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ABSTRACT

Interlaboratory Comparison 09/2018

Proftest SYKE carried out the interlaboratory comparison in cooperation with Finnish Institute of Occupational Health (FIOH) for VOC thermodesorption measurements (ISO 16000-6) from native indoor air samples in Tenax TA thermodesorption tubes (IDA 09/2018) in October 2018. Further, the measurements of alpha-pinene, 1-butanol, 2-butoxyethanol, 2EH (2-ethyl-1-hexanol), naphthalene, styrene, tetrachloroethylene, toluene, and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) were tested from the synthetic sample. In total eight participants took part in the comparison. In total 70 % of the results reported by the participants were satisfactory when deviation of 20–30 % from the assigned value was accepted. The calculated values were used as the assigned values for the results of the synthetic sample reported as compound specific responses. For the other measurands and samples the mean of the results of the homogeneity measurements of the expert laboratory were used as the assigned value. The performance 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 09/2018

Proftest SYKE järjesti yhteistyössä Työterveyslaitoksen (TTL) kanssa vertailumittauksen sisäilman VOC-määrityksiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille lokakuussa 2018 (IDA 09/2018). Vertailumittauksessa testattiin natiivinäytteistä kerättyjen TVOC-yhdisteiden määritysten vertailtavuutta Tenax TA-termodesorptioputkista sekä synteettisen näytteen alfa-pineeni, 1-butanoli, 2-butoksietanoli, 2EH (2-etyyli-1-heksanoli), naftaleeni, styreeni, tetrakloorietyleeni, tolueeni ja TXIB (2,2,4-trimetyyli-1,3-pentaanidioli di-isobutyraatti) määritysten vertailtavuutta. Vertailumittaukseen osallistui yhteensä 8 laboratoriota. Koko tulosaineistossa hyväksyttäviä tuloksia oli 70 %, kun vertailuarvosta sallittiin 20–30 % poikkeama 95 % luottamusvälillä. Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella raportoiduille tuloksille. Muille testisuureille ja näytteille käytettiin vertailuarvona asiantuntijalaboratorion homogeenisuusmääritystulosten 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 09/2018

Proftest SYKE genomförde tillsammans med Arbetshälsoinstitutet (TTL) i oktober 2018 en interkalibrering (IDA 09/18) av omfattade bestämningen av Tenax TA-termodynamiska rör som används för inomhus VOC mätningar (ISO 16000-6). I interkalibrering testades analyserna jämförbarheten av halten TVOC-ämnen som samlats från nativa prover i Tenax TA-termodynamiska rör samt jämförbarheten av halten av alfa-pinen, 1-butanol, 2-butoxietanol, 2EH (2-etyl-1-hexanol), naftalen, styren, tetrakloroetylen, toluen och TXIB (2,2,4-trimetyl-1,3-pentandioldiisobutyrat) som samlats från syntetiska prov. Totalt 8 deltagare deltog i interkalibreringen. Som referensvärde för de syntetiska provernas ämnesspecifika resultat användes beräkningskoncentrationerna. För övriga prov och mätstorheter användes som referensvärde medelvärdet av expertlaboratoriets homogenitetsanalysresultat. Resultaten värderades med hjälp av z värden. I interkalibrering var 70 % 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

CONTENTS

1 Introduction

Proftest SYKE carried out the interlaboratory comparison (ILC) in cooperation with the Finnish Institute of Occupational Health (FIOH) for VOC thermodesorption measurements (ISO 16000-6 [1]) from native indoor air samples in Tenax TA thermodesorption tubes (IDA 09/2018) in October 2018. Further, the measurements of alpha-pinene,1-butanol, 2-butoxyethanol, 2EH (2-ethyl-1-hexanol), naphthalene, styrene, tetrachloroethylene, toluene, and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) were tested from 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 Proftest SYKE is accredited by the Finnish Accreditation Service (FINAS) as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). This interlaboratory comparison has not been carried out under the accreditation scope of the Proftest SYKE.

2 Organizing the interlaboratory comparison

2.1 Responsibilities

Organizer:
Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4 (formerly Hakuninmaantie 6), FI-00430 Helsinki, Finland
Phone: +358 295 251 000, e-mail: proftest@environmenti.fi

The responsibilities in organizing the proficiency test were as follows:

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

Co-operation and the analytical expert:
Hanna Hovi, Finnish Institute of Occupational Health (FIOH)

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).

2.2 Participants

In total 8 participants took part in this interlaboratory comparison. Seven of these were from Finland and one from abroad (Appendix 1). Two of the participants reported several sets of results for the synthetic sample.

Seven participants used accredited analytical methods for at least part of the measurements. The samples were prepared and tested at the laboratory of FIOH and their participant code is 3 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 interlaboratory comparison the used chamber samples were collected from one sample batch.
- Blank chamber sample (IDA4Blank)

The synthetic sample was prepared gravimetrically in the laboratory of the FIOH. 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]. The chamber samples 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 2 October 2018 and they arrived to the participants at the latest on 4 October 2018.

The reporting of results was prolonged by one day due to sample delivery problems and all participants reported their results accordingly latest on 23 October 2018. The preliminary results were delivered to the participants on 29 October 2018. The participants were requested to return the Tenax TA thermodesorption tubes to the provider latest on 12 November 2018. 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

Homogeneity of the synthetic sample IDA1Synt was tested by measuring the reference compound response factors (RCRF) for all the tested measurands from six to seven subsamples (Appendix 3). Homogeneity of IDA3TVOC samples was tested by measuring TVOC as

toluene equivalent (TE) from six samples. In the calculations the samples collected from the same duct adapter were treated as parallel samples making three parallel measurements (Appendix 3). As the samples are known to be stable some of 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 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 the erroneous sample delivery for the blank sample of the synthetic sample. The comments from the provider mainly focused on the reported zero values for the blank 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 $5 \times s_{rob}$ 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 value was used as the assigned value for the synthetic sample measurands for which the results were reported as compound specific responses (IDA1Synt, RCRF). For the other measurands and samples the mean of the results of the homogeneity measurements of the expert laboratory was used as the assigned value. Due to low number of reported results the mean of the reported results was calculated only for some measurands in the blank samples (IDA2Blank, IDA4Blank, Table 1), and thus the performance was not estimated. The expert laboratory integrated the TVOC area and deleted the background as described in ISO16000-6 [1]. The used assigned values were not metrologically traceable.

For the calculated assigned values the expanded 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 as combined uncertainty of standard deviations within and between sub samples.

For the calculated assigned values the expanded uncertainties were between 1.9 % and 2.3 % for the results based on compound responses (RCRF) and between 2.5 % and 5.4 % 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 $TVOC_{Lab}$, the expanded uncertainties of the assigned were lower than 7 % (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 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 report **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 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 of the 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 summary of the z scores is shown in Appendix 9 and the z scores in the ascending order in Appendix 10.

Two TVOC samples, collected from the chamber, were delivered to the participants and the results were processed as parallel results. Participants reported TVOC results (toluene equivalents, TE) using their own method of calculation ($TVOC_{Lab}$). The TVOC results were reported both directly and as subtracted by the result of the chamber blank ($TVOC_{Lab}$-Chamber blank). The results of the individual measurands analysed from the synthetic sample (IDA1Synt) and from the tube blank sample were reported both as compound responses (RCRF, Reference Compound Response Factor) and as toluene equivalents (TE).

The robust standard deviation for the results of the synthetic sample (IDA1Synt) varied from 11 to 38% and for the chamber sample (IDA3TVOC) varied from 30 to 31 % (Table 1). The variability was somewhat higher than in the previous ILC IDA 09/2017 [7].

Table 1. The summary of the results in the interlaboratory comparison IDA 09/2018.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob}	s_{rob} %	2 x s_{pt} %	n (all)	Acc z %
Alpha-Pinene$_{RCRF}$	IDA1Synt	ng/sample	153	146	152	140	30	19.8	20	8	75
(CAS No 80-568)	IDA2Blank	ng/sample		0.01					-	5	-
Alpha-Pinene$_{TE}$	IDA1Synt	ng/sample	162	164	173	163	30	17.3	20	12	83
	IDA2Blank	ng/sample		0.10					-	7	-
1-Butanol$_{RCRF}$	IDA1Synt	ng/sample	157	136	132	136	14	10.9	20	8	63
(CAS No 71-26-3)	IDA2Blank	ng/sample		0.54					-	5	-
1-Butanol$_{TE}$	IDA1Synt	ng/sample	55.7	57	57	49	19	33.6	25	12	42
	IDA2Blank	ng/sample		0.13					-	7	-
2-Butoxyethanol$_{RCRF}$	IDA1Synt	ng/sample	156	125	125	135	20	16.3	20	8	50
(CAS No 111-76-2)	IDA2Blank	ng/sample		0.27					-	5	-
2-Butoxyethanol$_{TE}$	IDA1Synt	ng/sample	61.5	62.7	62.7	57.0	22.2	35.4	25	12	42
	IDA2Blank	ng/sample		0.08					-	7	-
2EH$_{RCRF}$	IDA1Synt	ng/sample	130	137	138	134	33	24.0	20	11	64
(CAS No 104-76-7)	IDA2Blank	ng/sample		2.85		0.69			-	6	-
2EH$_{TE}$	IDA1Synt	ng/sample	82.5	89.4	89.4	76.3	33.5	37.5	20	12	42
	IDA2Blank	ng/sample		2.82					-	7	-
Naphthalene$_{RCRF}$	IDA1Synt	ng/sample	248	257	251	252	35	13.8	20	11	82
(CAS No 91-20-3)	IDA2Blank	ng/sample	0.34	0.34		0.17			-	6	-
Naphthalene$_{TE}$	IDA1Synt	ng/sample	333	319	322	321	52	16.0	20	12	83
	IDA2Blank	ng/sample		0.33					-	7	-
Styrene$_{RCRF}$	IDA1Synt	ng/sample	230	232	232	231	43	18.7	20	11	82
(CAS No 100-42-5)	IDA2Blank	ng/sample		0.12		0.07			-	6	-
Styrene$_{TE}$	IDA1Synt	ng/sample	214	222	222	225	30	13.3	20	12	83
	IDA2Blank	ng/sample		0.08					-	7	-
Tetrachloroethylene$_{RCRF}$	IDA1Synt	ng/sample	80.5	81.3	81.3	79.0	10.9	13.4	20	8	100
(CAS No 127-18-4)	IDA2Blank	ng/sample		0.02					-	5	-
Tetrachloroethylene$_{TE}$	IDA1Synt	ng/sample	65.5	54.0	54.2	57.5	16.5	30.4	20	12	50
	IDA2Blank	ng/sample		0.01					-	7	-
Toluene$_{RCRF}$	IDA1Synt	ng/sample	86.1	82.6	81.9	79.3	12.3	15.0	20	12	92
(CAS No 108-88-3)	IDA2Blank	ng/sample	0.51	0.51		0.57			-	7	-
TXIB$_{RCRF}$	IDA1Synt	ng/sample	121	124	124	117	25	20.1	25	11	82
(CAS No 6846-50-0)	IDA2Blank	ng/sample		13.5		5.5			-	6	-
TXIB$_{TE}$	IDA1Synt	ng/sample	139	135	135	146	39	29.1	25	12	67
	IDA2Blank	ng/sample		7.74					-	7	-
TVOC$_{Lab}$	IDA3TVOC	µg/m^3	305	275	273	261	81	29.5	30	8	75
	IDA4Blank	µg/m^3	14.4	14.4	14.4	15.2	8.7	60.7	-	8	-
TVOC$_{Lab}$-Chamber blank	IDA3TVOC	µg/m^3	288	260	260	255	80	30.6	30	8	75

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob}%: the robust standard deviation as percent, $2\times s_{pt}$ %: 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 is possible for the data where the number of the results is ≥ 5. However, in this ILC there were not enough results for statistical comparison.

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.

Most of the listed compounds were identified quite well, also the compounds with lower concentrations. The expert laboratory (participant 3) reported 13 identified compounds, for which the concentration as compounds own response (RCRF) was higher than 5 µg/m^3. The participants reported identification of 5–12 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).

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. Only one participant 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.

In the interlaboratory comparison the participants were requested to report the results for the synthetic sample based on the compound specific response (RCRF) and the toluene equivalent (TE). One participant reported only the results based on the toluene equivalent. The reported results are shown in Table 2 with the calculated ratio of compound specific response results and toluene equivalent results (RCRF/TE). The calculated ratio varies both between participants and measurands.

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
Alpha-Pinene				1-Butanol			
3	130.5	142.1	0.92	3	132.5	48.1	2.75
5	157.2	155.6	1.01	5	147.1	44.2	3.33
6	278	250	1.11	6	365	155	2.35
7	118	146	0.81	7	118	146	0.81
8	179	190	0.94	8	121	41.2	2.94
9	160	170.4	0.94	9	143.3	63.04	2.27
11	139.9	153.4	0.91	11	137.7	38.6	3.57
12	134.4	146.8	0.92	12	133.5	37	3.61
2-Butoxyethanol				2EH (2-ethyl-1-hexanol)			
3	109.6	49.4	2.22	3	105.9	70	1.51
5	140.1	45.8	3.06	4	178.6	134	1.33
6	365	109	3.35	5	135.9	64	2.12
7	135	57.3	2.36	6	151	167	0.90
8	141	76.6	1.84	7	73	51.7	1.41
9	139.9	57.02	2.45	8	134	107	1.25
11	103.2	43	2.40	9	125.3	66.73	1.88
12	104.7	41.1	2.55	10	166	132.7	1.25
				11	127.2	76.3	1.67
				12	123.4	72.8	1.70
				13	181.4	123.1	1.47
Naphthalene				Styrene			
3	244.3	289.5	0.84	3	190.4	186.9	1.02
4	264.1	320.9	0.82	4	292.3	252.1	1.16
5	255.6	321.7	0.79	5	219.9	211.2	1.04
6	314	426	0.74	6	241	366	0.66
7	152	181	0.84	7	191	188	1.02
8	205	393	0.52	8	233	252	0.92
9	281.6	346.9	0.81	9	230.6	228.4	1.01
10	244.9	292.8	0.84	10	263.1	262.3	1.00
11	248.9	348.9	0.71	11	201.2	207.3	0.97
12	239	333.3	0.72	12	194	199.7	0.97
13	272	299.4	0.91	13	295.3	232.9	1.27
Tetrachloroethylene				TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate)			
3	76.6	58.8	1.30	3	95.5	109.4	0.87
5	81.2	61.3	1.32	4	259	163.7	1.58
6	95.8	26.6	3.60	5	110.5	108.2	1.02
7	76.8	51.6	1.49	6	137	95.6	1.43
8	91.3	73.8	1.24	7	97.1	75.1	1.29
9	87.82	60.08	1.46	8	148	159	0.93
11	71.9	58.6	1.23	9	147.1	106.5	1.38
12	68.7	56.3	1.22	10	149.9	184.1	0.81
				11	117.1	148	0.79
				12	111.8	143.1	0.78
				13	264.1	153.5	1.72

The ratio varied between: 0.92 and1.11 for alpha-pinene, 0.81 and 3.61 for 1-butanol, 1.84 and 3.06 for 2-butoxyethanol, 0.90 and 2.12 for 2EH, 0.52 and 0.91 for naphthalene, 0.66-1.27 for styrene, 1.22 and 3.60 for tetrachloroethylene and between 0.78 and 1.72 for TXIB (Table 2). 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.

3.3 Uncertainties of the results

Almost all participants reported the expanded measurement uncertainties (k=2) with their results for at least some of their results (Table 4, Appendix 13). Two participants did not report measurement uncertainty for some measurands.

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. Two participants used modelling approach for some measurands. For the estimation of uncertainties the MUkit measurement uncertainty software is available, but it was not used in the estimations [8]. The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach to estimate the measurement uncertainty did not make definite impact on the uncertainty estimates.

The estimated uncertainties varied for the tested measurands and samples (Table 4). Within the optimal measuring range, the expanded measurement uncertainty (k=2) should be typically 20-40 %. Close to the limit of quantification the relative measurement is higher. When reporting measurement uncertainties, the accuracy of the numeric values should correlate with the accuracy of the result. It is evident that harmonization is still needed for the estimation of the expanded measurement uncertainties.

Table 3. The range of the reported expanded measurement uncertainties (k=2, U_i%).

Measurand	U_i%, IDA1Synt / IDA3TVOC
Alpha-pinene$_{RCRF}$	17.65-40
Alpha-pinene$_{TE}$	4.99-40
1-Butanol$_{RCRF}$	14.6-30
1-Butanol$_{TE}$	4.99-35
2-Butoxyethanol$_{RCRF}$	5.82-30
2-Butoxyethanol$_{RCRF}$	4.99-35
2EH$_{RCRF}$	11.72-40
2EH$_{TE}$	4.99-38.5
Naphthalene$_{RCRF}$	13.23-40
Naphthalene$_{TE}$	4.99-50
Styrene$_{RCRF}$	16.76-45.5
Styrene$_{TE}$	4.99-50
Tetrachloroethylene$_{RCRF}$	15.94-30
Tetrachloroethylene$_{TE}$	4.99-35
Toluene$_{RCRF}$	4.99-50
TXIB$_{RCRF}$	10.88-65
TXIB$_{TE}$	4.99-70
TVOC$_{Lab}$	27.5-40
TVOC$_{Lab}$-Chamber blank	27.5-40

4 Evaluation of the results

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

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

In total, 70 % of the results evaluated based on z scores were satisfactory when accepted deviation from the assigned value was 20–30 % at the 95 % confidence level (Appendix 9). Almost 90 % of the participants used the accredited methods for at least some of the mesurands and 66 % of those results were satisfactory. In the previous ILC IDA 09/2017, the performance was satisfactory for 68 % of the all participants when accepted deviation from the assigned value was 20–30 % [7].

The summary of the performance evaluation is shown in Table 4. The percentage of the satisfactory results varied between 61 % and 75 % 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 4). In the previous similar ILC IDA 09/2017 the percentage of the satisfactory results varied between 58 - 72 % for the tested sample types [7].

Table 4. Summary of the performance evaluation in the interlaboratory comparison IDA 09/2018.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value at 95 % confidence level (%)	Remarks
IDA1Synt, RCRF	76	20–25	• Four more measurands than in the previous ILC IDA 09/2017 [7]. • Difficulties in measurements for some of the participants; satisfactory results < 80 % for alpha-pinene, 1-butanol, 2-butoxyethanol, 2EH. • In the previous ILC IDA 09/2017 the performance was satisfactory for 67 % of the results when accepting the deviation of 20 % from the assigned value [7].
IDA1Synt, TE	61	20–25	• Four more measurands than in the previous ILC IDA 09/2017 [7]. • Difficulties in measurements for some of the participants; satisfactory results < 80 % for 1-butanol, 2-butoxyethanol, 2EH, tetrachloroethylene, TXIB. • In the previous ILC IDA 09/2017 the performance was satisfactory for 58 % of the results [7].
IDA3TVOC$_{Lab}$, IDA3TVOC$_{Lab}$-Chamber blank	75	30	• Difficulties in measurements for some of the participants. • In the previous ILC IDA 09/2017 the performance was satisfactory for 72 % of the results [7].

Based on the results of this ILC as well as on the results of the previous similar ILC, IDA 09/2017 and ISO 16000-6, it is further recommended to increase the number of the pure compounds in calibrations [1, 7].

5 Summary

Proftest SYKE carried out in cooperation with the Finnish Institute of Occupational Health (FIOH) the interlaboratory comparison (ILC) for VOC thermodesorption measurements (ISO 16000-6 [1]) from native indoor air samples in Tenax TA thermodesorption tubes (IDA 09/2018) in October 2018. Further, the measurements of alpha-pinene, 1-butanol, 2-butoxyethanol, 2EH (2-ethyl-1-hexanol), naphthalene, styrene, tetrachloroethylene, toluene, and TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate) were tested from the synthetic sample. In total eight participants took part in the interlaboratory comparison.

The calculated value was used as the assigned value for the measurands of the synthetic sample for which the results were reported as compound specific responses (RCRF). For the other measurands and samples the mean of the results of the homogeneity measurements of the expert laboratory was used as the assigned value. For the calculated assigned values the expanded uncertainties were between 1.9 % and 2.3 % for the results based on compound responses and between 2.5 % and 5.4 % 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 $TVOC_{Lab}$, the expanded uncertainties of the assigned values were lower than 7 %.

