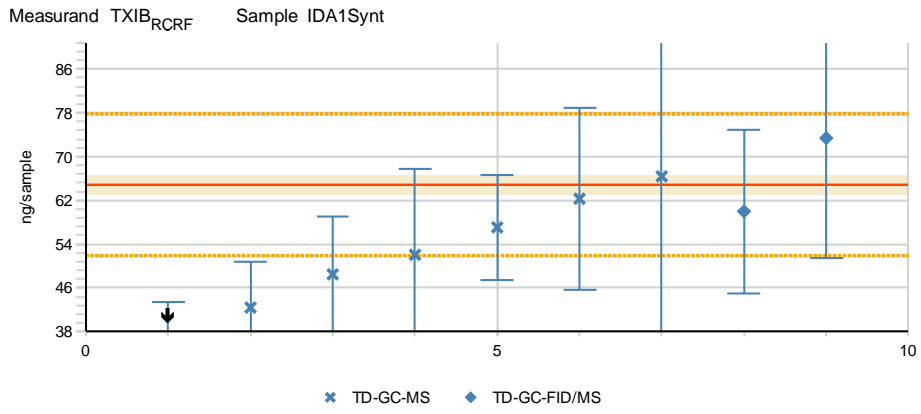
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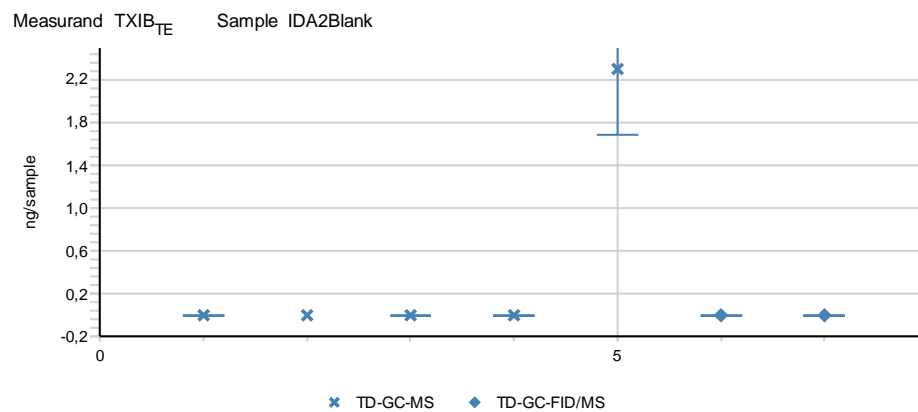






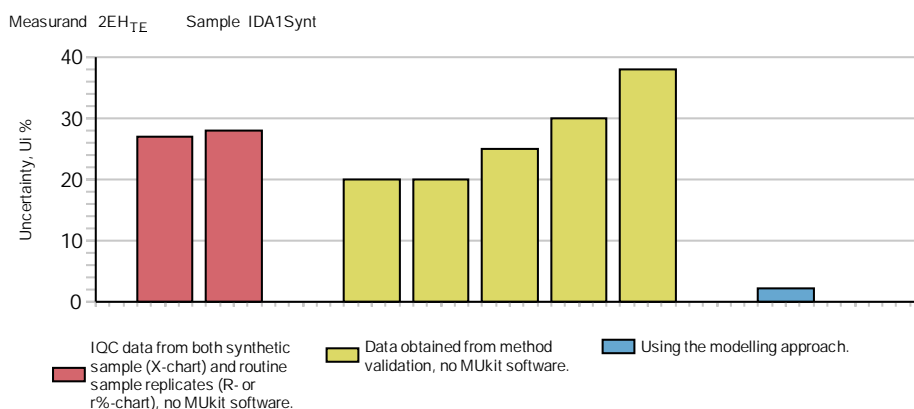
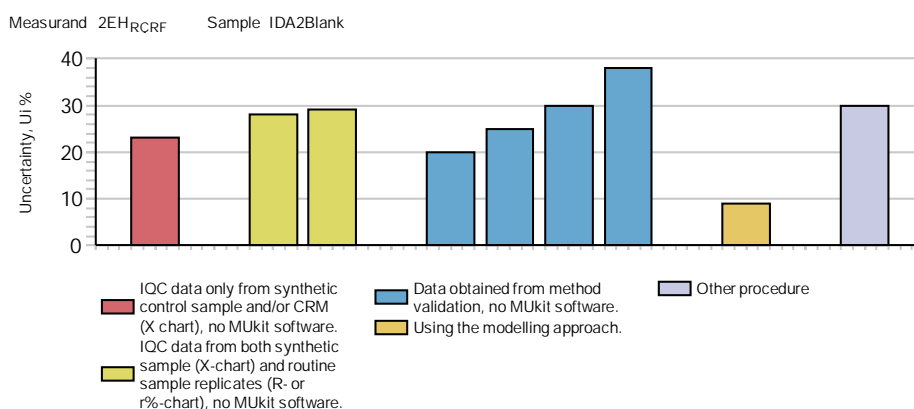
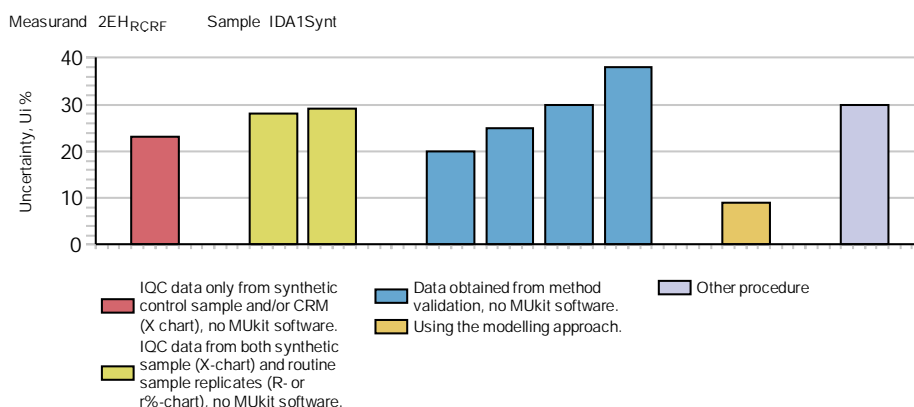