The evaluation of the performance was based on the z scores. In this interlaboratory comparison 70 % 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. Almost 90 % of the participants used accredited methods and 66 % of those results were satisfactory. In the interlaboratory comparison the participants were requested to report the results for the synthetic sample both 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

Proftest SYKE järjesti vertailumittauksen yhteistyössä Työterveyslaitoksen (TTL) kanssa sisäilman VOC-määrityksiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille lokakuussa 2018 (IDA 09/2018). Vertailumittauksessa testattiin natiivinäytteistä kerättyjen TVOC-yhdisteiden määritysten vertailtavuutta Tenax TA-termodesorptioputkista sekä synteettisen näytteen alfa-pineeni, 1-butanoli, 2-butoksietanoli, 2EH (2-etyyli-1-heksanoli), naftaleeni, styreeni, tetrakloorietyleeni, tolueeni ja TXIB (2,2,4-trimetyyli-1,3-pentaanidioli di-isobutyraatti) määritysten vertailtavuutta. Vertailumittaukseen osallistui yhteensä 8 laboratoriota.

Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella (RCRF) raportoiduille tuloksille. Muille testisuureille ja näytteille käytettiin asiantuntijalaboratorion homogeenisuusmääritystulosten keskiarvoa.

Synteettisen näytteen vertailuarvon laajennettu epävarmuus vaihteli välillä 1,9–2,3 % omalla vasteella raportoiduille tuloksille ja välillä 2,5–5,4 % tolueeniekvivalenttina (TE) raportoiduille tuloksille. Kammionäytteiden vertailuarvojen laajennettu epävarmuus oli alle 7 %.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa hyväksyttäviä tuloksia oli 70 %, kun vertailuarvosta sallittiin 20–30 % poikkeama 95 % luottamusvälillä. Noin 90 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 66 %. Vertailumittauksessa pyydettiin osallistuja raportoimaan synteettisen näytteen tulokset sekä yhdisteen omalla vasteella että tolueeniekvivalenttina. Vertailumittauksen tulosten mukaan on vaikea arvioida yhtä ainoaa muuntokerrointa tuloksen muuntamiseksi yhdisteen omasta vasteesta tolueenin ekvivalentiksi tai päinvastoin.

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APPENDIX 1: Participants in the proficiency test

Country	Participant
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, Jyväskylä
Portugal	INEGI - Institute of Science and Innovation in Mechanical and Industrial Engineering, Laboratory for Indoor Air

APPENDIX 2: Preparation of the samples

The sample preparation 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	Producer, Producer code, Purity, Batch
Alpha-Pinene	Sigma Aldrich 80599, ≥99.0 %, LOT BCBR2614V
1-Butanol	Sigma Aldrich 19422, ≥99.9 %, LOT BCBV0379
2-Butoxyethanol	Sigma Aldrich 53071, ≥99.5 %, LOT BCBV1447
2-Ethyl-1-hexanol, 2EH	Sigma Aldrich 08607, ≥99.5 %, LOT BCBT9323
Methanol	VWR 20864.292 GPR Rectapur, 100 %, LOT 15L220518
Naphthalene	Merck 8.20846.0100 for synthesis, ≥99.8%, LOT S6827746
Styrene	Merck 8.07679.0100 (stabilized) for Synthesis, ≥99.9 %, LOT S7213279
Tetrachloroethylene	VWR 83950.290 Spectronorm for spectroscopy, ≥99.9 %, LOT 15K260511
Toluene	Merck 1.00849.1000 MS Suprasolv, ≥99.8 %, LOT 1764349
2,2,4-Trimethyl-1,3-pentanediol diisobutyrate, TXIB	Sigma Aldrich 41601, ≥98.5 %, LOT BCBT1338

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

Measurand/Solvent	Mass (g)	Concentration (ng/ml) (V_{tot} = 20 ml)	Addition of 2 µl to each termodesorption tube, (ng/sample)	Assigned value RCRF (ng/sample)
Alpha-Pinene	0.01541	77.05	154.1	153
1-Butanol	0.01566	78.3	156.6	157
2-Butoxyethanol	0.01561	78.05	156.1	156
2EH	0.01307	65.35	130.7	130
Methanol	15.62402			
Naphthalene	0.02482	124.2	248.4	248
Styrene	0.02301	115.1	230.1	230
Tetrachloroethylene	0.00806	40.3	80.6	80.5
Toluene	0.00863	43.15	86.3	86.1
TXIB	0.01219	60.95	121.9	121

Preparation of the Chamber samples

The native samples were prepared using a controllable chamber at the laboratory of FIOH as in the previous ILC IDA 09/2017 [7]. Air flow, temperature and humidity were controlled in the chamber. The chamber had twelve sampling ports and parallel samples were collected from each port, providing in total 24 samples. Calibrated air pumps provided by FIOH were used for sample collection. The used TA-Tenax thermodesorption tubes were produced by Markes and the dimensios 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 tubing was changed. Temperature was adjusted to 23°C ± 1°C and humidity to 50 RH% ± 5.

The collection of the samples started on 23 August 2018 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.

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 started 24 hours after the chamber was closed, on 24 August 2018.

APPENDIX 3: Homogeneity of the samples

Homogeneity of the synthetic sample IDA1Synt was tested by measuring alpha-pinene, 1-butanol, 2-butoxyethanol, 2EH, naphthalene, styrene, tetrachloroethylene, toluene and TXIB as compound specific response (RCRF, Reference Compound Response Factor) from six or seven subsamples. The samples collected from the chamber (IDA3TVOC) were tested measuring TVOC as toluene equivalents (TE) from six samples. In the calculations the samples collected from the same duct adapter were treated as parallel samples making three parallel measurements.

Criteria for homogeneity:

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

s_{anal} = analytical deviation, standard deviation of the results within sub samples
s_{pt}% = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_{pt})^2$,
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/IDA3TVOC	Concentration [TE, µg/m³]	n	s_{pt} %	s_{pt}	s_{anal}	s_{anal}/s_{pt}	$s_{anal}/s_{pt}<0.5$?	s_{sam}^2	c	$s_{sam}^2<c$?
$TVOC_{Lab}$	305	3	15	45.8	11.3	0.25	Yes	144	1116	Yes
$TVOC_{Lab}$-Chamber Blank	288	3	15	43.3	11.3	0.26	Yes	125	1055	Yes

Criterion for homogeneity without parallel results:

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

s_{pt} = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of results between sub samples

Measurand/IDA1Synt	Concentration [RCRF, ng/sample]	n	s_{pt} %	s_{pt}	s_{sam}	s_{sam}/s_{pt}	$s_{sam}/s_{pt} < 0.5$?
Alpha-Pinene	164	6	10	16.4	5.43	0.33	Yes
1-Butanol	135	6	10	13.5	3.83	0.28	Yes
2-Butoxyethanol	111	7	10	11.1	4.40	0.40	Yes
2EH	100	7	10	10.0	4.90	0.49	Yes
Naphthalene	228	7	10	22.8	9.72	0.43	Yes
Styrene	200	7	10	20.0	7.18	0.36	Yes
Tetrachloroethylene	70.8	6	10	7.08	3.18	0.45	Yes
Toluene	71.4	7	10	7.14	2.74	0.38	Yes
TXIB	94.7	7	10	9.47	2.15	0.23	Yes

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

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest
1, 4, 5, 8, 9	The participants received incorrect blank sample for the synthetic sample, IDA2Blank.	The provider apologized the delivery errors. The new samples were delivered to the participants. The provider will be more careful in the sample delivery for the future rounds.
7	To the participant was erroneously sent information about the incorrect synthetic blank sample.	The provider apologized from the erroneous information and will be more carefully delivering of information in the future rounds.

Participant	Comments to the results	Action / Proftest
9	Participant reported results also for another synthetic sample IDA1Synt (ng/sample): Alpha-Pinene$_{RCRF}$:158.7, Alpha-Pinene$_{TE}$: 168.9; 1-Butanol$_{RCRF}$: 141.1, 1-Butanol$_{TE}$: 62.06, 2-Butoxyethanol$_{RCRF}$: 136.8, 2-Butoxyethanol$_{TE}$: 55.74; 2EH$_{RCRF}$: 120.4, 2EH$_{TE}$: 64.12; Napthalene$_{RCRF}$: 278.7, Napthalene$_{TE}$: 343.3; Styrene$_{RCRF}$: 229.9; Styrene$_{TE}$: 227.7; Tetrachloroethylene$_{RCRF}$: 88.61, Tetrachloroethylene$_{TE}$:60.62; Toluene$_{RCRF}$: 80.03; TXIB$_{RCRF}$: 149.7; TXIB$_{TE}$: 108.4	All these results were satisfactory with the exception of questionable 2EH$_{TE}$ result. The participant can recalculate the z scores according to the Guide for participants [6].
2	During the previous similar ILC, VOC 09/2017, we commented the calculation of the TVOC. In the summary of the report it was concluded that the calculation of TVOC is very challenging. We agree with this but the original question was not about integration etc. We mentioned that the ISO standard does not clarify exactly how many peaks should be taken into account in TVOC calculation, e.g. is the right number 50 or 60. This has neither been told in the instructions of the ILC nor is this fact related to the skillfulness or education of the personnel. So, this gives possibilities for different results which all are equally correct answers. Especially 2-EH and also to some extend 1-butanol and 2-butoxyethanol were tailing strongly. We do not know the reason for this because normally the peaks are almost gaussian. This was also checked after the runs of the ILC samples. Is it possible that there was some moisture in the tubes or the volume of the solvent in spiking was too big.	The provider thanks for the feedback. Commonly, the integration parameters are selected so that the peaks higher than the detection limit are integrated and the baseline of the chromatogram follows the shape of the blank sample. The parameters are device specific, e.g. for three different analytical instrument from the same manufacturer, there will be different parameters for each. Based on the sample preparation there is no sign of moisture in the sample tubes. Also in the measurements the peak of eluent (methanol) is lower than the peaks of the measurands.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
2, 4, 5, 9	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.

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}
Alpha-Pinene$_{RCRF}$	IDA1Synt	ng/sample	153	3	2.1	Calculated value	0.11
Alpha-Pinene$_{TE}$	IDA1Synt	ng/sample	162	5	2.8	Mean value of the homogeneity testing data	0.14
1-Butanol$_{RCRF}$	IDA1Synt	ng/sample	157	3	2.0	Calculated value	0.10
1-Butanol$_{TE}$	IDA1Synt	ng/sample	55.7	2	2.9	Mean value of the homogeneity testing data	0.12
2-Butoxyethanol$_{RCRF}$	IDA1Synt	ng/sample	156	3	2.0	Calculated value	0.10
2-Butoxyethanol$_{TE}$	IDA1Synt	ng/sample	61.5	1.7	2.7	Mean value of the homogeneity testing data	0.11
2EH$_{RCRF}$	IDA1Synt	ng/sample	130	3	2.1	Calculated value	0.11
2EH$_{TE}$	IDA1Synt	ng/sample	82.5	3.2	3.9	Mean value of the homogeneity testing data	0.20
Naphthalene$_{RCRF}$	IDA1Synt IDA2Blank	ng/sample ng/sample	248 0.34	5	1.9	Calculated value Mean	0.10
Naphthalene$_{TE}$	IDA1Synt	ng/sample	333	9	2.6	Mean value of the homogeneity testing data	0.13
Styrene$_{RCRF}$	IDA1Synt	ng/sample	230	4	1.9	Calculated value	0.10
Styrene$_{TE}$	IDA1Synt	ng/sample	214	5	2.5	Mean value of the homogeneity testing data	0.13
Tetrachloroethylene$_{RCRF}$	IDA1Synt	ng/sample	80.5	1.9	2.3	Calculated value	0.12
Tetrachloroethylene$_{TE}$	IDA1Synt	ng/sample	65.5	1.7	2.6	Mean value of the homogeneity testing data	0.13
Toluene$_{RCRF}$	IDA1Synt IDA2Blank	ng/sample ng/sample	86.1 0.51	1.9	2.2	Calculated value Mean	0.11
TXIB$_{RCRF}$	IDA1Synt	ng/sample	121	3	2.2	Calculated value	0.09
TXIB$_{TE}$	IDA1Synt	ng/sample	139	8	5.4	Mean value of the homogeneity testing data	0.22
TVOC$_{Lab}$	IDA3TVOC IDA4Blank	µg/m3 µg/m3	305 14.4	19	6.1	Mean value of the homogeneity testing data Mean	0.20
TVOC$_{Lab}$-Chamber blank	IDA3TVOC	µg/m3	288	18	6.4	Mean value of the homogeneity testing data	0.21

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}= the standard deviation for proficiency assessment
u_{pt}= the 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

Measurand	The tested parameter
Sample	The code of the sample
z score	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
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participants's result	The result reported by the participant (the mean value of the replicates)
Md	Median
s	Standard deviation
s %	Standard deviation, %
n (stat)	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 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

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 $(i = 1, 2 \ldots p)$:

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

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 [3].

APPENDIX 7: Results of each participant

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{TE}$	ng/sample	IDA1Synt		-0.99	55.7	25	49	49	57	17	29.6	11
	ng/sample	IDA2Blank					0.00	0.00	0.13	0.29	223.6	5
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		-1.16	61.5	25	52.6	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.18	223.6	5
2EH$_{TE}$	ng/sample	IDA1Synt		0.38	82.5	20	85.6	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					0.00	0.00	2.82	5.71	202.5	5
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		3.64	162	20	221	163	164	18	10.8	10
	ng/sample	IDA2Blank					0.50	0.00	0.10	0.22	213.0	5
Naphthalene$_{TE}$	ng/sample	IDA1Synt		-1.63	333	20	279	321	319	61	19.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.33	0.54	164.4	5
Styrene$_{TE}$	ng/sample	IDA1Synt		0.51	214	20	225	225	222	26	11.7	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.19	223.6	5
Tetrachloroethylene$_{TE}$	ng/sample	IDA1Synt		2.27	65.5	20	80.4	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.01	0.01	223.6	5
Toluene$_{RCRF}$	ng/sample	IDA1Synt		1.06	86.1	20	95.2	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		0.30	0.57	0.51	0.37	71.7	5
TVOC$_{Lab}$	µg/m3	IDA3TVOC		-0.97	305	30	261	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		3.8	15.2	14.4	7.7	53.5	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		-0.75	288	30	256	255	260	71	27.4	8
TXIB$_{TE}$	ng/sample	IDA1Synt		2.14	139	25	176	146	135	35	25.8	12
	ng/sample	IDA2Blank					0.00	0.00	7.74	13.48	174.1	5

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{RCRF}$	ng/sample	IDA1Synt		-1.56	157	20	133	136	136	9	6.8	6
	ng/sample	IDA2Blank					*<5*	0.00	0.54	0.94	173.2	3
1-Butanol$_{TE}$	ng/sample	IDA1Synt		-1.09	55.7	25	48	49	57	17	29.6	11
	ng/sample	IDA2Blank					*<5*	0.00	0.13	0.29	223.6	5
2-Butoxyethanol$_{RCRF}$	ng/sample	IDA1Synt		-2.97	156	20	110	135	125	18	14.4	7
	ng/sample	IDA2Blank					*<10*	0.00	0.27	0.47	173.2	3
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		-1.57	61.5	25	49.4	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					*<10*	0.00	0.08	0.18	223.6	5
2EH$_{RCRF}$	ng/sample	IDA1Synt		-1.85	130	20	106	134	137	32	23.4	11
	ng/sample	IDA2Blank					*<5*	0.69	2.85	4.81	169.2	4
2EH$_{TE}$	ng/sample	IDA1Synt		-1.52	82.5	20	70.0	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					*<5*	0.00	2.82	5.71	202.5	5
Alpha-Pinene$_{RCRF}$	ng/sample	IDA1Synt		-1.47	153	20	131	140	146	21	14.3	7
	ng/sample	IDA2Blank					*<5*	0.00	0.01	0.02	173.2	3
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		-1.23	162	20	142	163	164	18	10.8	10
	ng/sample	IDA2Blank					*<5*	0.00	0.10	0.22	213.0	5
Naphthalene$_{RCRF}$	ng/sample	IDA1Synt		-0.15	248	20	244	252	257	29	11.3	10
	ng/sample	IDA2Blank			0.34		*<4*	0.17	0.34	0.47	139.1	4
Naphthalene$_{TE}$	ng/sample	IDA1Synt		-1.31	333	20	290	321	319	61	19.2	12
	ng/sample	IDA2Blank					*<4*	0.00	0.33	0.54	164.4	5

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$Styrene_{RCRF}$	ng/sample	IDA1Synt		-1.72	230	20	190	231	232	38	16.5	11
	ng/sample	IDA2Blank					*<4*	0.07	0.12	0.17	137.6	4
$Styrene_{TE}$	ng/sample	IDA1Synt		-1.27	214	20	187	225	222	26	11.7	11
	ng/sample	IDA2Blank					*<4*	0.00	0.08	0.19	223.6	5
$Tetrachloroethylene_{RCRF}$	ng/sample	IDA1Synt		-0.48	80.5	20	76.6	79.0	81.3	9.6	11.8	8
	ng/sample	IDA2Blank					*<4*	0.00	0.02	0.03	173.2	3
$Tetrachloroethylene_{TE}$	ng/sample	IDA1Synt		-1.02	65.5	20	58.8	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					*<4*	0.00	0.01	0.01	223.6	5
$Toluene_{RCRF}$	ng/sample	IDA1Synt		-1.95	86.1	20	69.3	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		*<4*	0.57	0.51	0.37	71.7	5
$TVOC_{Lab}$	µg/m3	IDA3TVOC		-1.71	305	30	227	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		15.5	15.2	14.4	7.7	53.5	8
$TVOC_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		-1.78	288	30	211	255	260	71	27.4	8
$TXIB_{RCRF}$	ng/sample	IDA1Synt		-1.69	121	25	96	117	124	22	17.8	9
	ng/sample	IDA2Blank					*<4*	5.5	13.5	20.3	150.4	4
$TXIB_{TE}$	ng/sample	IDA1Synt		-1.70	139	25	109	146	135	35	25.8	12
	ng/sample	IDA2Blank					*<4*	0.00	7.74	13.48	174.1	5

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol_{TE}	ng/sample	IDA1Synt		3.43	55.7	25	80	49	57	17	29.6	11
	ng/sample	IDA2Blank					0.00	0.00	0.13	0.29	223.6	5
$2\text{-Butoxyethanol}_{TE}$	ng/sample	IDA1Synt		3.55	61.5	25	88.8	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.18	223.6	5
$2EH_{RCRF}$	ng/sample	IDA1Synt		3.74	130	20	179	134	137	32	23.4	11
	ng/sample	IDA2Blank					1.38	0.69	2.85	4.81	169.2	4
$2EH_{TE}$	ng/sample	IDA1Synt		6.24	82.5	20	134.0	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					1.10	0.00	2.82	5.71	202.5	5
$Alpha\text{-}Pinene_{TE}$	ng/sample	IDA1Synt		1.57	162	20	187	163	164	18	10.8	10
	ng/sample	IDA2Blank					0.00	0.00	0.10	0.22	213.0	5
$Naphthalene_{RCRF}$	ng/sample	IDA1Synt		0.65	248	20	264	252	257	29	11.3	10
	ng/sample	IDA2Blank			0.34		0.03	0.17	0.34	0.47	139.1	4
$Naphthalene_{TE}$	ng/sample	IDA1Synt		-0.36	333	20	321	321	319	61	19.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.33	0.54	164.4	5
$Styrene_{RCRF}$	ng/sample	IDA1Synt		2.71	230	20	292	231	232	38	16.5	11
	ng/sample	IDA2Blank					0.13	0.07	0.12	0.17	137.6	4
$Styrene_{TE}$	ng/sample	IDA1Synt		1.78	214	20	252	225	222	26	11.7	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.19	223.6	5
$Tetrachloroethylene_{TE}$	ng/sample	IDA1Synt		-3.62	65.5	20	41.8	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.01	0.01	223.6	5
$Toluene_{RCRF}$	ng/sample	IDA1Synt		0.22	86.1	20	88.0	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		0.80	0.57	0.51	0.37	71.7	5
$TVOC_{Lab}$	µg/m3	IDA3TVOC		0.42	305	30	324	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		23.0	15.2	14.4	7.7	53.5	8
$TVOC_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		0.30	288	30	301	255	260	71	27.4	8
$TXIB_{RCRF}$	ng/sample	IDA1Synt		9.12	121	25	259	117	124	22	17.8	9
	ng/sample	IDA2Blank					0.2	5.5	13.5	20.3	150.4	4

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$TXIB_{TE}$	ng/sample	IDA1Synt		1.42	139	25	164	146	135	35	25.8	12
	ng/sample	IDA2Blank					0.00	0.00	7.74	13.48	174.1	5

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-$Butanol_{RCRF}$	ng/sample	IDA1Synt		-0.63	157	20	147	136	136	9	6.8	6
	ng/sample	IDA2Blank					0.00	0.00	0.54	0.94	173.2	3
1-$Butanol_{TE}$	ng/sample	IDA1Synt		-1.65	55.7	25	44	49	57	17	29.6	11
	ng/sample	IDA2Blank					0.00	0.00	0.13	0.29	223.6	5
2-$Butoxyethanol_{RCRF}$	ng/sample	IDA1Synt		-1.02	156	20	140	135	125	18	14.4	7
	ng/sample	IDA2Blank					0.00	0.00	0.27	0.47	173.2	3
2-$Butoxyethanol_{TE}$	ng/sample	IDA1Synt		-2.04	61.5	25	45.8	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.18	223.6	5
$2EH_{RCRF}$	ng/sample	IDA1Synt		0.45	130	20	136	134	137	32	23.4	11
	ng/sample	IDA2Blank					0.00	0.69	2.85	4.81	169.2	4
$2EH_{TE}$	ng/sample	IDA1Synt		-2.24	82.5	20	64.0	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					0.00	0.00	2.82	5.71	202.5	5
Alpha-$Pinene_{RCRF}$	ng/sample	IDA1Synt		0.27	153	20	157	140	146	21	14.3	7
	ng/sample	IDA2Blank					0.00	0.00	0.01	0.02	173.2	3
Alpha-$Pinene_{TE}$	ng/sample	IDA1Synt		-0.40	162	20	156	163	164	18	10.8	10
	ng/sample	IDA2Blank					0.00	0.00	0.10	0.22	213.0	5
$Naphthalene_{RCRF}$	ng/sample	IDA1Synt		0.31	248	20	256	252	257	29	11.3	10
	ng/sample	IDA2Blank			0.34		0.00	0.17	0.34	0.47	139.1	4
$Naphthalene_{TE}$	ng/sample	IDA1Synt		-0.34	333	20	322	321	319	61	19.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.33	0.54	164.4	5
$Styrene_{RCRF}$	ng/sample	IDA1Synt		-0.44	230	20	220	231	232	38	16.5	11
	ng/sample	IDA2Blank					0.00	0.07	0.12	0.17	137.6	4
$Styrene_{TE}$	ng/sample	IDA1Synt		-0.13	214	20	211	225	222	26	11.7	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.19	223.6	5
$Tetrachloroethylene_{RCRF}$	ng/sample	IDA1Synt		0.09	80.5	20	81.2	79.0	81.3	9.6	11.8	8
	ng/sample	IDA2Blank					0.00	0.00	0.02	0.03	173.2	3
$Tetrachloroethylene_{TE}$	ng/sample	IDA1Synt		-0.64	65.5	20	61.3	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.01	0.01	223.6	5
$Toluene_{RCRF}$	ng/sample	IDA1Synt		-1.21	86.1	20	75.7	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		0.00	0.57	0.51	0.37	71.7	5
$TVOC_{Lab}$	µg/m3	IDA3TVOC		-3.04	305	30	166	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		18.3	15.2	14.4	7.7	53.5	8
$TVOC_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		-3.25	288	30	147	255	260	71	27.4	8
$TXIB_{RCRF}$	ng/sample	IDA1Synt		-0.69	121	25	111	117	124	22	17.8	9
	ng/sample	IDA2Blank					0.0	5.5	13.5	20.3	150.4	4
$TXIB_{TE}$	ng/sample	IDA1Synt		-1.77	139	25	108	146	135	35	25.8	12
	ng/sample	IDA2Blank					0.00	0.00	7.74	13.48	174.1	5

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{RCRF}$	ng/sample	IDA1Synt		13.25	157	20	365	136	136	9	6.8	6
	ng/sample	IDA2Blank					1.62	0.00	0.54	0.94	173.2	3
1-Butanol$_{TE}$	ng/sample	IDA1Synt		14.26	55.7	25	155	49	57	17	29.6	11
	ng/sample	IDA2Blank					0.65	0.00	0.13	0.29	223.6	5
2-Butoxyethanol$_{RCRF}$	ng/sample	IDA1Synt		3.65	156	20	213	135	125	18	14.4	7
	ng/sample	IDA2Blank					0.81	0.00	0.27	0.47	173.2	3
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		6.18	61.5	25	109.0	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					0.41	0.00	0.08	0.18	223.6	5
2EH$_{RCRF}$	ng/sample	IDA1Synt		1.62	130	20	151	134	137	32	23.4	11
	ng/sample	IDA2Blank					10.00	0.69	2.85	4.81	169.2	4
2EH$_{TE}$	ng/sample	IDA1Synt		10.24	82.5	20	167.0	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					13.00	0.00	2.82	5.71	202.5	5
Alpha-Pinene$_{RCRF}$	ng/sample	IDA1Synt		8.17	153	20	278	140	146	21	14.3	7
	ng/sample	IDA2Blank					0.03	0.00	0.01	0.02	173.2	3
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		5.43	162	20	250	163	164	18	10.8	10
	ng/sample	IDA2Blank					0.02	0.00	0.10	0.22	213.0	5
Naphthalene$_{RCRF}$	ng/sample	IDA1Synt		2.66	248	20	314	252	257	29	11.3	10
	ng/sample	IDA2Blank			0.34		0.31	0.17	0.34	0.47	139.1	4
Naphthalene$_{TE}$	ng/sample	IDA1Synt		2.79	333	20	426	321	319	61	19.2	12
	ng/sample	IDA2Blank					0.40	0.00	0.33	0.54	164.4	5
Styrene$_{RCRF}$	ng/sample	IDA1Synt		0.48	230	20	241	231	232	38	16.5	11
	ng/sample	IDA2Blank					0.35	0.07	0.12	0.17	137.6	4
Styrene$_{TE}$	ng/sample	IDA1Synt		7.10	214	20	366	225	222	26	11.7	11
	ng/sample	IDA2Blank					0.42	0.00	0.08	0.19	223.6	5
Tetrachloroethylene$_{RCRF}$	ng/sample	IDA1Synt		1.90	80.5	20	95.8	79.0	81.3	9.6	11.8	8
	ng/sample	IDA2Blank					0.06	0.00	0.02	0.03	173.2	3
Tetrachloroethylene$_{TE}$	ng/sample	IDA1Synt		-5.94	65.5	20	26.6	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					0.03	0.00	0.01	0.01	223.6	5
Toluene$_{RCRF}$	ng/sample	IDA1Synt		2.66	86.1	20	109.0	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		0.57	0.57	0.51	0.37	71.7	5
TVOC$_{Lab}$	µg/m3	IDA3TVOC		2.28	305	30	410	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		25.0	15.2	14.4	7.7	53.5	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		2.22	288	30	384	255	260	71	27.4	8
TXIB$_{RCRF}$	ng/sample	IDA1Synt		1.06	121	25	137	117	124	22	17.8	9
	ng/sample	IDA2Blank					10.8	5.5	13.5	20.3	150.4	4
TXIB$_{TE}$	ng/sample	IDA1Synt		-2.50	139	25	96	146	135	35	25.8	12
	ng/sample	IDA2Blank					7.58	0.00	7.74	13.48	174.1	5

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{RCRF}$	ng/sample	IDA1Synt		-4.64	157	20	84	136	136	9	6.8	6
	ng/sample	IDA2Blank					*<20*	0.00	0.54	0.94	173.2	3
1-Butanol$_{TE}$	ng/sample	IDA1Synt		1.90	55.7	25	69	49	57	17	29.6	11
	ng/sample	IDA2Blank					*<17*	0.00	0.13	0.29	223.6	5
2-Butoxyethanol$_{RCRF}$	ng/sample	IDA1Synt		-1.35	156	20	135	135	125	18	14.4	7
	ng/sample	IDA2Blank					*<50*	0.00	0.27	0.47	173.2	3
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		-0.55	61.5	25	57.3	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					*<22*	0.00	0.08	0.18	223.6	5

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$2EH_{RCRF}$	ng/sample	IDA1Synt		-4.38	130	20	73	134	137	32	23.4	11
	ng/sample	IDA2Blank					*<5,0*	0.69	2.85	4.81	169.2	4
$2EH_{TE}$	ng/sample	IDA1Synt		-3.73	82.5	20	51.7	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					*<3,5*	0.00	2.82	5.71	202.5	5
Alpha-$Pinene_{RCRF}$	ng/sample	IDA1Synt		-2.29	153	20	118	140	146	21	14.3	7
	ng/sample	IDA2Blank					*<0,5*	0.00	0.01	0.02	173.2	3
Alpha-$Pinene_{TE}$	ng/sample	IDA1Synt		-0.99	162	20	146	163	164	18	10.8	10
	ng/sample	IDA2Blank					*<0,6*	0.00	0.10	0.22	213.0	5
$Naphthalene_{RCRF}$	ng/sample	IDA1Synt		-3.87	248	20	152	252	257	29	11.3	10
	ng/sample	IDA2Blank			0.34		*<3,1*	0.17	0.34	0.47	139.1	4
$Naphthalene_{TE}$	ng/sample	IDA1Synt		-4.56	333	20	181	321	319	61	19.2	12
	ng/sample	IDA2Blank					*<3,7*	0.00	0.33	0.54	164.4	5
$Styrene_{RCRF}$	ng/sample	IDA1Synt		-1.70	230	20	191	231	232	38	16.5	11
	ng/sample	IDA2Blank					*<2,1*	0.07	0.12	0.17	137.6	4
$Styrene_{TE}$	ng/sample	IDA1Synt		-1.21	214	20	188	225	222	26	11.7	11
	ng/sample	IDA2Blank					*<2,1*	0.00	0.08	0.19	223.6	5
$Tetrachloroethylene_{RCRF}$	ng/sample	IDA1Synt		-0.46	80.5	20	76.8	79.0	81.3	9.6	11.8	8
	ng/sample	IDA2Blank					*<0,5*	0.00	0.02	0.03	173.2	3
$Tetrachloroethylene_{TE}$	ng/sample	IDA1Synt		-2.12	65.5	20	51.6	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					*<0,34*	0.00	0.01	0.01	223.6	5
$Toluene_{RCRF}$	ng/sample	IDA1Synt		-1.66	86.1	20	71.8	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		*<3,4*	0.57	0.51	0.37	71.7	5
$TVOC_{Lab}$	µg/m3	IDA3TVOC		-1.62	305	30	231	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		7.7	15.2	14.4	7.7	53.5	8
$TVOC_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		-1.50	288	30	223	255	260	71	27.4	8
$TXIB_{RCRF}$	ng/sample	IDA1Synt		-1.58	121	25	97	117	124	22	17.8	9
	ng/sample	IDA2Blank					*<5,0*	5.5	13.5	20.3	150.4	4
$TXIB_{TE}$	ng/sample	IDA1Synt		-3.68	139	25	75	146	135	35	25.8	12
	ng/sample	IDA2Blank					*<3,9*	0.00	7.74	13.48	174.1	5

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-$Butanol_{RCRF}$	ng/sample	IDA1Synt		-2.29	157	20	121	136	136	9	6.8	6
1-$Butanol_{TE}$	ng/sample	IDA1Synt		-2.08	55.7	25	41	49	57	17	29.6	11
2-$Butoxyethanol_{RCRF}$	ng/sample	IDA1Synt		-0.96	156	20	141	135	125	18	14.4	7
2-$Butoxyethanol_{TE}$	ng/sample	IDA1Synt		1.96	61.5	25	76.6	57.0	62.7	19.6	31.2	11
$2EH_{RCRF}$	ng/sample	IDA1Synt		0.31	130	20	134	134	137	32	23.4	11
$2EH_{TE}$	ng/sample	IDA1Synt		2.97	82.5	20	107.0	76.3	89.4	29.5	33.0	11
Alpha-$Pinene_{RCRF}$	ng/sample	IDA1Synt		1.70	153	20	179	140	146	21	14.3	7
Alpha-$Pinene_{TE}$	ng/sample	IDA1Synt		1.73	162	20	190	163	164	18	10.8	10
$Naphthalene_{RCRF}$	ng/sample	IDA1Synt		-1.73	248	20	205	252	257	29	11.3	10
$Naphthalene_{TE}$	ng/sample	IDA1Synt		1.80	333	20	393	321	319	61	19.2	12
$Styrene_{RCRF}$	ng/sample	IDA1Synt		0.13	230	20	233	231	232	38	16.5	11
$Styrene_{TE}$	ng/sample	IDA1Synt		1.78	214	20	252	225	222	26	11.7	11
$Tetrachloroethylene_{RCRF}$	ng/sample	IDA1Synt		1.34	80.5	20	91.3	79.0	81.3	9.6	11.8	8
$Tetrachloroethylene_{TE}$	ng/sample	IDA1Synt		1.27	65.5	20	73.8	57.5	54.0	15.2	28.2	12
$Toluene_{RCRF}$	ng/sample	IDA1Synt		-0.81	86.1	20	79.1	79.3	82.6	12.4	15.0	12

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
$TVOC_{Lab}$	µg/m3	IDA3TVOC		0.37	305	30	322	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		14.9	15.2	14.4	7.7	53.5	8
$TVOC_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		0.42	288	30	306	255	260	71	27.4	8
$TXIB_{RCRF}$	ng/sample	IDA1Synt		1.79	121	25	148	117	124	22	17.8	9
$TXIB_{TE}$	ng/sample	IDA1Synt		1.15	139	25	159	146	135	35	25.8	12

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-$Butanol_{RCRF}$	ng/sample	IDA1Synt		-0.87	157	20	143	136	136	9	6.8	6
	ng/sample	IDA2Blank					0.00	0.00	0.54	0.94	173.2	3
1-$Butanol_{TE}$	ng/sample	IDA1Synt		1.05	55.7	25	63	49	57	17	29.6	11
	ng/sample	IDA2Blank					0.00	0.00	0.13	0.29	223.6	5
2-$Butoxyethanol_{RCRF}$	ng/sample	IDA1Synt		-1.03	156	20	140	135	125	18	14.4	7
	ng/sample	IDA2Blank					0.00	0.00	0.27	0.47	173.2	3
2-$Butoxyethanol_{TE}$	ng/sample	IDA1Synt		-0.58	61.5	25	57.0	57.0	62.7	19.6	31.2	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.18	223.6	5
$2EH_{RCRF}$	ng/sample	IDA1Synt		-0.36	130	20	125	134	137	32	23.4	11
	ng/sample	IDA2Blank					0.00	0.69	2.85	4.81	169.2	4
$2EH_{TE}$	ng/sample	IDA1Synt		-1.91	82.5	20	66.7	76.3	89.4	29.5	33.0	11
	ng/sample	IDA2Blank					0.00	0.00	2.82	5.71	202.5	5
Alpha-$Pinene_{RCRF}$	ng/sample	IDA1Synt		0.46	153	20	160	140	146	21	14.3	7
	ng/sample	IDA2Blank					0.00	0.00	0.01	0.02	173.2	3
Alpha-$Pinene_{TE}$	ng/sample	IDA1Synt		0.52	162	20	170	163	164	18	10.8	10
	ng/sample	IDA2Blank					0.00	0.00	0.10	0.22	213.0	5
$Naphthalene_{RCRF}$	ng/sample	IDA1Synt		1.35	248	20	282	252	257	29	11.3	10
	ng/sample	IDA2Blank			0.34		1.01	0.17	0.34	0.47	139.1	4
$Naphthalene_{TE}$	ng/sample	IDA1Synt		0.42	333	20	347	321	319	61	19.2	12
	ng/sample	IDA2Blank					1.25	0.00	0.33	0.54	164.4	5
$Styrene_{RCRF}$	ng/sample	IDA1Synt		0.03	230	20	231	231	232	38	16.5	11
	ng/sample	IDA2Blank					0.00	0.07	0.12	0.17	137.6	4
$Styrene_{TE}$	ng/sample	IDA1Synt		0.67	214	20	228	225	222	26	11.7	11
	ng/sample	IDA2Blank					0.00	0.00	0.08	0.19	223.6	5
$Tetrachloroethylene_{RCRF}$	ng/sample	IDA1Synt		0.91	80.5	20	87.8	79.0	81.3	9.6	11.8	8
	ng/sample	IDA2Blank					0.00	0.00	0.02	0.03	173.2	3
$Tetrachloroethylene_{TE}$	ng/sample	IDA1Synt		-0.83	65.5	20	60.1	57.5	54.0	15.2	28.2	12
	ng/sample	IDA2Blank					0.00	0.00	0.01	0.01	223.6	5
$Toluene_{RCRF}$	ng/sample	IDA1Synt		-0.77	86.1	20	79.4	79.3	82.6	12.4	15.0	12
	ng/sample	IDA2Blank			0.51		0.90	0.57	0.51	0.37	71.7	5
$TVOC_{Lab}$	µg/m3	IDA3TVOC		-0.97	305	30	261	261	275	75	27.3	8
	µg/m3	IDA4Blank			14.4		7.0	15.2	14.4	7.7	53.5	8
$TVOC_{Lab}$-Chamber blank	µg/m3	IDA3TVOC		-0.79	288	30	254	255	260	71	27.4	8
$TXIB_{RCRF}$	ng/sample	IDA1Synt		1.73	121	25	147	117	124	22	17.8	9
	ng/sample	IDA2Blank					43.0	5.5	13.5	20.3	150.4	4
$TXIB_{TE}$	ng/sample	IDA1Synt		-1.87	139	25	107	146	135	35	25.8	12
	ng/sample	IDA2Blank					31.14	0.00	7.74	13.48	174.1	5

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{TE}$	ng/sample	IDA1Synt		3.63	55.7	25	81	49	57	17	29.6	11
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		4.46	61.5	25	95.8	57.0	62.7	19.6	31.2	11
2EH$_{RCRF}$	ng/sample	IDA1Synt		2.77	130	20	166	134	137	32	23.4	11
2EH$_{TE}$	ng/sample	IDA1Synt		6.08	82.5	20	132.7	76.3	89.4	29.5	33.0	11
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		1.01	162	20	178	163	164	18	10.8	10
Naphthalene$_{RCRF}$	ng/sample	IDA1Synt		-0.13	248	20	245	252	257	29	11.3	10
Naphthalene$_{TE}$	ng/sample	IDA1Synt		-1.21	333	20	293	321	319	61	19.2	12
Styrene$_{RCRF}$	ng/sample	IDA1Synt		1.44	230	20	263	231	232	38	16.5	11
Styrene$_{TE}$	ng/sample	IDA1Synt		2.26	214	20	262	225	222	26	11.7	11
Tetrachloroethylene$_{TE}$	ng/sample	IDA1Synt		-3.76	65.5	20	40.9	57.5	54.0	15.2	28.2	12
Toluene$_{RCRF}$	ng/sample	IDA1Synt		0.89	86.1	20	93.8	79.3	82.6	12.4	15.0	12
TXIB$_{RCRF}$	ng/sample	IDA1Synt		1.91	121	25	150	117	124	22	17.8	9
TXIB$_{TE}$	ng/sample	IDA1Synt		2.60	139	25	184	146	135	35	25.8	12