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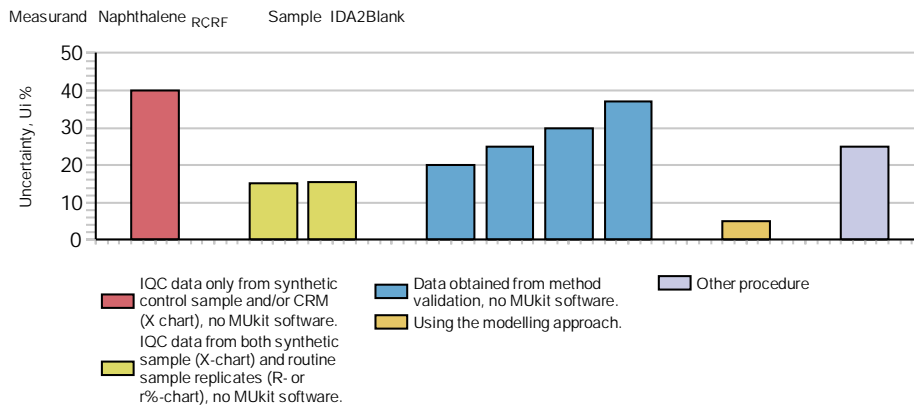
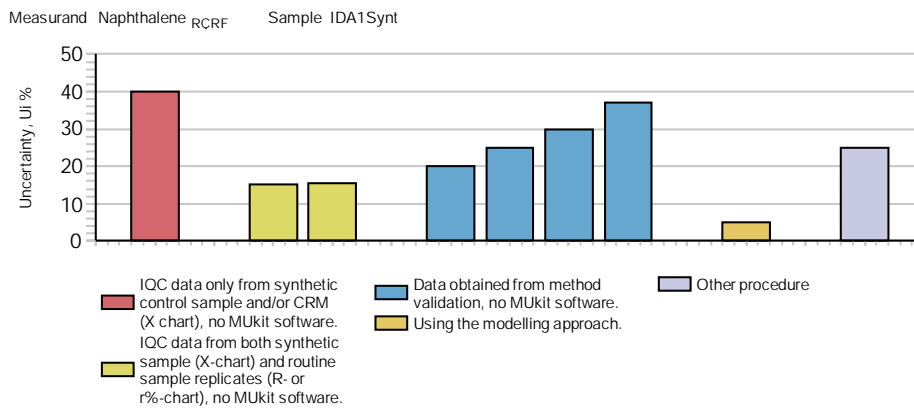
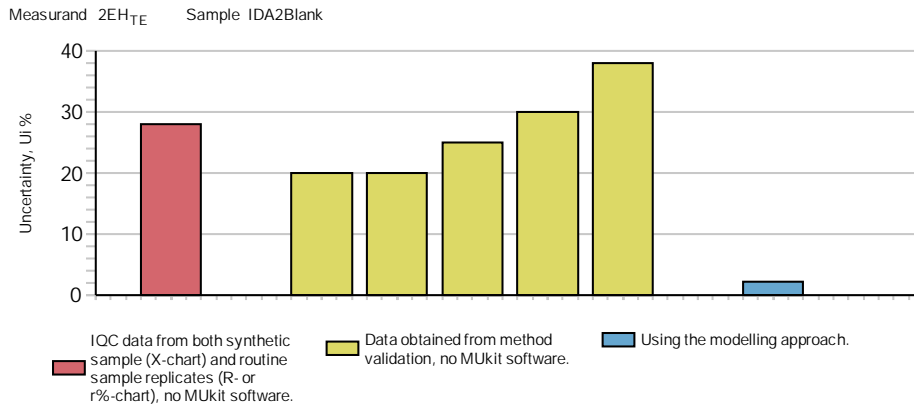




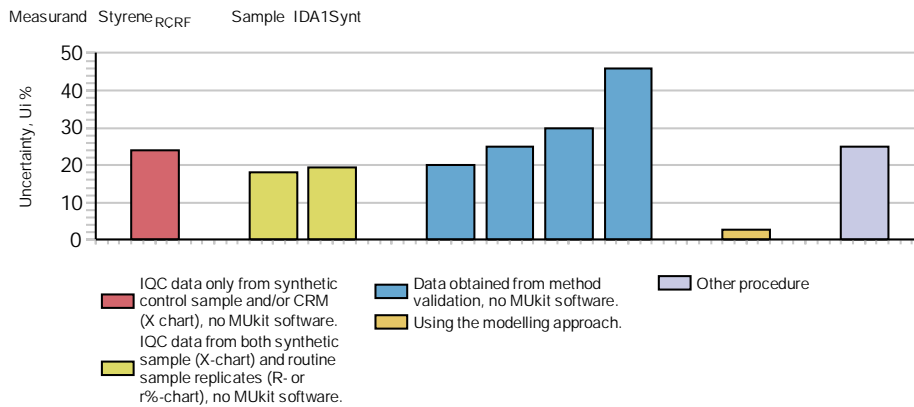