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{RCRF}$	ng/sample	IDA1Synt		-1.23	157	20	138	136	136	9	6.8	6
1-Butanol$_{TE}$	ng/sample	IDA1Synt		-2.46	55.7	25	39	49	57	17	29.6	11
2-Butoxyethanol$_{RCRF}$	ng/sample	IDA1Synt		-3.38	156	20	103	135	125	18	14.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		-2.41	61.5	25	43.0	57.0	62.7	19.6	31.2	11
2EH$_{RCRF}$	ng/sample	IDA1Synt		-0.22	130	20	127	134	137	32	23.4	11
2EH$_{TE}$	ng/sample	IDA1Synt		-0.75	82.5	20	76.3	76.3	89.4	29.5	33.0	11
Alpha-Pinene$_{RCRF}$	ng/sample	IDA1Synt		-0.86	153	20	140	140	146	21	14.3	7
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		-0.53	162	20	153	163	164	18	10.8	10
Naphthalene$_{RCRF}$	ng/sample	IDA1Synt		0.04	248	20	249	252	257	29	11.3	10
Naphthalene$_{TE}$	ng/sample	IDA1Synt		0.48	333	20	349	321	319	61	19.2	12
Styrene$_{RCRF}$	ng/sample	IDA1Synt		-1.25	230	20	201	231	232	38	16.5	11
Styrene$_{TE}$	ng/sample	IDA1Synt		-0.31	214	20	207	225	222	26	11.7	11
Tetrachloroethylene$_{RCRF}$	ng/sample	IDA1Synt		-1.07	80.5	20	71.9	79.0	81.3	9.6	11.8	8
Tetrachloroethylene$_{TE}$	ng/sample	IDA1Synt		-1.05	65.5	20	58.6	57.5	54.0	15.2	28.2	12
Toluene$_{RCRF}$	ng/sample	IDA1Synt		-1.64	86.1	20	72.0	79.3	82.6	12.4	15.0	12
TXIB$_{RCRF}$	ng/sample	IDA1Synt		-0.26	121	25	117	117	124	22	17.8	9
TXIB$_{TE}$	ng/sample	IDA1Synt		0.52	139	25	148	146	135	35	25.8	12

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{RCRF}$	ng/sample	IDA1Synt		-1.50	157	20	134	136	136	9	6.8	6
1-Butanol$_{TE}$	ng/sample	IDA1Synt		-2.69	55.7	25	37	49	57	17	29.6	11
2-Butoxyethanol$_{RCRF}$	ng/sample	IDA1Synt		-3.29	156	20	105	135	125	18	14.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		-2.65	61.5	25	41.1	57.0	62.7	19.6	31.2	11
2EH$_{RCRF}$	ng/sample	IDA1Synt		-0.51	130	20	123	134	137	32	23.4	11
2EH$_{TE}$	ng/sample	IDA1Synt		-1.18	82.5	20	72.8	76.3	89.4	29.5	33.0	11
Alpha-Pinene$_{RCRF}$	ng/sample	IDA1Synt		-1.22	153	20	134	140	146	21	14.3	7
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		-0.94	162	20	147	163	164	18	10.8	10
Naphthalene$_{RCRF}$	ng/sample	IDA1Synt		-0.36	248	20	239	252	257	29	11.3	10
Naphthalene$_{TE}$	ng/sample	IDA1Synt		0.01	333	20	333	321	319	61	19.2	12
Styrene$_{RCRF}$	ng/sample	IDA1Synt		-1.57	230	20	194	231	232	38	16.5	11
Styrene$_{TE}$	ng/sample	IDA1Synt		-0.67	214	20	200	225	222	26	11.7	11

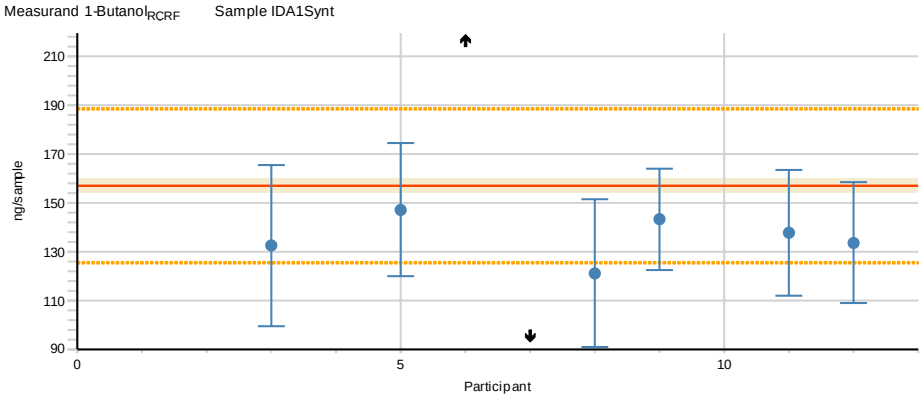
Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
Tetrachloroethylene$_{RCRF}$	ng/sample	IDA1Synt		-1.47	80.5	20	68.7	79.0	81.3	9.6	11.8	8
Tetrachloroethylene$_{TE}$	ng/sample	IDA1Synt		-1.40	65.5	20	56.3	57.5	54.0	15.2	28.2	12
Toluene$_{RCRF}$	ng/sample	IDA1Synt		-1.89	86.1	20	69.8	79.3	82.6	12.4	15.0	12
TXIB$_{RCRF}$	ng/sample	IDA1Synt		-0.61	121	25	112	117	124	22	17.8	9
TXIB$_{TE}$	ng/sample	IDA1Synt		0.24	139	25	143	146	135	35	25.8	12

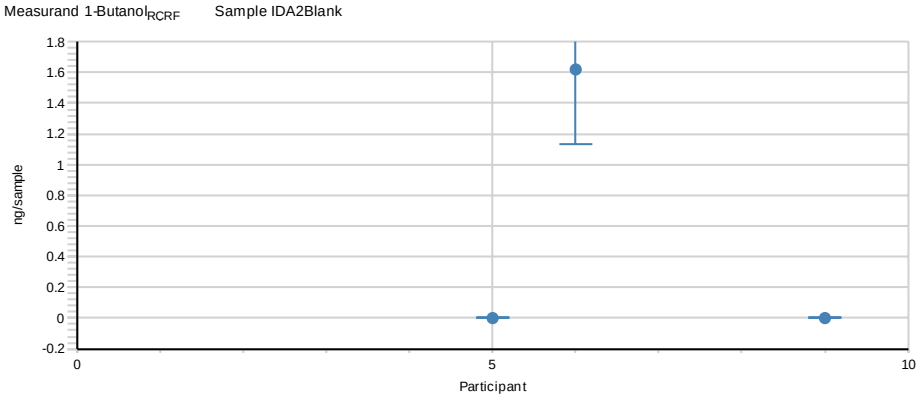
Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	s	s %	n (stat)
1-Butanol$_{TE}$	ng/sample	IDA1Synt		2.48	55.7	25	73	49	57	17	29.6	11
2-Butoxyethanol$_{TE}$	ng/sample	IDA1Synt		2.71	61.5	25	82.3	57.0	62.7	19.6	31.2	11
2EH$_{RCRF}$	ng/sample	IDA1Synt		3.95	130	20	181	134	137	32	23.4	11
2EH$_{TE}$	ng/sample	IDA1Synt		4.92	82.5	20	123.1	76.3	89.4	29.5	33.0	11
Alpha-Pinene$_{TE}$	ng/sample	IDA1Synt		0.75	162	20	174	163	164	18	10.8	10
Naphthalene$_{RCRF}$	ng/sample	IDA1Synt		0.97	248	20	272	252	257	29	11.3	10
Naphthalene$_{TE}$	ng/sample	IDA1Synt		-1.01	333	20	299	321	319	61	19.2	12
Styrene$_{RCRF}$	ng/sample	IDA1Synt		2.84	230	20	295	231	232	38	16.5	11
Styrene$_{TE}$	ng/sample	IDA1Synt		0.88	214	20	233	225	222	26	11.7	11
Tetrachloroethylene$_{TE}$	ng/sample	IDA1Synt		-4.14	65.5	20	38.4	57.5	54.0	15.2	28.2	12
Toluene$_{RCRF}$	ng/sample	IDA1Synt		0.24	86.1	20	88.2	79.3	82.6	12.4	15.0	12
TXIB$_{RCRF}$	ng/sample	IDA1Synt		9.46	121	25	264	117	124	22	17.8	9
TXIB$_{TE}$	ng/sample	IDA1Synt		0.83	139	25	154	146	135	35	25.8	12

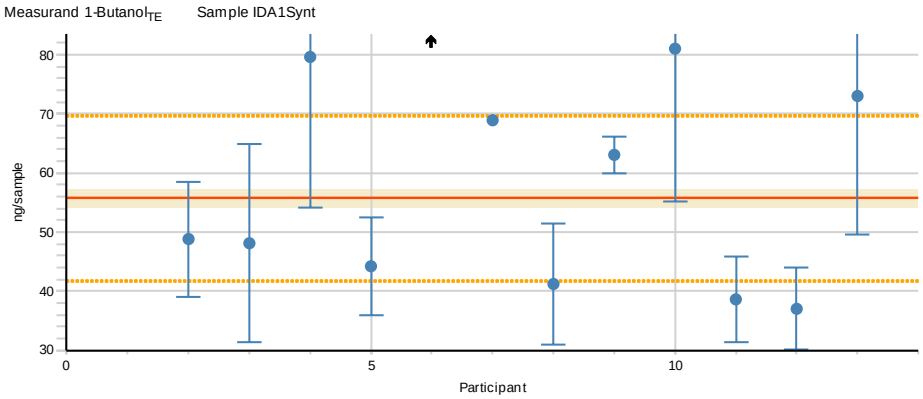
APPENDIX 8: Results of participants and their uncertainties

In figures:

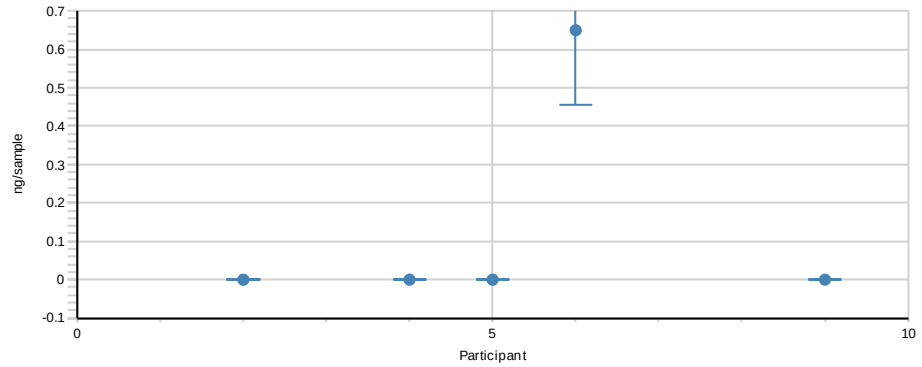
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



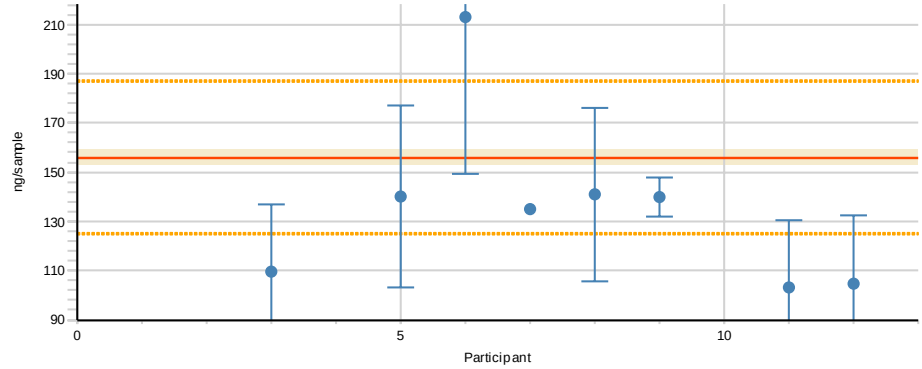




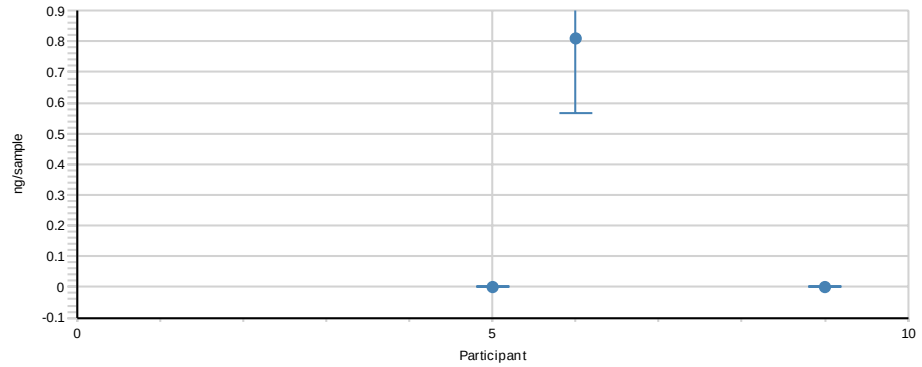
Measurand 1-Butanol$_{TE}$ Sample IDA2Blank

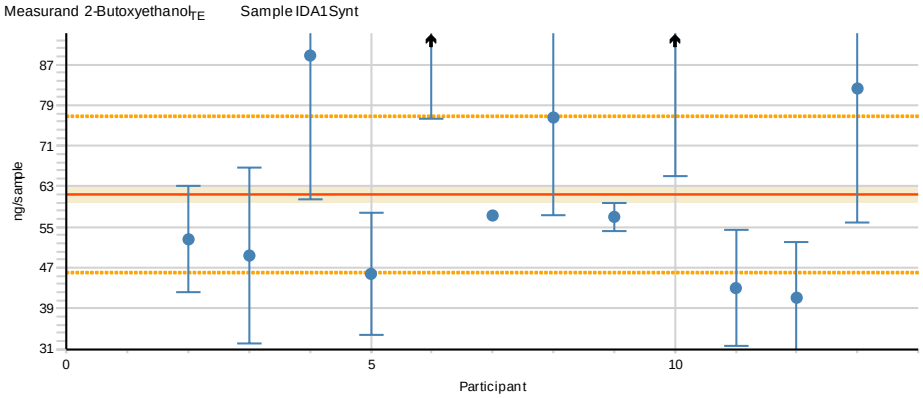


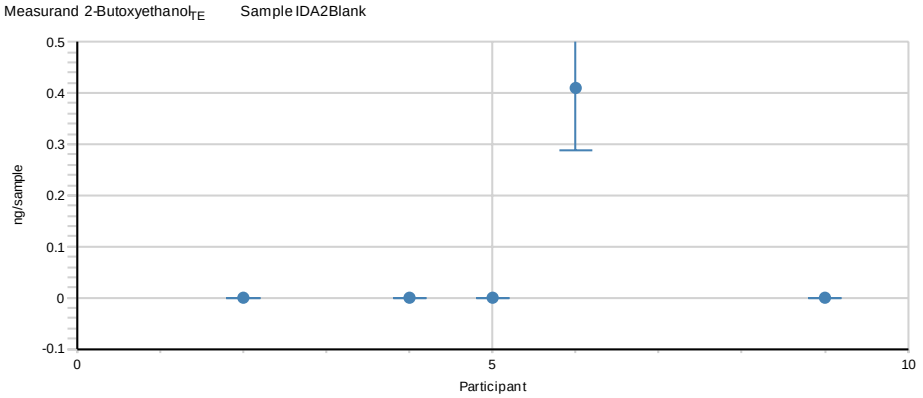
Measurand 2-Butoxyethanol$_{RCRF}$ Sample IDA1Synt

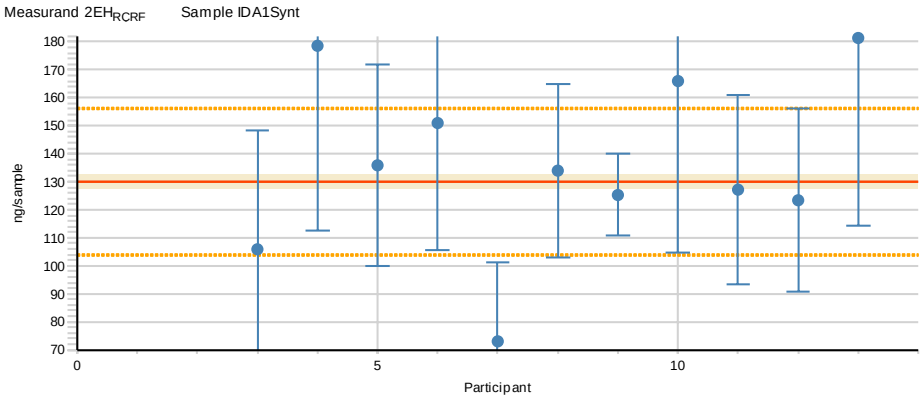


Measurand 2-Butoxyethanol$_{RCRF}$ Sample IDA2Blank

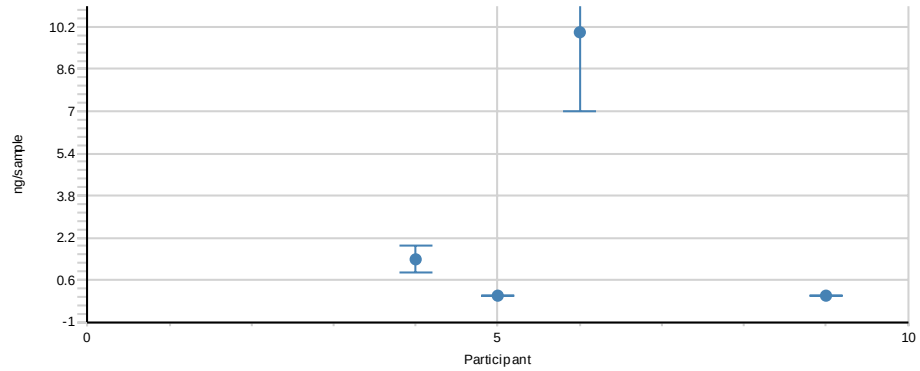



Measurand 2-Butoxyethanol$_{TE}$
Sample IDA1Synt
ng/sample
87
79
71
63
55
47
39
31
0
5
10
Participant

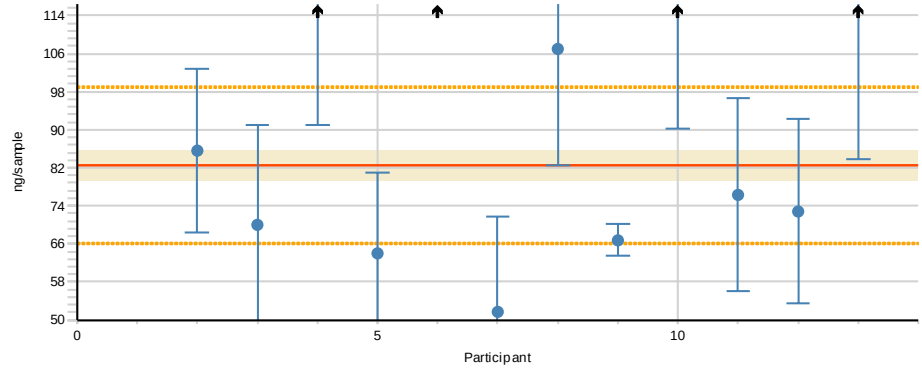

Measurand 2-Butoxyethanol$_{TE}$
Sample IDA2Blank
ng/sample
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
5
10
Participant


Measurand 2EH$_{RCRF}$
Sample IDA1Synt
ng/sample
180
170
160
150
140
130
120
110
100
90
80
70
0
5
10
Participant

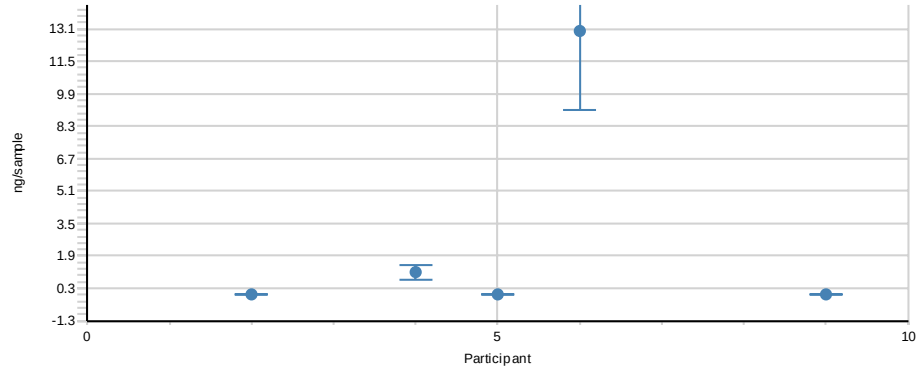
Measurand $2EH_{RCRF}$ Sample IDA2Blank

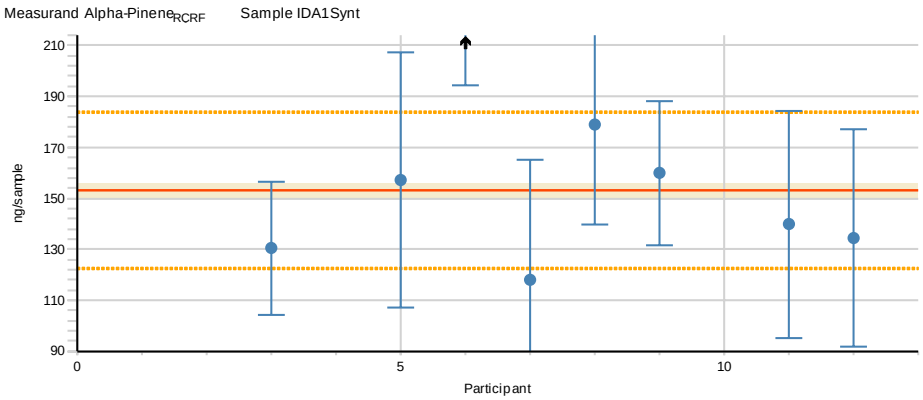


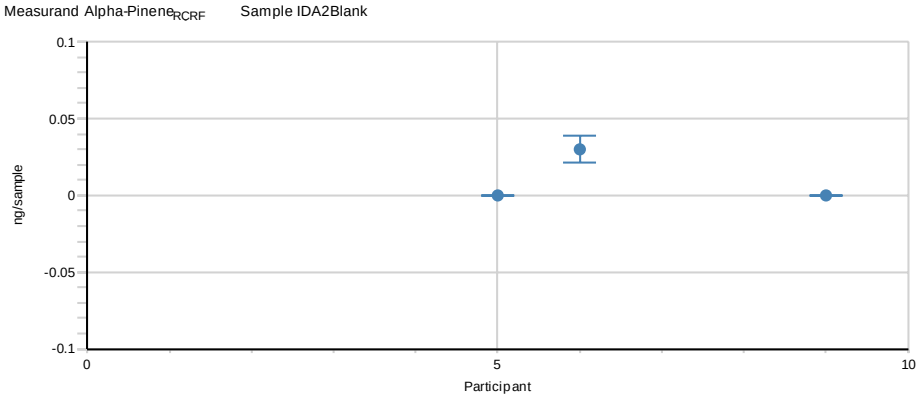
Measurand $2EH_{TE}$ Sample IDA1Synt

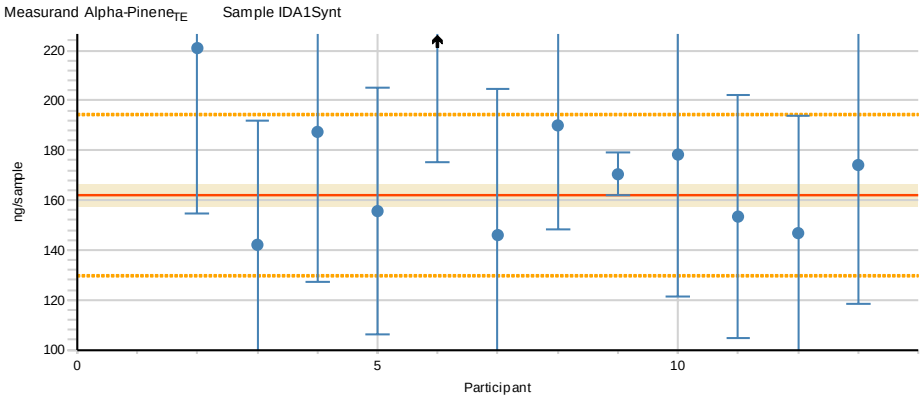


Measurand $2EH_{TE}$ Sample IDA2Blank

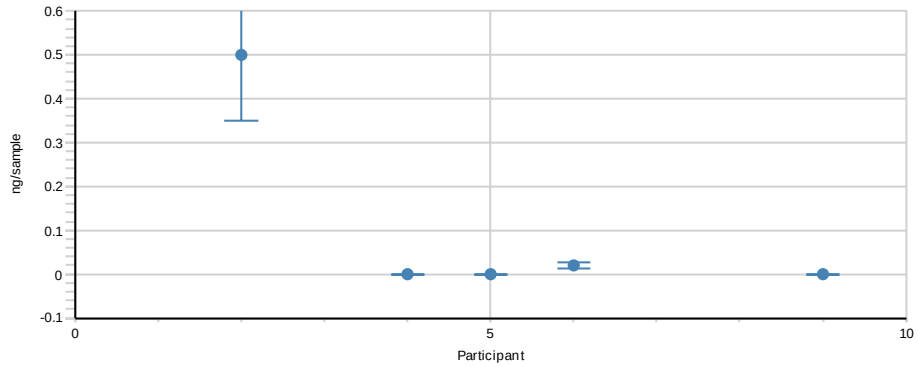



Measurand Alpha-Pinene$_{RCRF}$ Sample IDA1Synt
ng/sample
210
190
170
150
130
110
90
0
5
10
Participant

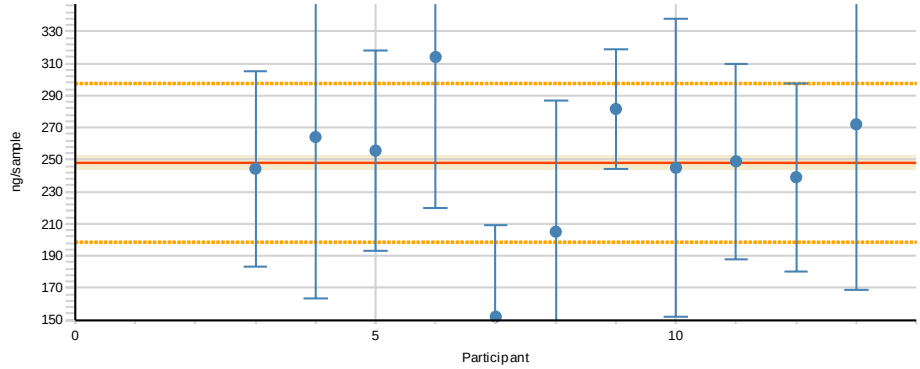

Measurand Alpha-Pinene$_{RCRF}$ Sample IDA2Blank
ng/sample
0.1
0.05
0
-0.05
-0.1
0
5
10
Participant


Measurand Alpha-Pinene$_{TE}$ Sample IDA1Synt
ng/sample
220
200
180
160
140
120
100
0
5
10
Participant

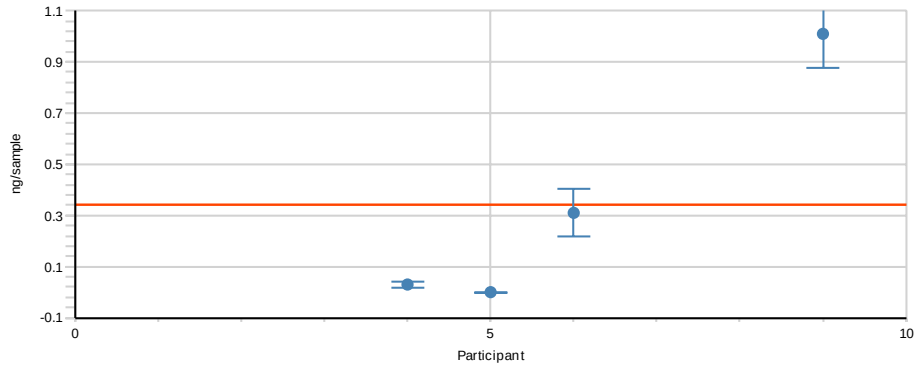
Measurand Alpha-Pinene$_{TE}$ Sample IDA2Blank

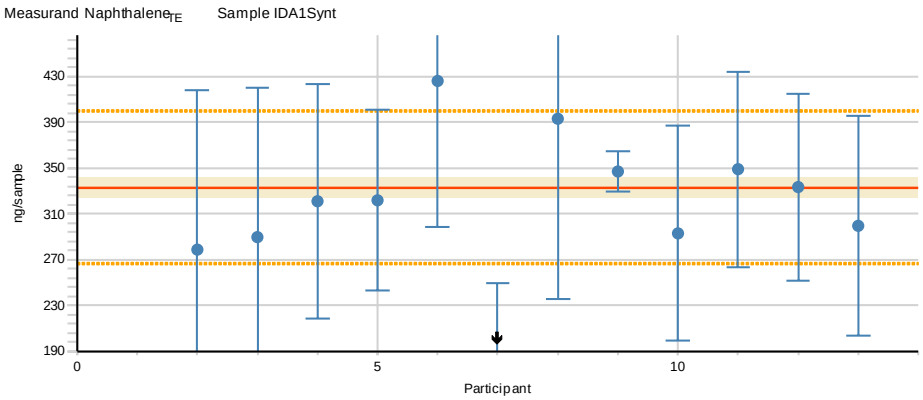


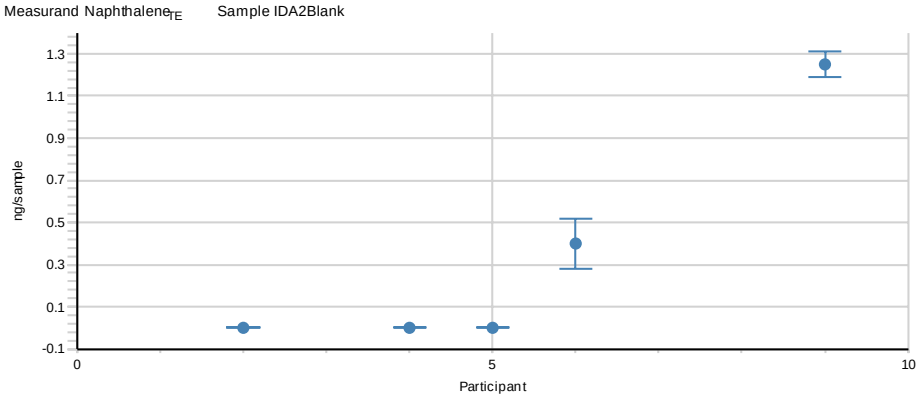
Measurand Naphthalene$_{RCRF}$ Sample IDA1Synt

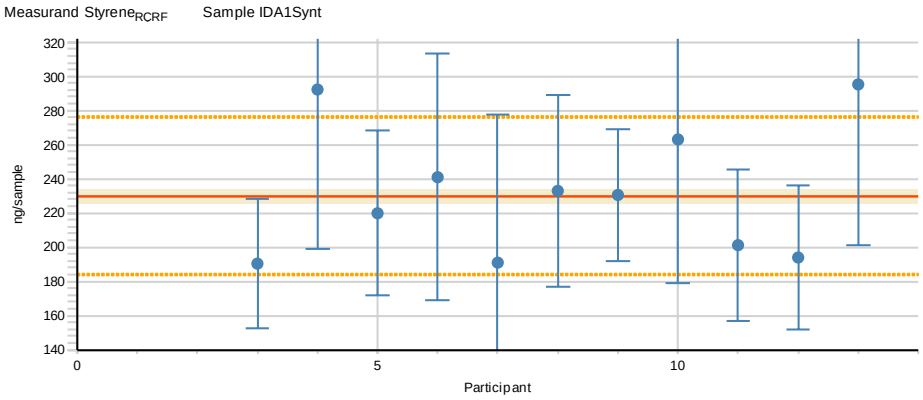


Measurand Naphthalene$_{RCRF}$ Sample IDA2Blank

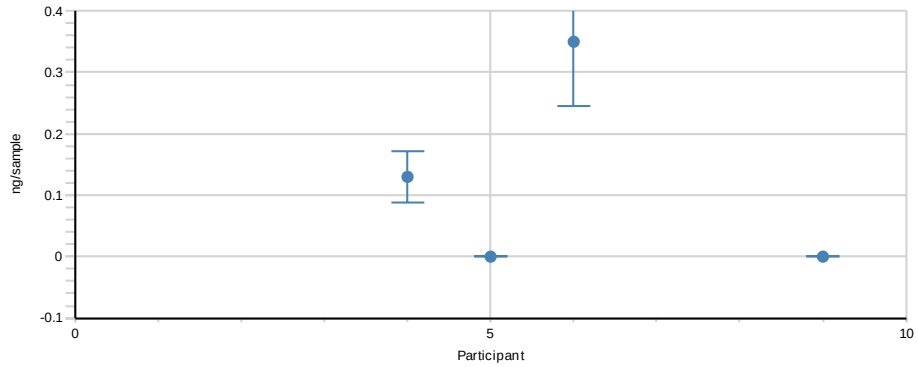



Measurand Naphthalene$_{TE}$
Sample IDA1Synt
ng/sample
430
390
350
310
270
230
190
0
5
10
Participant

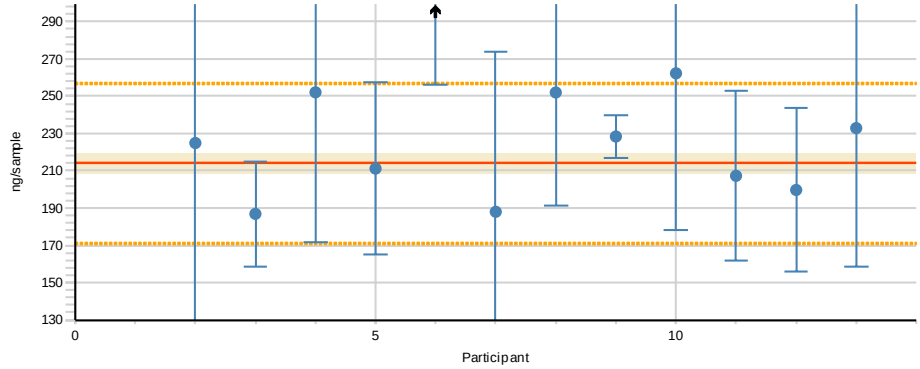

Measurand Naphthalene$_{TE}$
Sample IDA2Blank
ng/sample
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
0
5
10
Participant


Measurand Styrene$_{RCRF}$
Sample IDA1Synt
ng/sample
320
300
280
260
240
220
200
180
160
140
0
5
10
Participant

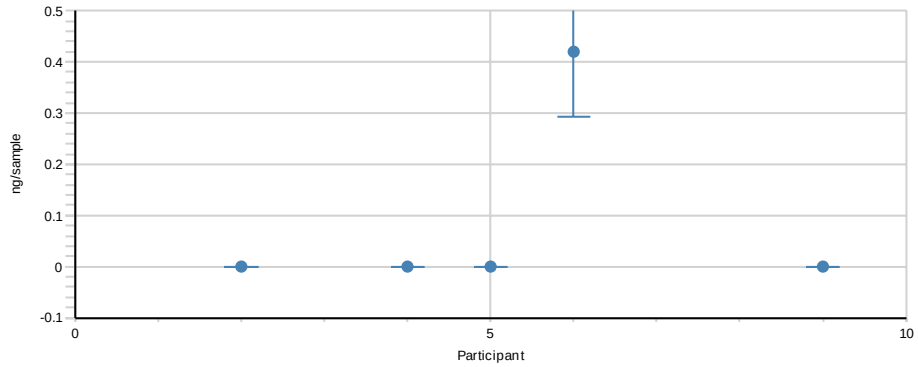
Measurand $Styrene_{RCRF}$ Sample IDA2Blank

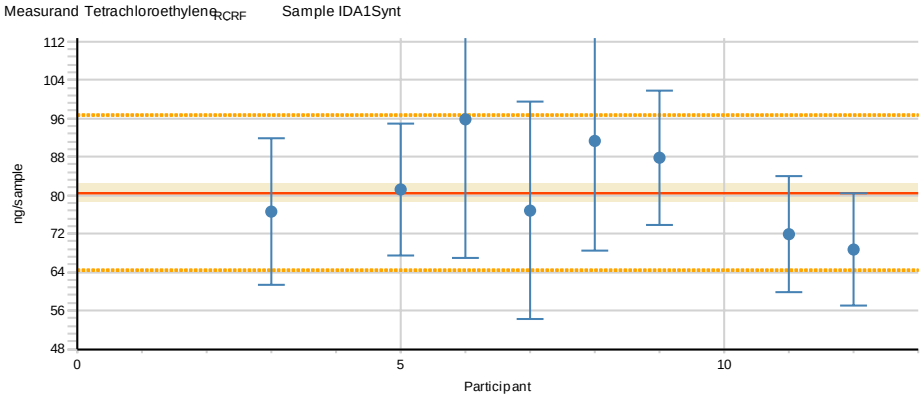


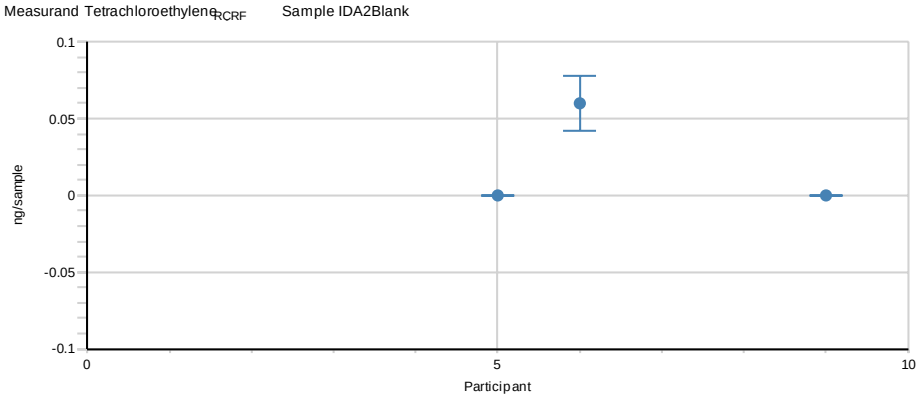
Measurand $Styrene_{TE}$ Sample IDA1Synt

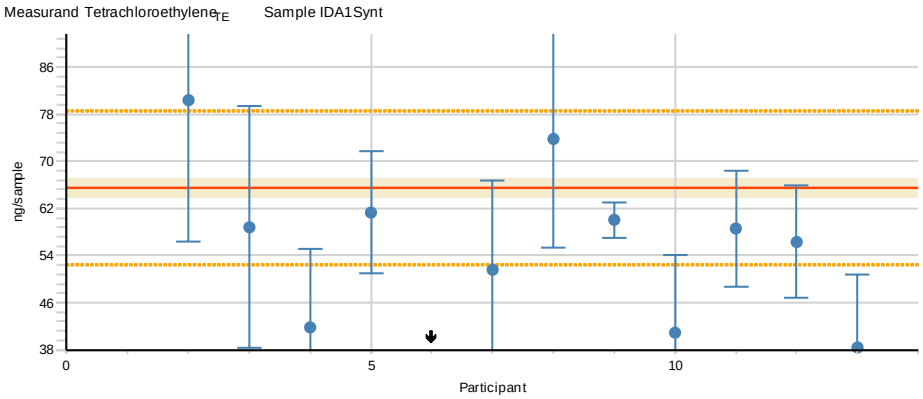


Measurand $Styrene_{TE}$ Sample IDA2Blank

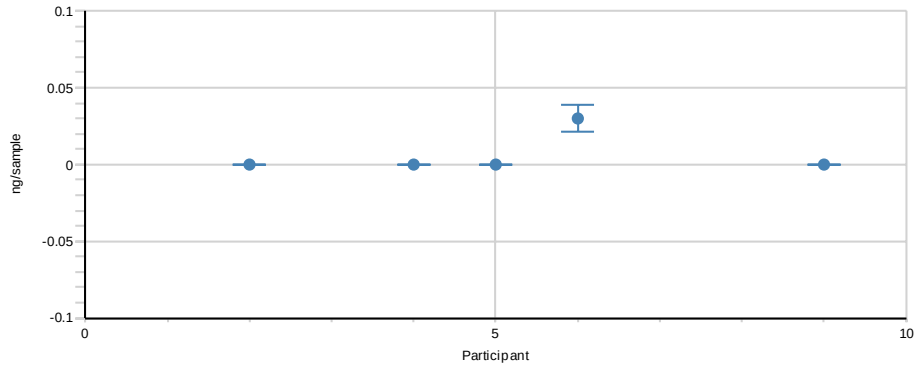



Measurand Tetrachloroethylene RCRF
Sample IDA1Synt
ng/sample
112
104
96
88
80
72
64
56
48
0
5
10
Participant