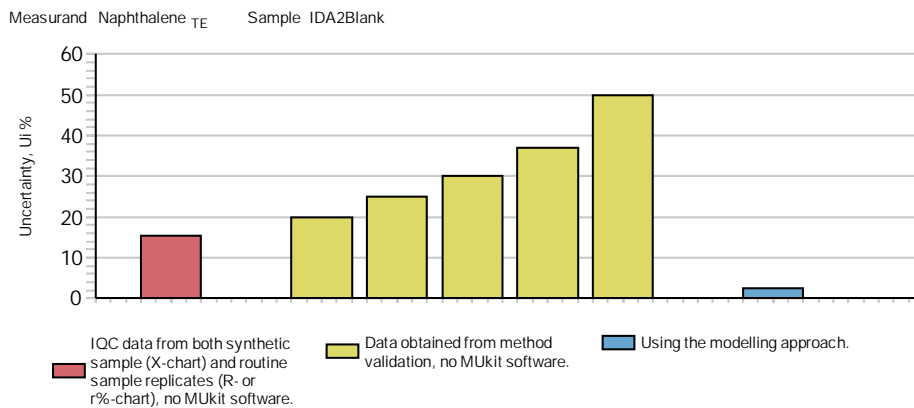
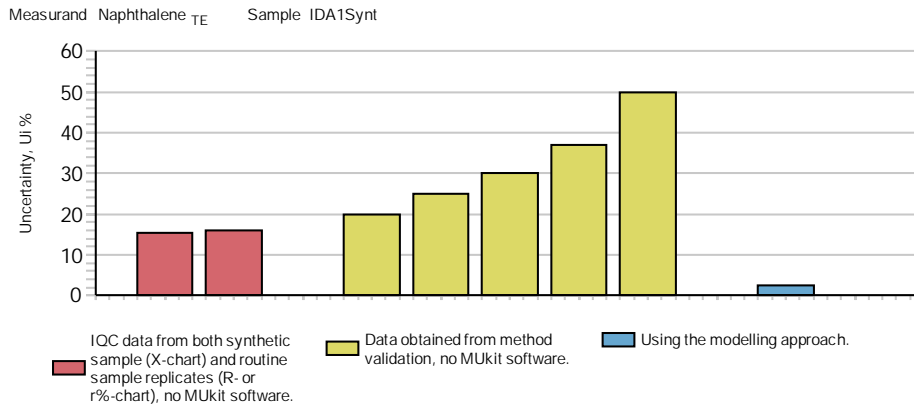
## APPENDIX 13: Examples of measurement uncertainties reported by the participants

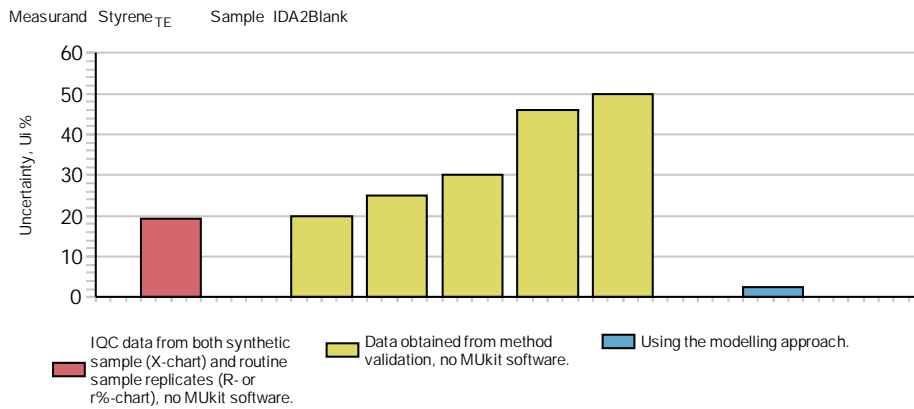
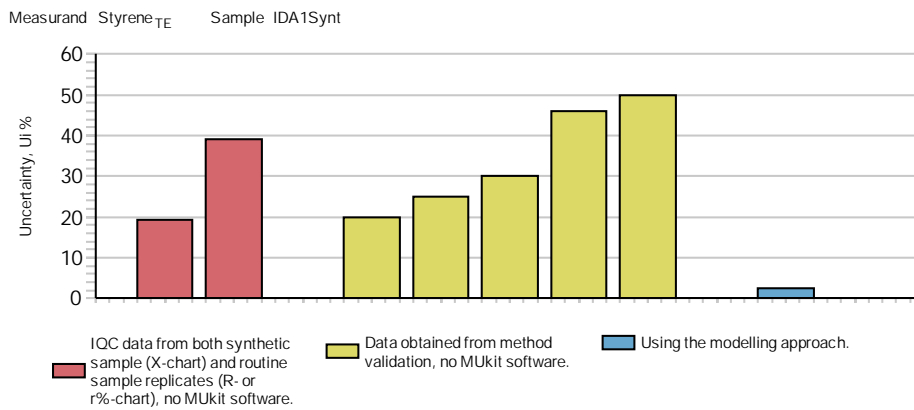