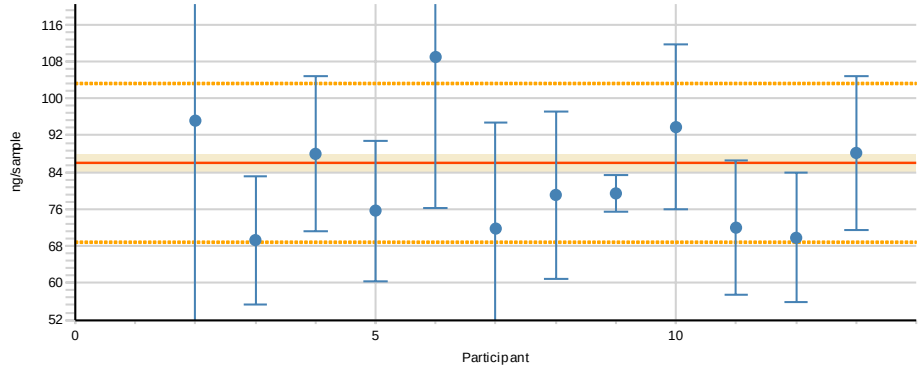

Measurand Tetrachloroethylene RCRF
Sample IDA2Blank
ng/sample
0.1
0.05
0
-0.05
-0.1
0
5
10
Participant


Measurand Tetrachloroethylene TE
Sample IDA1Synt
ng/sample
86
78
70
62
54
46
38
0
5
10
Participant

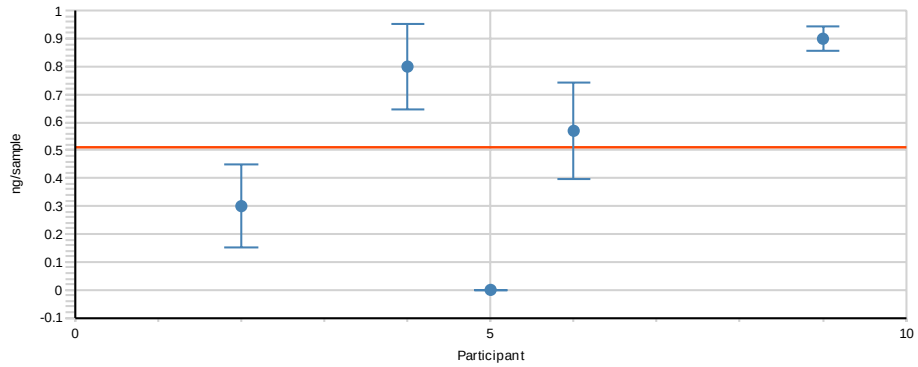
Measurand Tetrachloroethylene$_{TE}$ Sample IDA2Blank



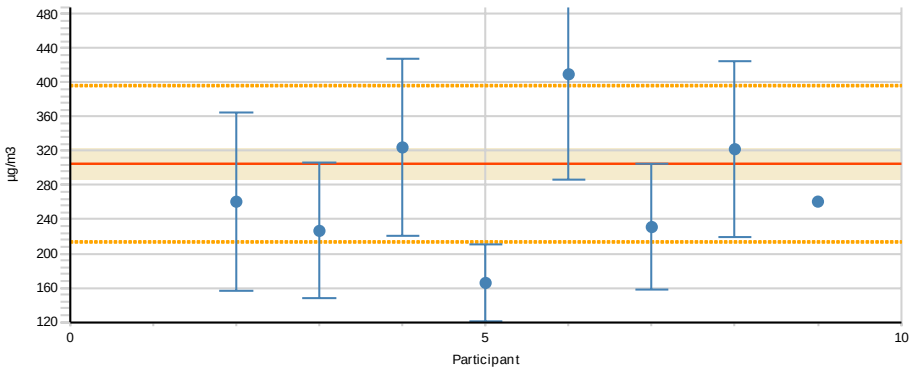
Measurand Toluene$_{RCRF}$ Sample IDA1Synt



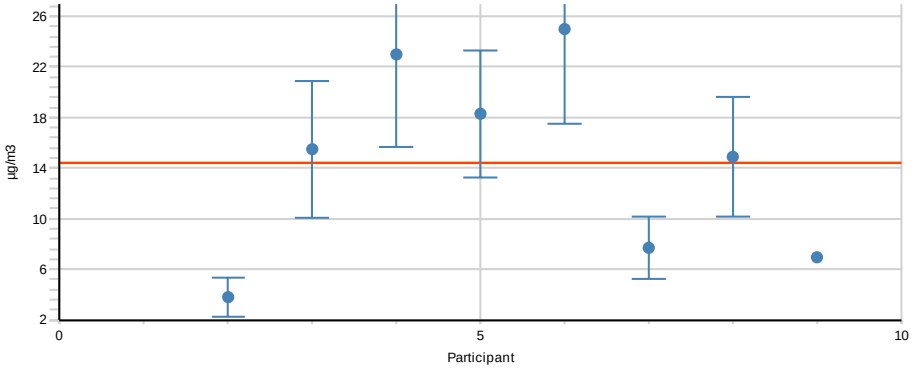
Measurand Toluene$_{RCRF}$ Sample IDA2Blank



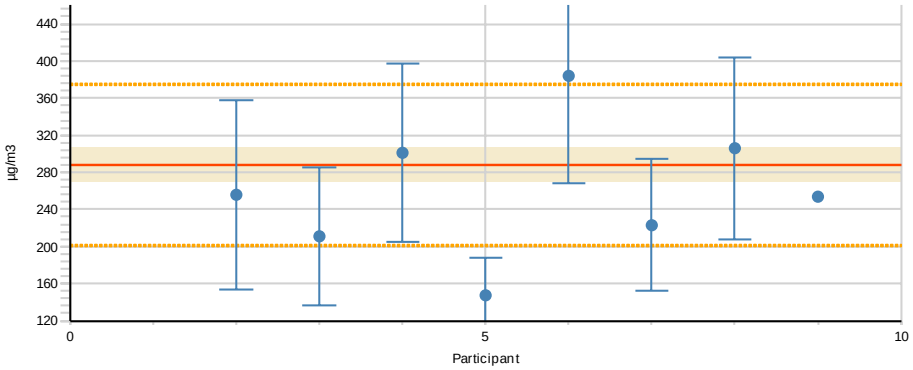
Measurand $TVOC_{Lab}$ Sample IDA3TVOC



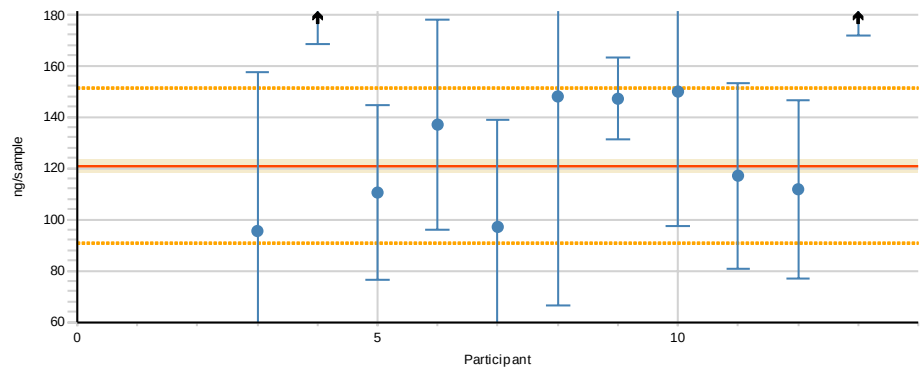
Measurand $TVOC_{Lab}$ Sample IDA4Blank



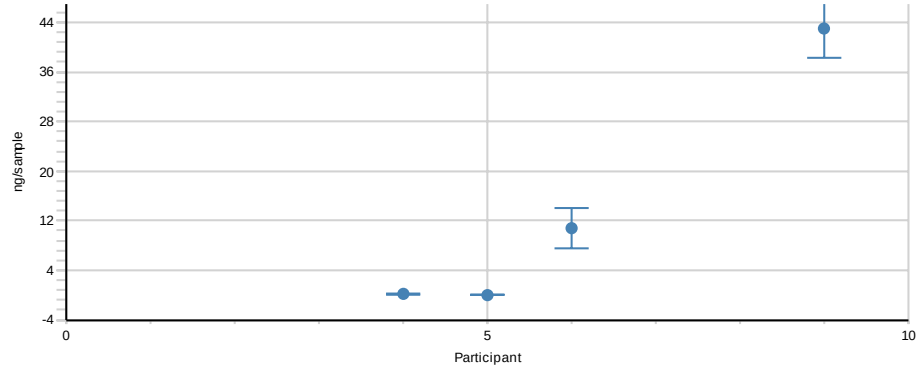
Measurand $TVOC_{Lab}$- Chamber blank Sample IDA3TVOC



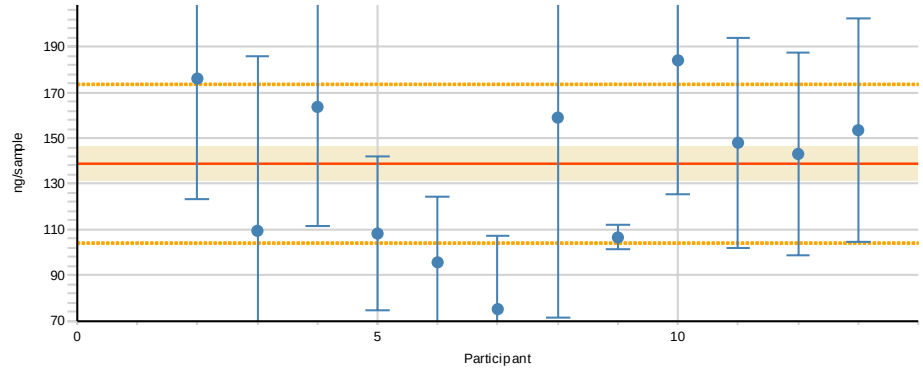
Measurand $TXIB_{RCRF}$ Sample IDA1Synt

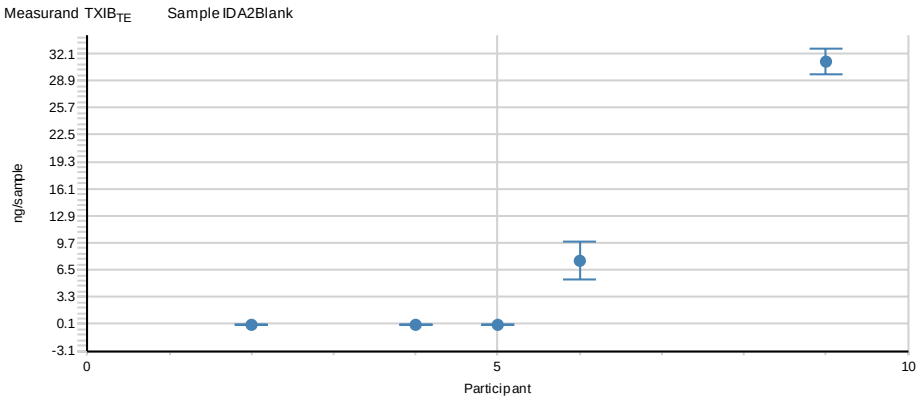


Measurand $TXIB_{RCRF}$ Sample IDA2Blank



Measurand $TXIB_{TE}$ Sample IDA1Synt




Measurand TXIB$_{TE}$
Sample IDA2Blank
32.1
28.9
25.7
22.5
19.3
16.1
12.9
9.7
6.5
3.3
0.1
-3.1
ng/sample
0
5
10
Participant

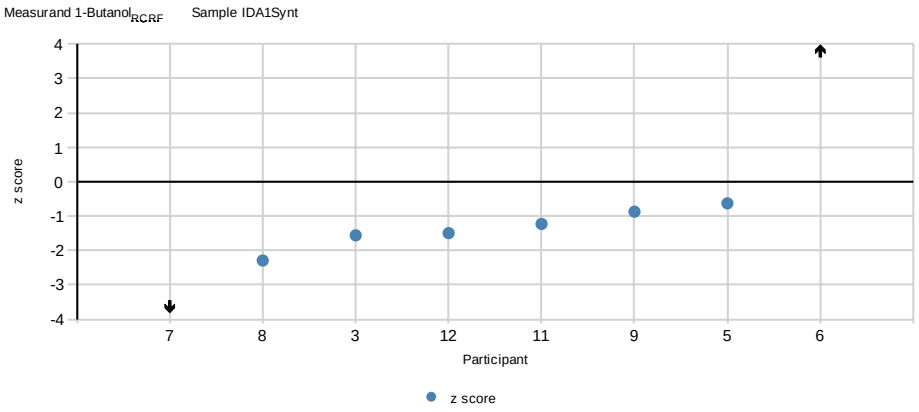
APPENDIX 9: Summary of the z scores

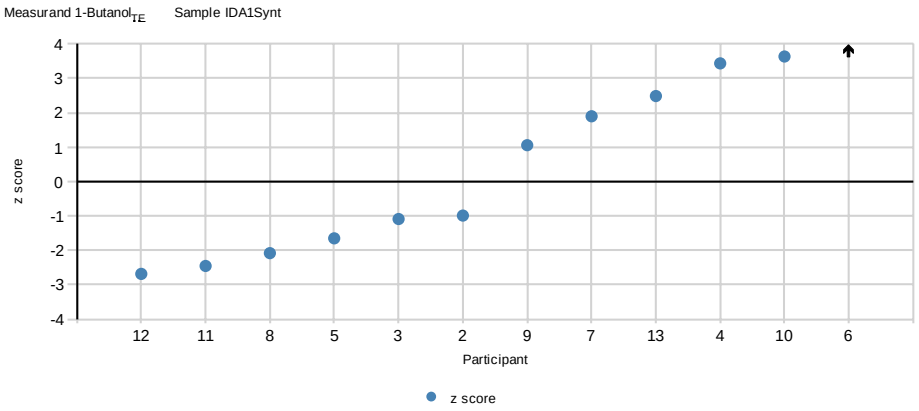
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
1-Butanol$_{RCRF}$	IDA1Synt	.	.	S	.	S	U	*u*	*q*	*S*	.	S	S	.	.	.	.	.	.	.	.	.	.	.	62.5
1-Butanol$_{TE}$	IDA1Synt	.	S	S	U	S	U	*S*	*q*	S	U	q	q	Q	.	.	.	.	.	.	.	.	.	.	41.7
2-Butoxyethanol$_{RCRF}$	IDA1Synt	.	.	q	.	S	U	*S*	*S*	*S*	.	u	u	.	.	.	.	.	.	.	.	.	.	.	50.0
2-Butoxyethanol$_{TE}$	IDA1Synt	.	S	S	U	q	U	*S*	*S*	*S*	U	q	q	Q	.	.	.	.	.	.	.	.	.	.	41.7
2EH$_{RCRF}$	IDA1Synt	.	.	S	U	S	S	u	S	*S*	Q	S	S	U	.	.	.	.	.	.	.	.	.	.	63.6
2EH$_{TE}$	IDA1Synt	.	S	S	U	q	U	u	Q	*S*	U	S	S	U	.	.	.	.	.	.	.	.	.	.	41.7
Alpha-Pinene$_{RCRF}$	IDA1Synt	.	.	S	.	S	U	q	S	*S*	.	S	S	.	.	.	.	.	.	.	.	.	.	.	75.0
Alpha-Pinene$_{TE}$	IDA1Synt	.	U	S	S	S	U	S	S	*S*	S	S	S	S	.	.	.	.	.	.	.	.	.	.	83.3
Naphthalene$_{RCRF}$	IDA1Synt	.	.	S	S	S	Q	u	S	*S*	S	S	S	S	.	.	.	.	.	.	.	.	.	.	81.8
Naphthalene$_{TE}$	IDA1Synt	.	S	S	S	S	Q	u	S	*S*	S	S	S	S	.	.	.	.	.	.	.	.	.	.	83.3
Styrene$_{RCRF}$	IDA1Synt	.	.	S	Q	S	S	S	S	*S*	S	S	S	Q	.	.	.	.	.	.	.	.	.	.	81.8
Styrene$_{TE}$	IDA1Synt	.	S	S	S	S	U	S	S	S	Q	S	S	S	.	.	.	.	.	.	.	.	.	.	83.3
Tetrachloroethylene$_{RCRF}$	IDA1Synt	.	.	S	.	S	S	S	*S*	*S*	.	S	S	.	.	.	.	.	.	.	.	.	.	.	100
Tetrachloroethylene$_{TE}$	IDA1Synt	.	Q	S	u	S	u	q	*S*	*S*	u	S	S	u	.	.	.	.	.	.	.	.	.	.	50.0
Toluene$_{RCRF}$	IDA1Synt	.	S	S	S	S	Q	S	S	S	S	S	S	S	.	.	.	.	.	.	.	.	.	.	91.7
TVOC$_{Lab}$	IDA3TVOC	.	S	S	S	u	Q	S	S	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
TVOC$_{Lab}$-Chamber blank	IDA3TVOC	.	S	S	S	u	Q	S	S	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
TXIB$_{RCRF}$	IDA1Synt	.	.	S	U	S	S	S	S	*S*	S	S	S	U	.	.	.	.	.	.	.	.	.	.	81.8
TXIB$_{TE}$	IDA1Synt	.	Q	S	S	S	q	u	S	*S*	Q	S	S	S	.	.	.	.	.	.	.	.	.	.	66.7
%			75	95	56	75	20	60	85	100	46	82	82	46										
accredited			12	20	16	20	20	16	14		13	17	17	13										

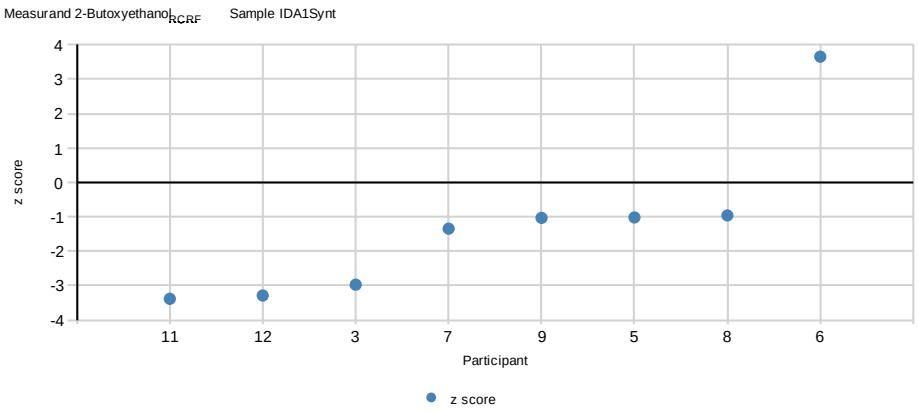
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited,
% - percentage of satisfactory results

Totally satisfactory, % in all: 70 % in accredited: 66 % in non-accredited: 90

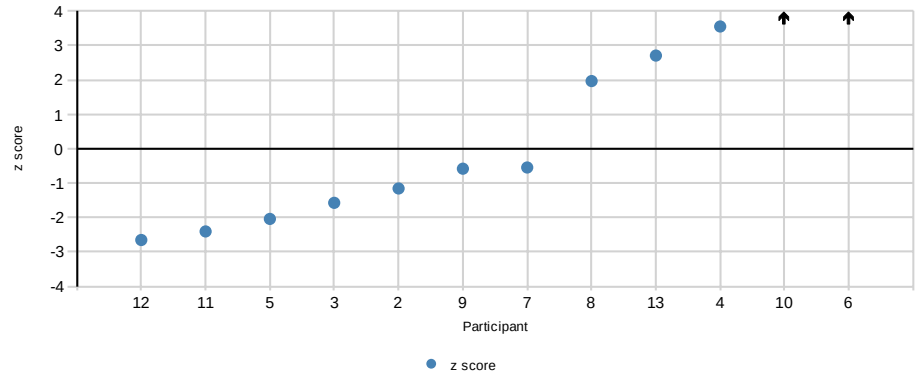
APPENDIX 10: z scores in ascending order