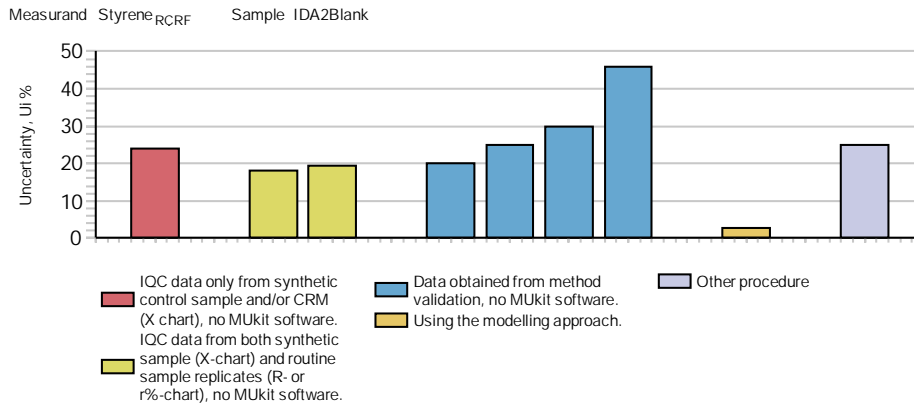
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level ( $k=2$ ). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUKIT software for uncertainty estimation [7, 8] or using a modelling approach based [9, 10].



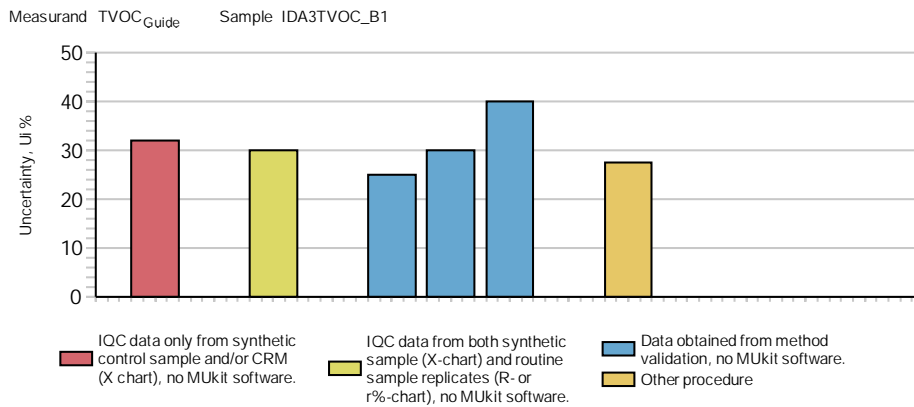
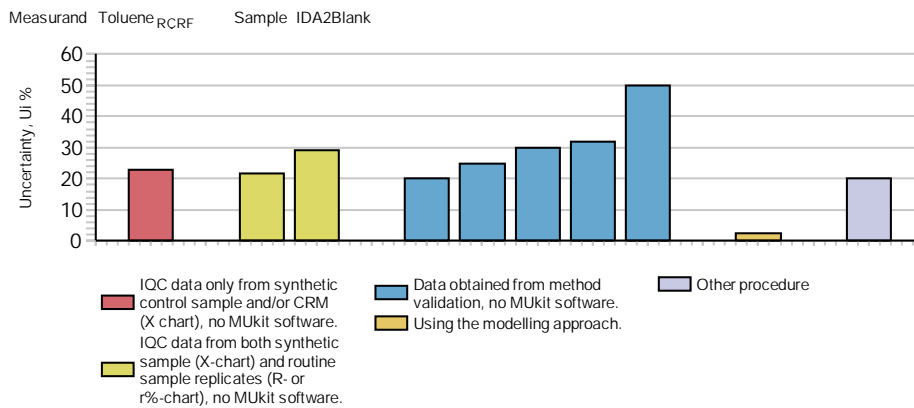
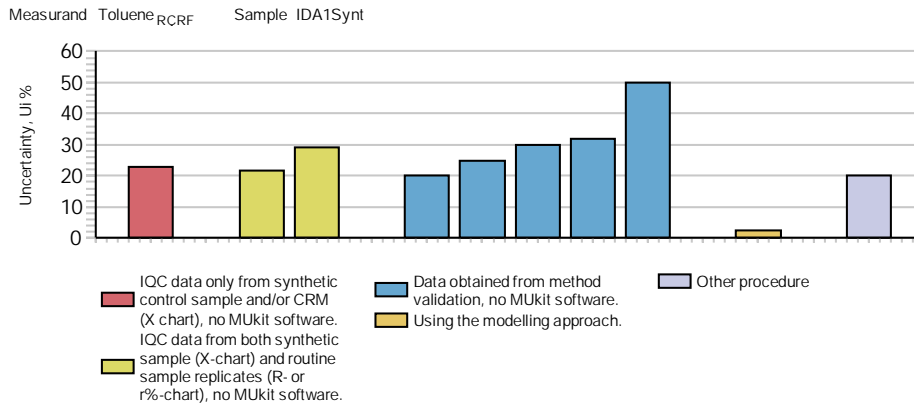


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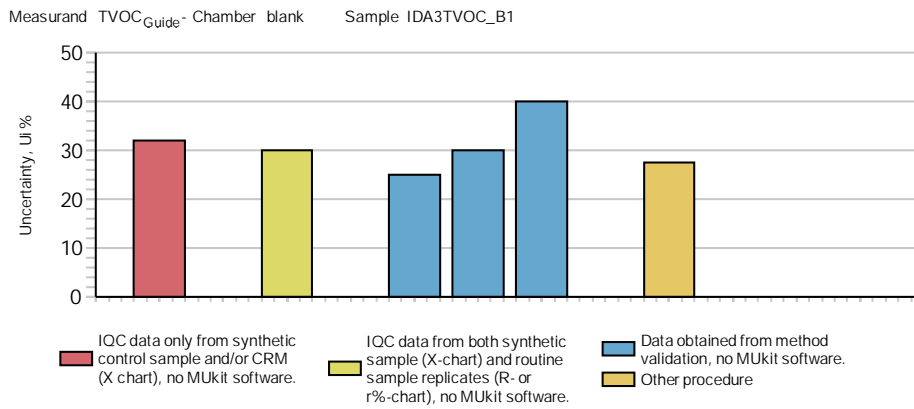