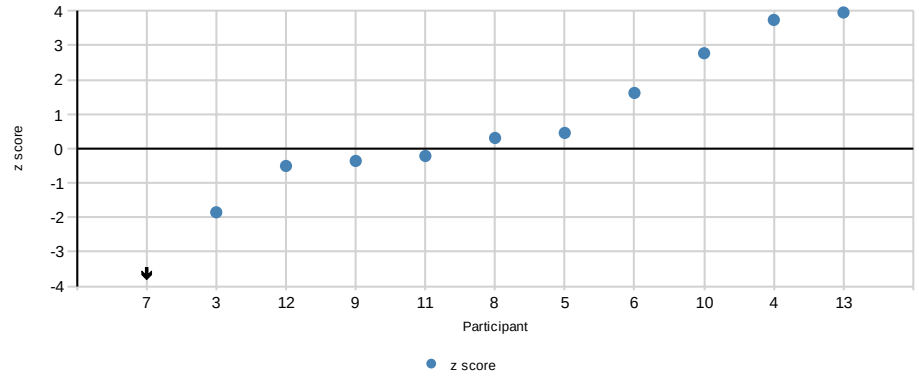




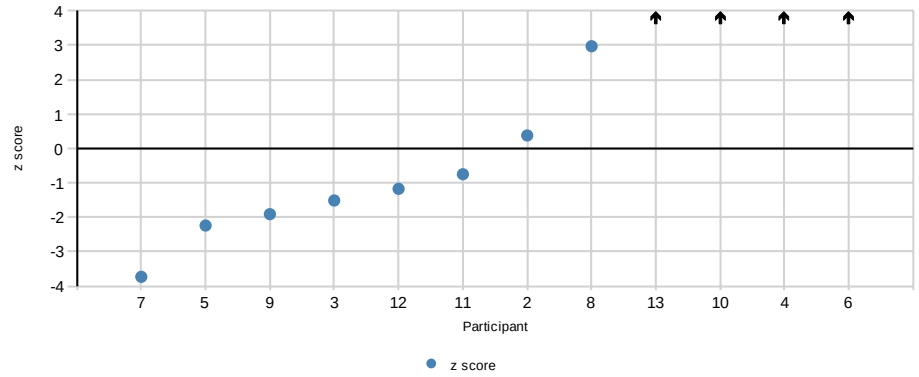
Measurand 2-Butoxyethanol$_{TE}$ Sample IDA1Synt

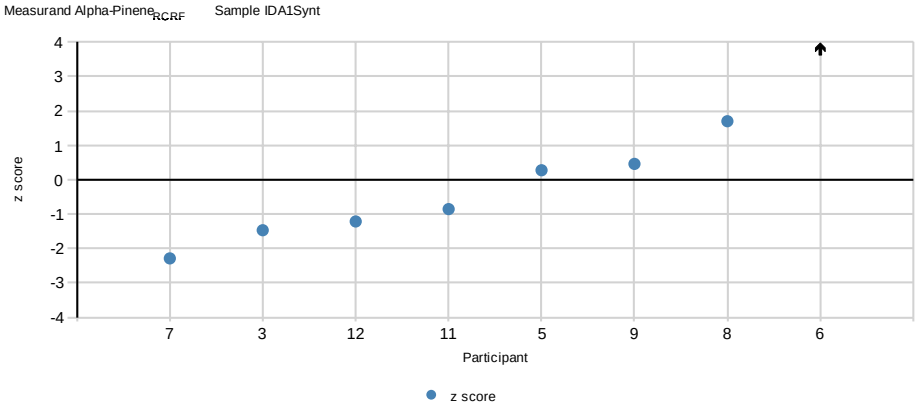


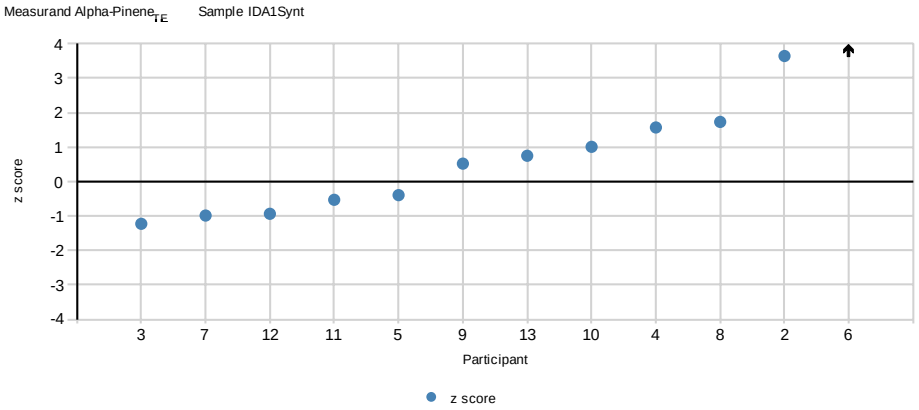
Measurand 2EH$_{RCRF}$ Sample IDA1Synt

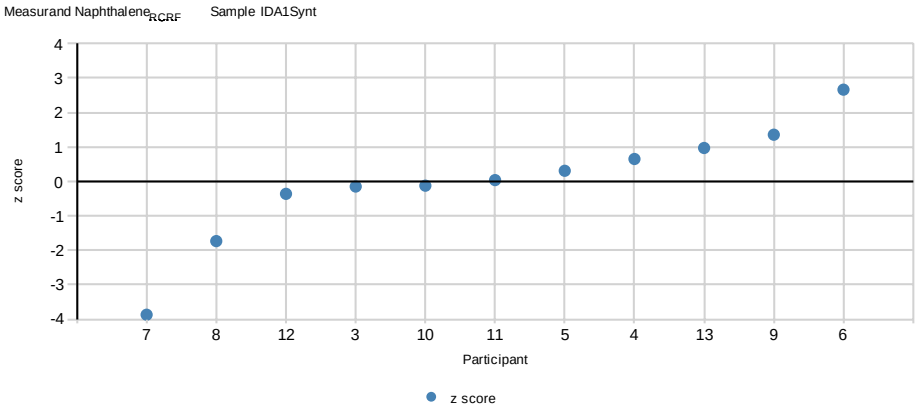


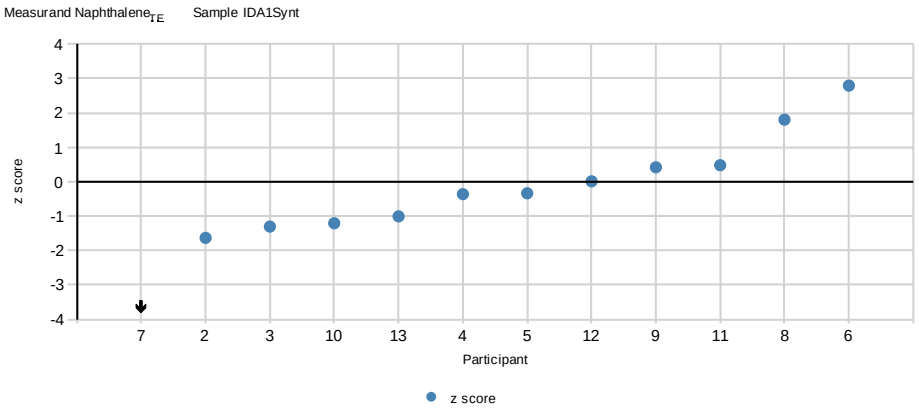
Measurand 2EH$_{TE}$ Sample IDA1Synt

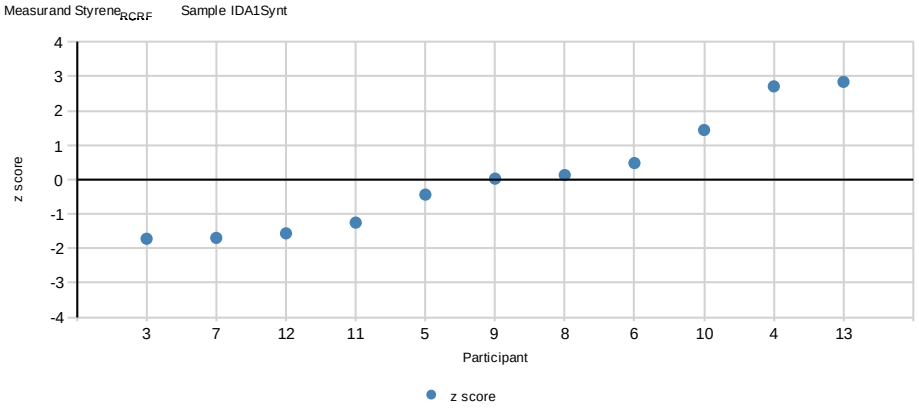


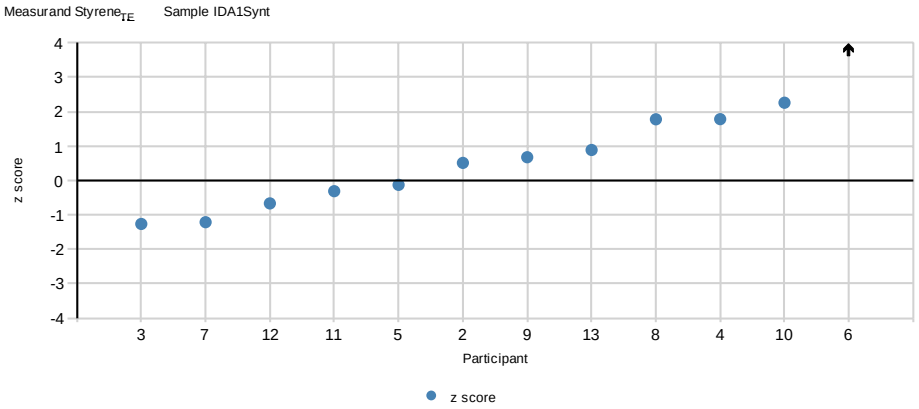

Measurand Alpha-Pinene RCRF
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
7
3
12
11
5
9
8
6
Participant
z score

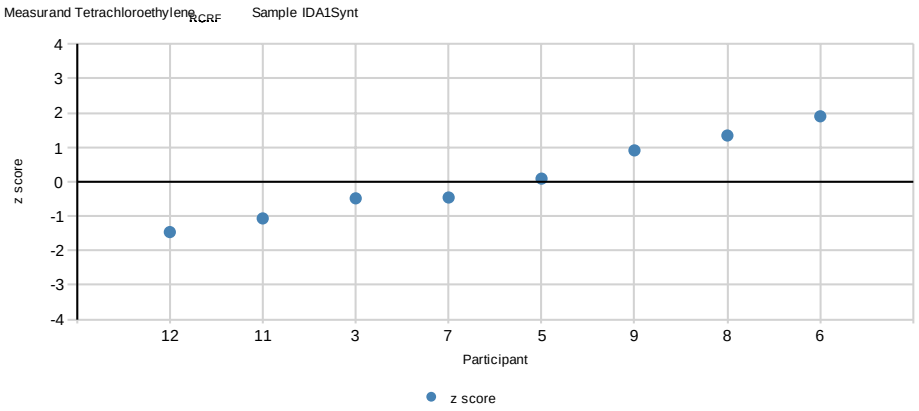

Measurand Alpha-Pinene TE
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
3
7
12
11
5
9
13
10
4
8
2
6
Participant
z score

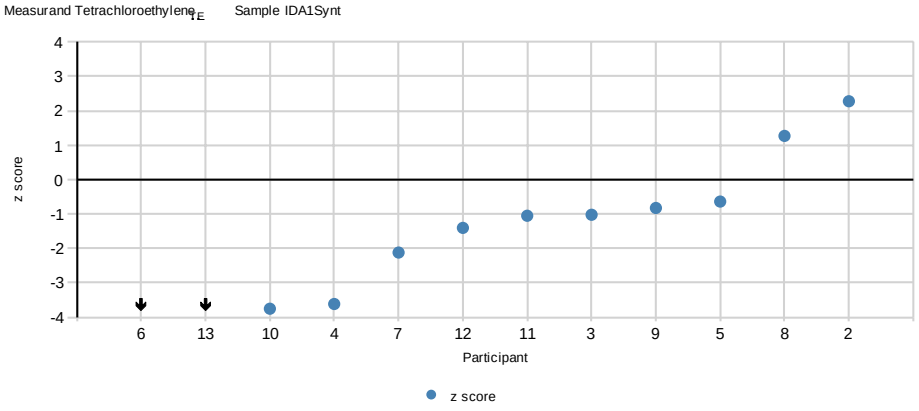

Measurand Naphthalene RCRF
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
7
8
12
3
10
11
5
4
13
9
6
Participant
z score

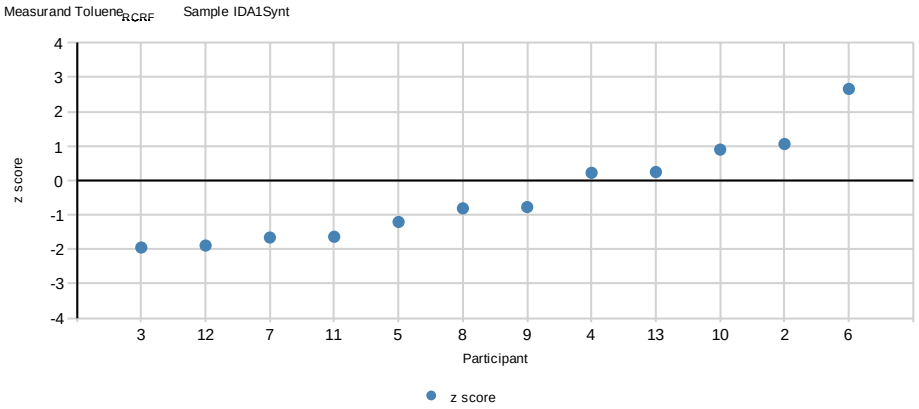

Measurand Naphthalene$_{TE}$ Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
7 2 3 10 13 4 5 12 9 11 8 6
Participant
z score


Measurand Styrene$_{RCRF}$ Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
3 7 12 11 5 9 8 6 10 4 13
Participant
z score

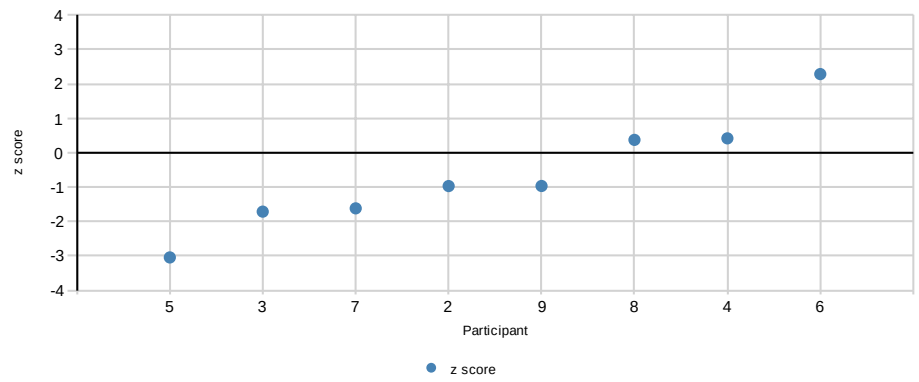

Measurand Styrene$_{TE}$ Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
3 7 12 11 5 2 9 13 8 4 10 6
Participant
z score


Measurand Tetrachloroethylene RCRF
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
12
11
3
7
5
9
8
6
Participant
z score

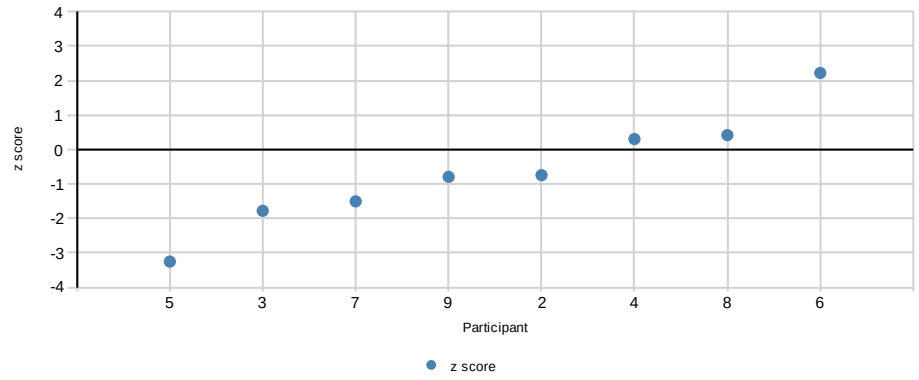

Measurand Tetrachloroethylene TE
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
6
13
10
4
7
12
11
3
9
5
8
2
Participant
z score


Measurand Toluene RCRF
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
3
12
7
11
5
8
9
4
13
10
2
6
Participant
z score

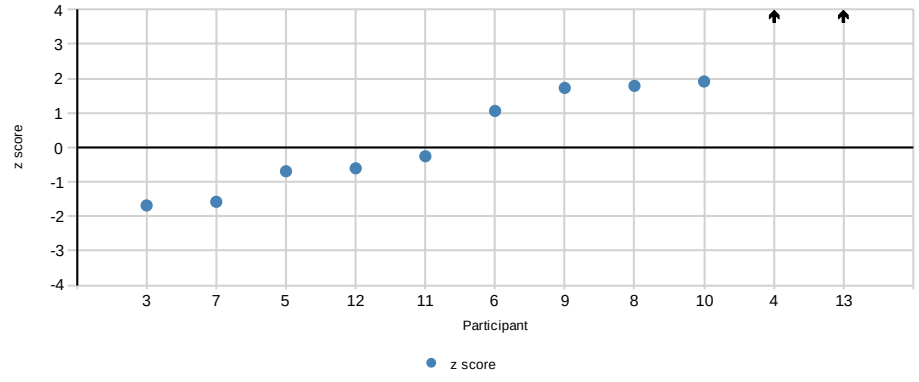
Measurand $TVOC_{Lab}$ Sample IDA3TVOC

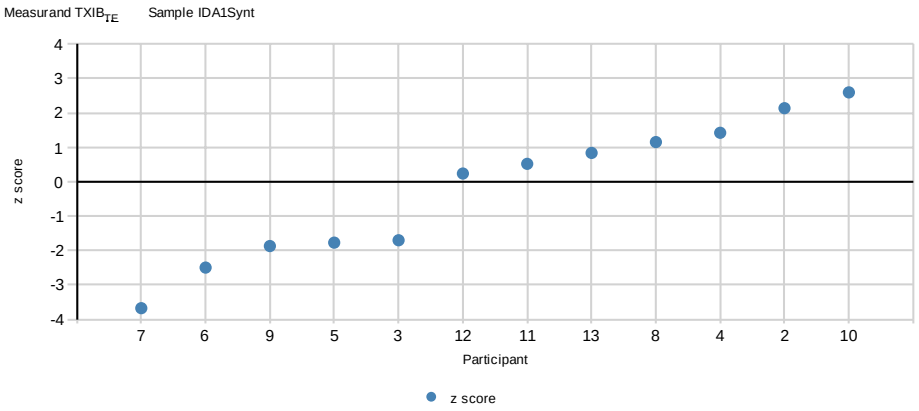


Measurand $TVOC_{Lab}$- Chamber blank Sample IDA3TVOC



Measurand $TXIB_{RCRF}$ Sample IDA1Synt




Measurand TXIB$_{TE}$
Sample IDA1Synt
z score
4
3
2
1
0
-1
-2
-3
-4
7
6
9
5
3
12
11
13
8
4
2
10
Participant
z score

APPENDIX 11: Analytical methods and recognized compounds

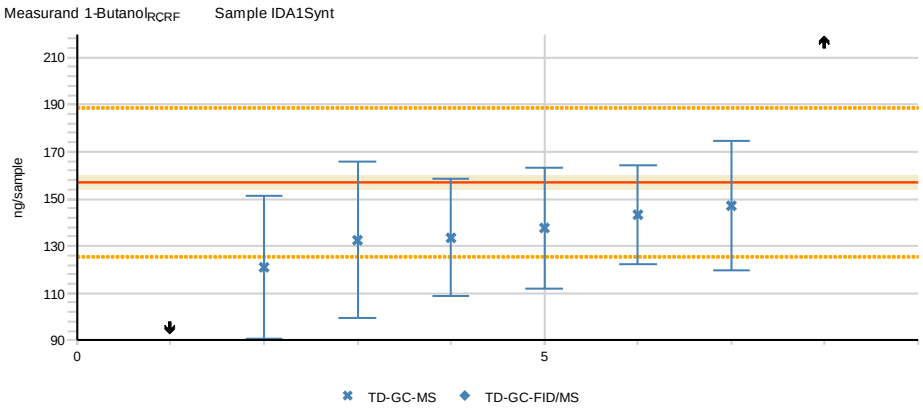
Participant/Question	2	3	4	5	6	7	8	9
What kind of thermodesorption system/instrument was used?	TD-GC-MS -Markes TD100 -GC Agilent 7890A -MS Agilent 5975C	Markes TD-100	Shimadzu TD-GC-MS	TD-100 (Markes) 7890B (Agilent) 5977A (Agilent)	Markes TD 100, Agilent GC 7890B, Agilent 5977A MSD	Perkin Elmer Turbomatrix 650	Markes TD	STD DANI, model TD MASTER
What desorption temperature was used, in (°C)?	280	280	280	320	300	300	270	260ºC
What desorption flow was the used, in ml/min?	50	50	50	50	20	50	30	34 ml/min
How long was desorption time, in minutes?	5	10	5	8	8	15	10	10 min
What was the temperature of the cryo cold trap and the heating temperature, in °C ?	0 and 300	-20 300	-20, +280	15 and 320	-10 / 310	-30 300	-10, 300	-35ºC and 300ºC
What was flow rate of carrier gas, in ml/min?	1	1	0.8	1 ml/min in column and 30 ml/min in split	2	1,2	2	0.44 ml/min
Which type of analytical column was used?	HP5MS	HP-5MS	ZB-5MSplus, 60x0,25x0,25	HP5-MS (50 m x 0,2 mm x 0,33 m)	HP5-MSUI, 30x0,25x0,25	DB-1701	HP-5MS	HP-5MS 50m x 200 um x 0.33 um
What kind of detector(s) was used?	MSD	MSD	single quadrupole MS	Agilent inert mass selective detector	MSD and FID	MSD	MSD	MSD
Did your results include the recovery rate?	no	no		no	No	No	No	yes
Do you have suggestions for substances for the next intercomparison?			Mixture of oil compounds with narrow boiling point area or different C8-C10 alcohols, difficult to observe with MS					1,2,4-trimethylbenzene, limonene, ethylbenzene, benzene