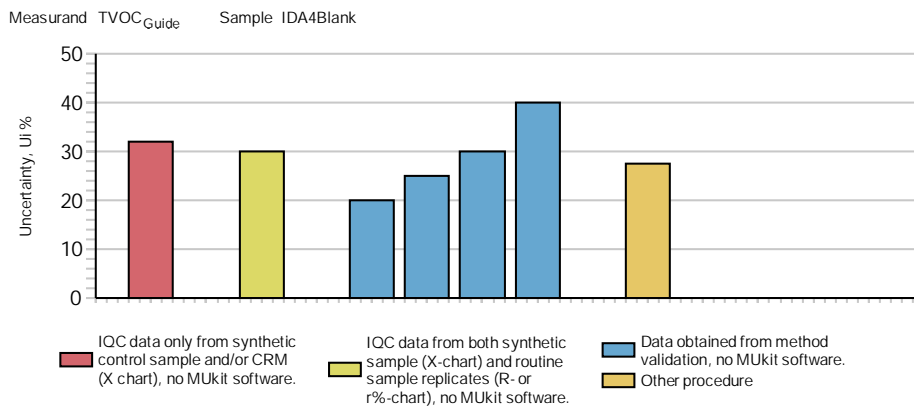
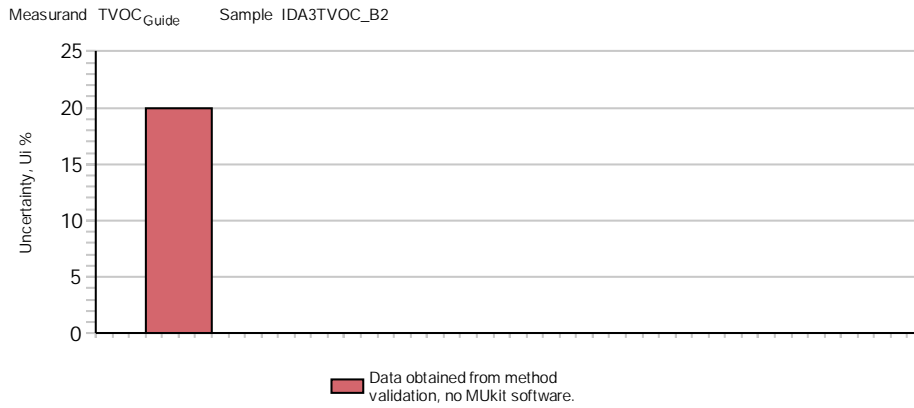




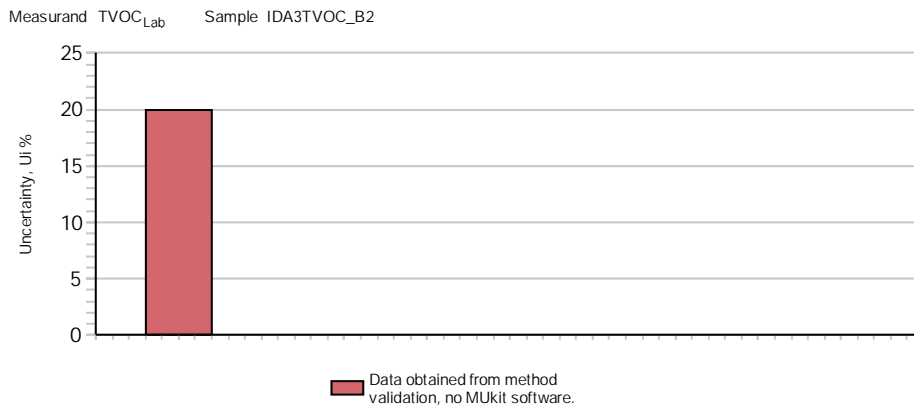
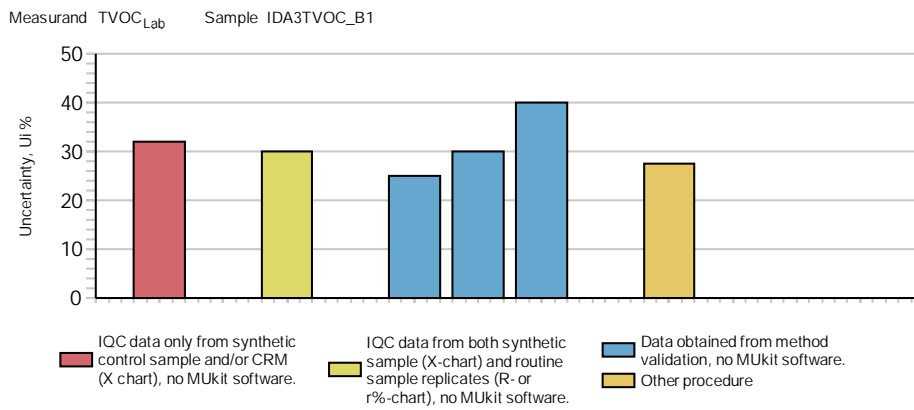
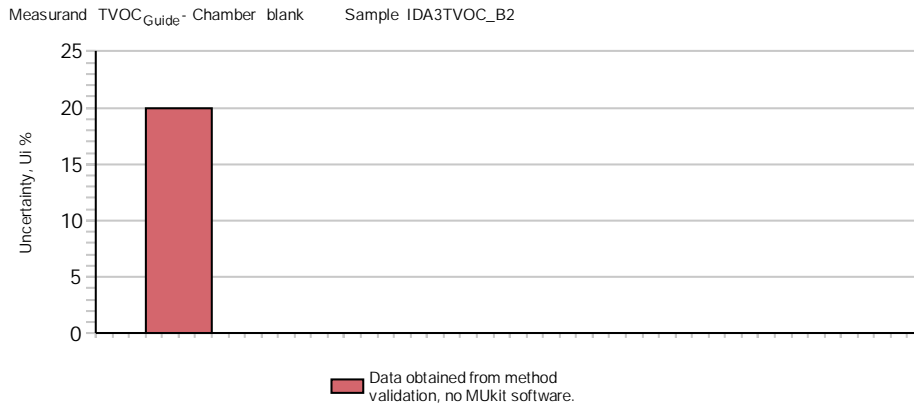
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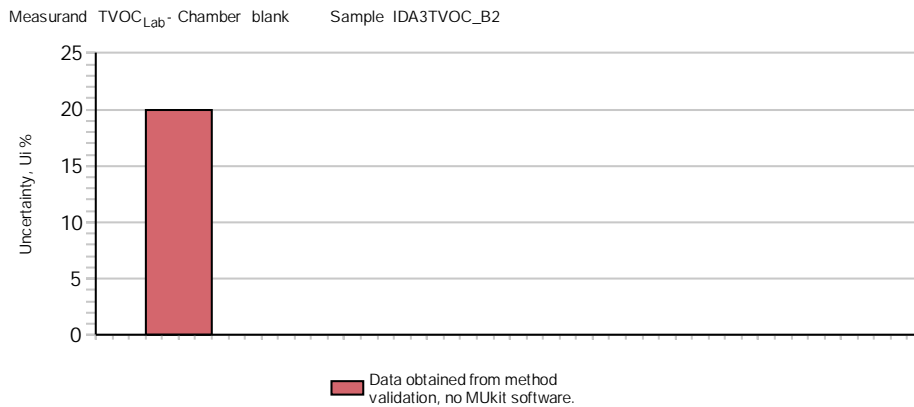
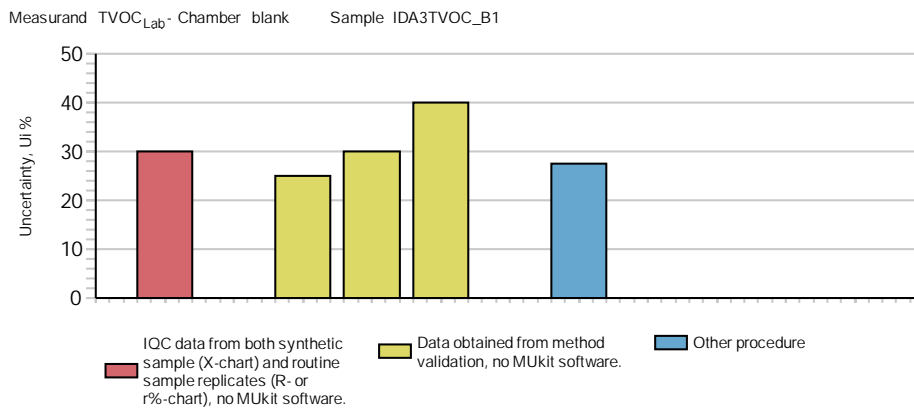
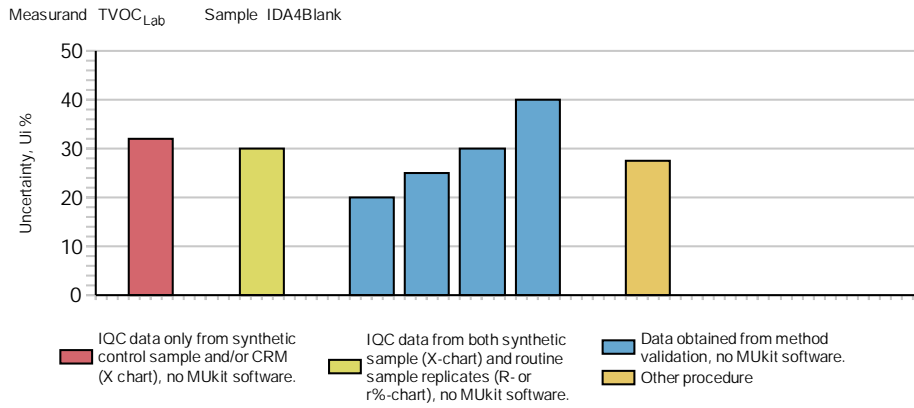




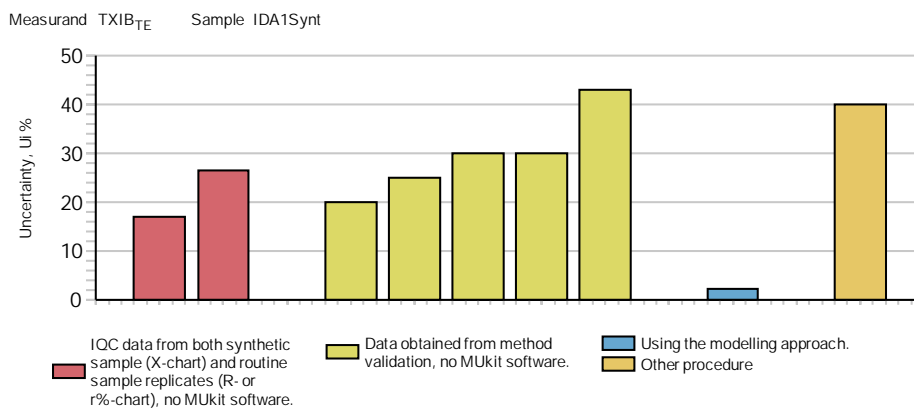
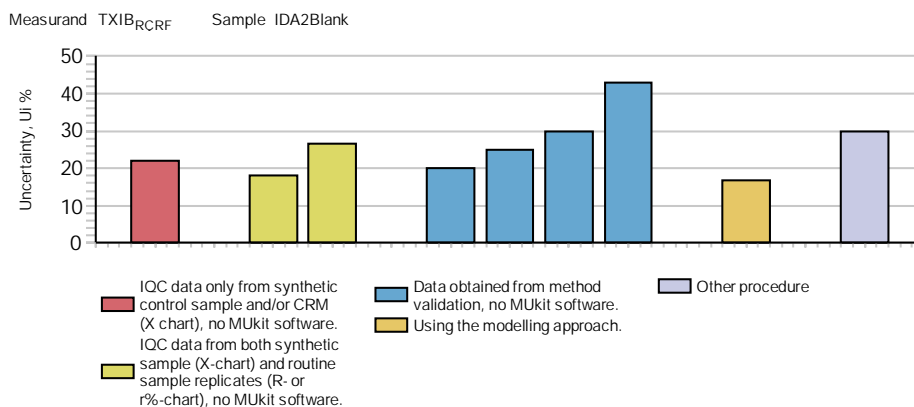
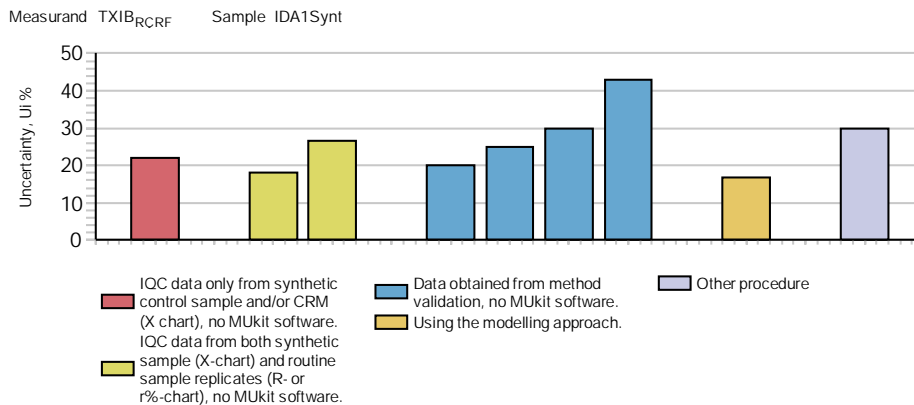


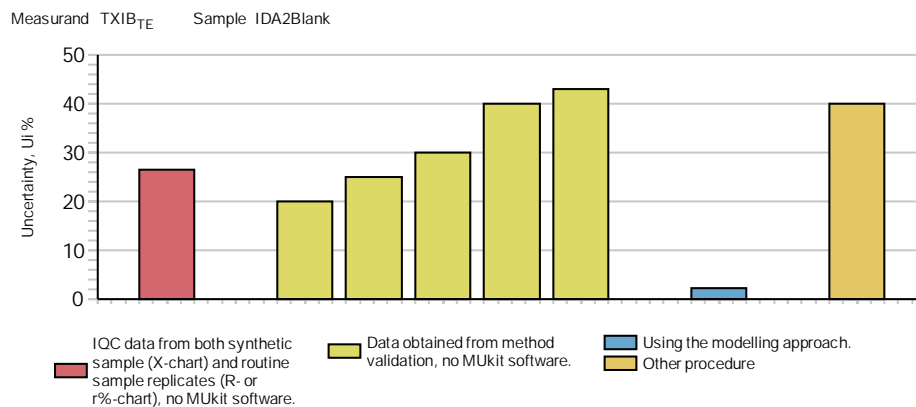
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