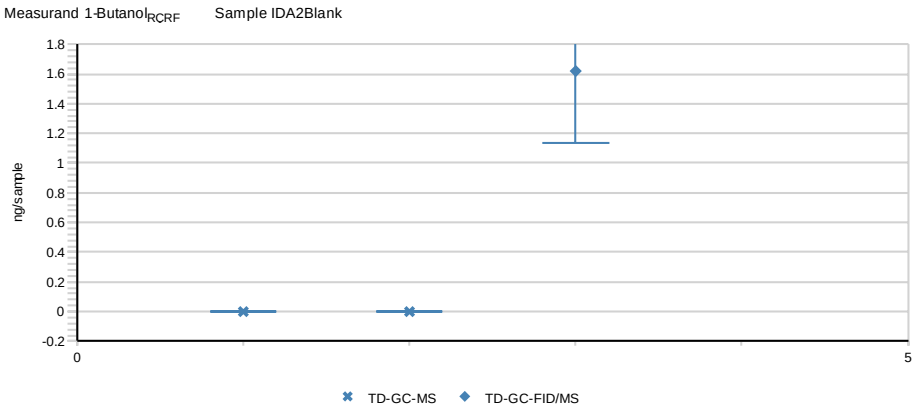
Participant/Question	2	3	4	5	6	7	8	9
Which VOC compounds were recognized from the chamber samples? Report compounds founded> 5 µg/m3 as toluene equivalent. Please, select below (1/7).		**2-Bornanone, 464-49-3, Borneol, 464-45-9, 2-(2-Butoxyethoxy)ethanol, 112-34-5**	**2-(2-Butoxyethoxy)ethanol, 112-34-5**, 1-Butanol, 71-36-3, **Borneol, 464-45-9**	**2-Bornanone, 464-49-3, 2-(2-Butoxyethoxy)ethanol, 112-34-5**	Acetic acid glacial, 64-19-7, 2-Bornanone, 464-49-3, **Borneol, 464-45-9**, 1-Butanol, 71-36-3	1-Butanol, 71-36-3, **2-(2-Butoxyethoxy)ethanol, 112-34-5**	**2-(2-Butoxyethoxy)ethanol, 112-34-5**, 1-Butanol, 71-36-3, **Borneol, 464-45-9**, Acetic acid glacial, 64-19-7	**Borneol, 464-45-9**
Which one VOC compounds were recognized from the chamber samples? Report compounds founded>5 µg/m3 as toluene equivalent. Please, select below (2/7).	**Camphor, 76-22-2**, 3-Carene, 13466-78-9, **1,8-Cineole, 470-82-6**, Decanal, 112-31-2	**Camphor, 76-22-2, 1,8-Cineole, 470-82-6**	Decanal, 112-31-2, **Camphor, 76-22-2**		**Camphor, 76-22-2**	**Camphor, 76-22-**2	**1,8-Cineole, 470-82-6, Camphor, 76-22-2**	**Camphor, 76-22-2**
Which one VOC compounds were recognized from the chamber samples? Report compounds founded> 5 µg/m3 as toluene equivalent. Please, select below (3/7).		**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**	**Fenchyl alcohol, 1632-73-1, 2-Ethyl-1-hexanol, 104-76-7**	**2-Ethyl-1-hexanol, 104-76-7, Fenchyl alcohol, 1632-73-1**
Which one VOC compounds were recognized from the chamber samples? Report compounds founded> 5 µg/m3 as toluene equivalent. Please, select below (4/7).	**Limonene, 5989-27-5**	**Limonene, 5989-27-5, 1-Methyl-4-isopropylbenzene, 99-87-6, 1-Methyl-4-isopropyleneben zene, 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**	**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**	**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**
Which one VOC compounds were recognized from chamber the samples? Report compounds founded> 5 µg/m3 as toluene equivalent. Please, select below (5/7).	alpha-Pinene, 80-56-8, beta-Pinene, 127-91-3, **alpha-terpineol, 98-55-5**	**alpha-terpineol, 98-55-5**	**alpha-terpineol, 98-55-5**			**alpha-terpineol, 98-55-5**	**alpha-terpineol, 98-55-5**	**alpha-terpineol, 98-55-5**

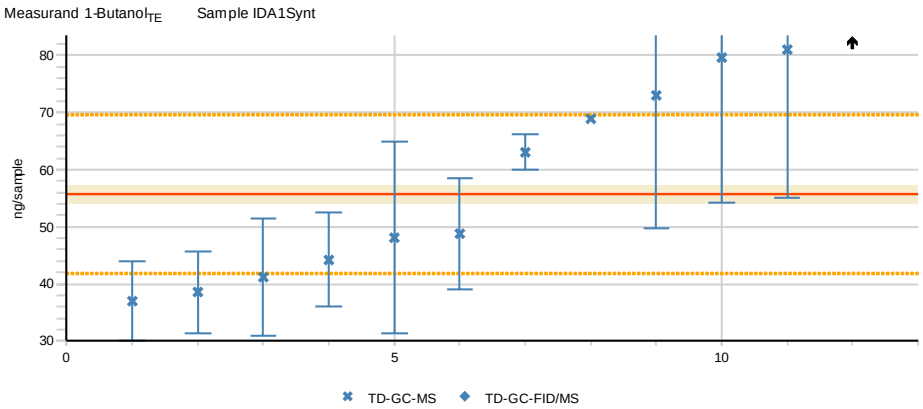
Participant/Question	2	3	4	5	6	7	8	9
Which one VOC compounds were recognized from the chamber samples? Report compounds founded> 5 µg/m3 as toluene equivalent. Please, select below (6/7).	**4-terpineol, 562-74-3, alpha-Terpinolene, 586-62-9**, Toluene, 108-88-3	**4-terpineol, 562-74-3, alpha-Terpinolene, 586-62-9**	**4-terpineol, 562-74-3**	**alpha-Terpinolene, 586-62-9**	**4-terpineol, 562-74-3**	**alpha-Terpinolene, 586-62-9**	**4-terpineol, 562-74-3, alpha-Terpinolene, 586-62-9**	**alpha-Terpinolene, 586-62-9, 4-terpineol, 562-74-3**
Which one VOC compounds were recognized from the chamber samples? Report compounds founded> 5 µg/m3 as toluene equivalent.Please, select below (7/7).	p-Xylene, 106-42-3							
Number of recognized results by the exert laboratory	5	13	9	8	5	9	12	9

APPENDIX 12: Results grouped according to the methods

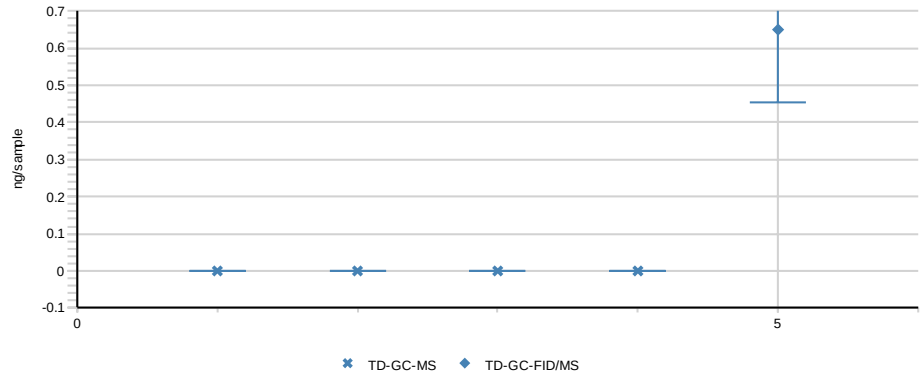
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



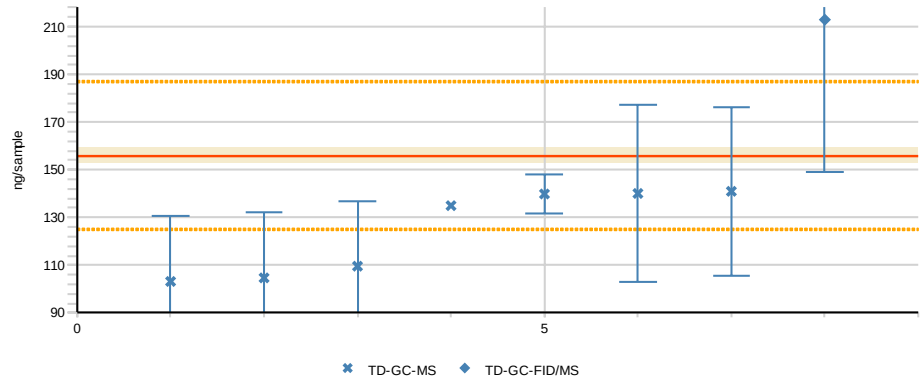




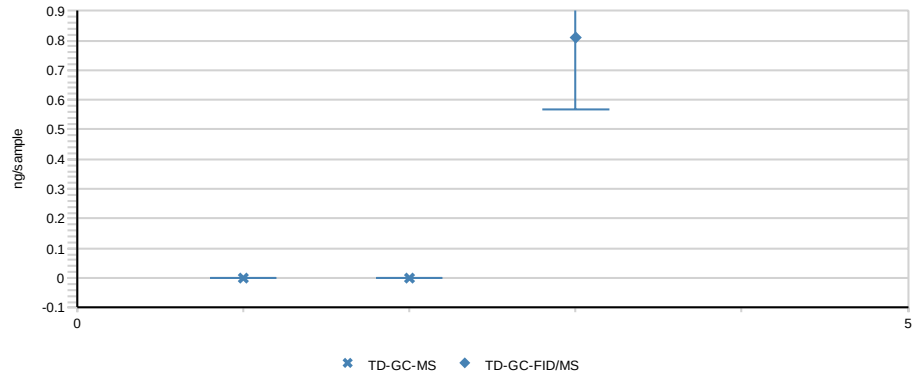
Measurand 1-Butanol$_{TE}$ Sample IDA2Blank

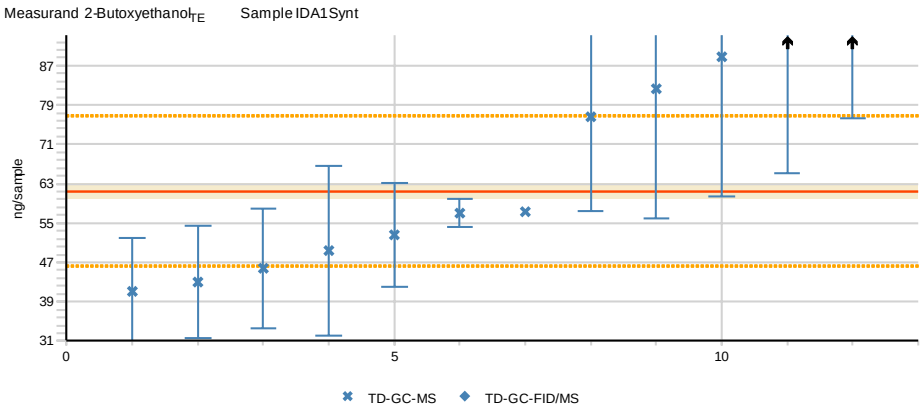


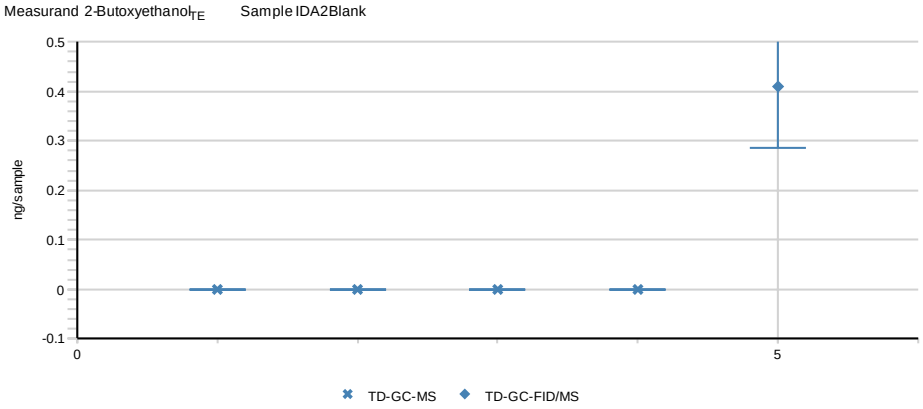
Measurand 2-Butoxyethanol$_{RCRF}$ Sample IDA1Synt

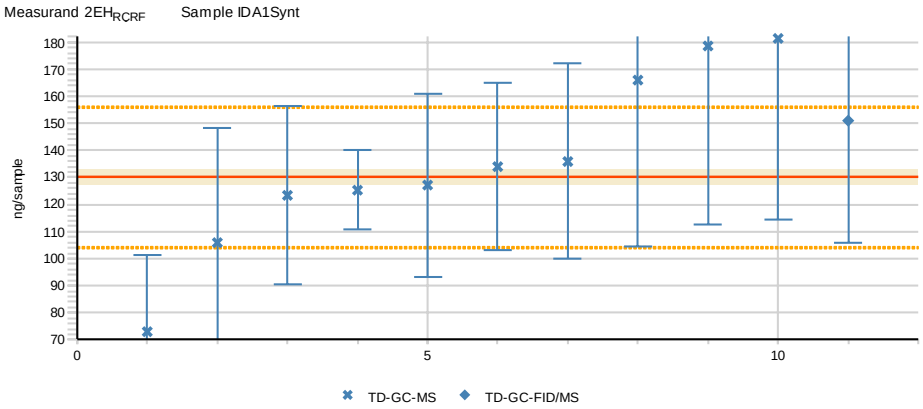


Measurand 2-Butoxyethanol$_{RCRF}$ Sample IDA2Blank

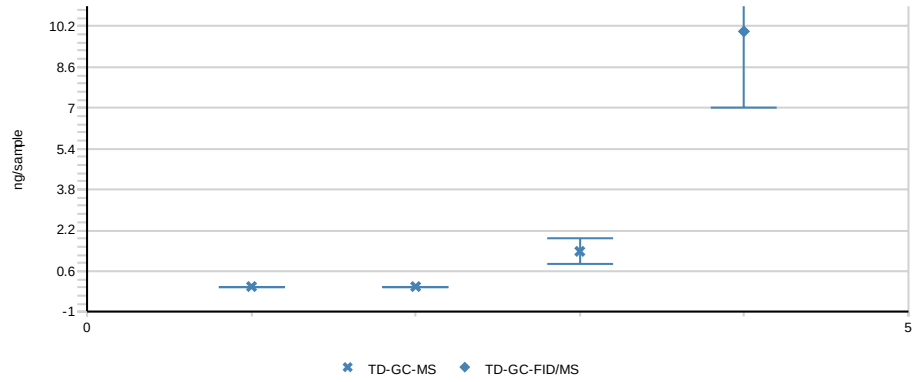



Measurand 2-Butoxyethanol$_{TE}$
Sample IDA1Synt
ng/sample
87
79
71
63
55
47
39
31
0
5
10
TD-GC-MS
TD-GC-FID/MS

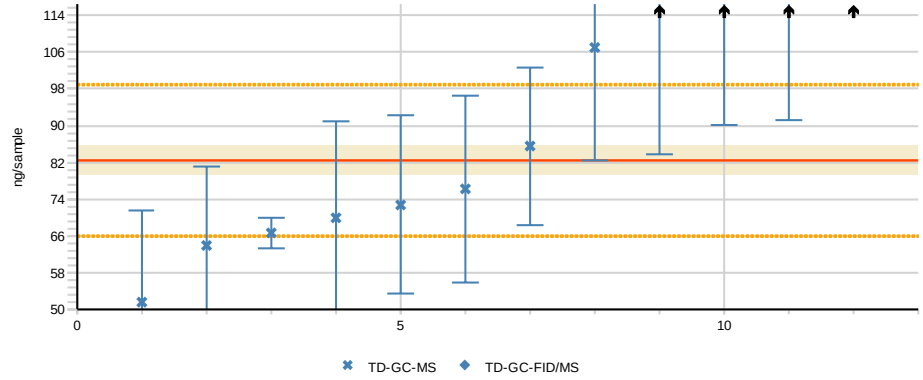

Measurand 2-Butoxyethanol$_{TE}$
Sample IDA2Blank
ng/sample
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand 2EH$_{RCRF}$
Sample IDA1Synt
ng/sample
180
170
160
150
140
130
120
110
100
90
80
70
0
5
10
TD-GC-MS
TD-GC-FID/MS

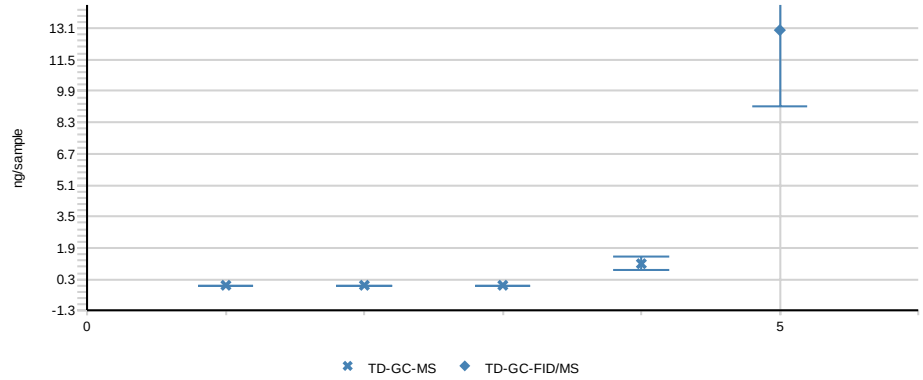
Measurand $2EH_{RCRF}$ Sample IDA2Blank

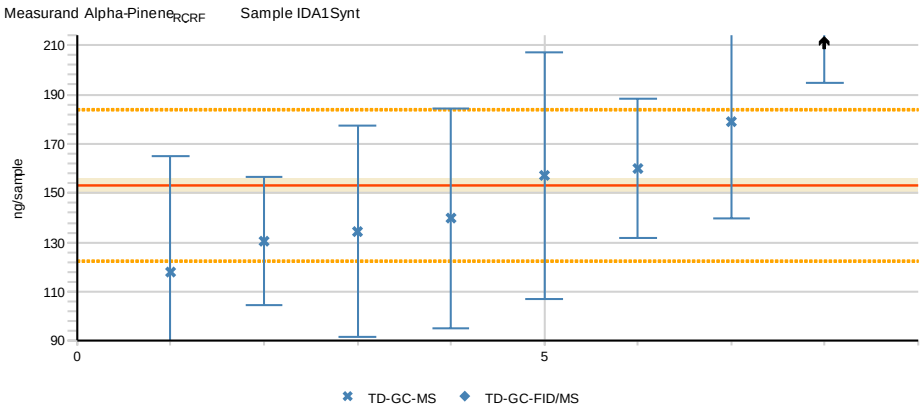


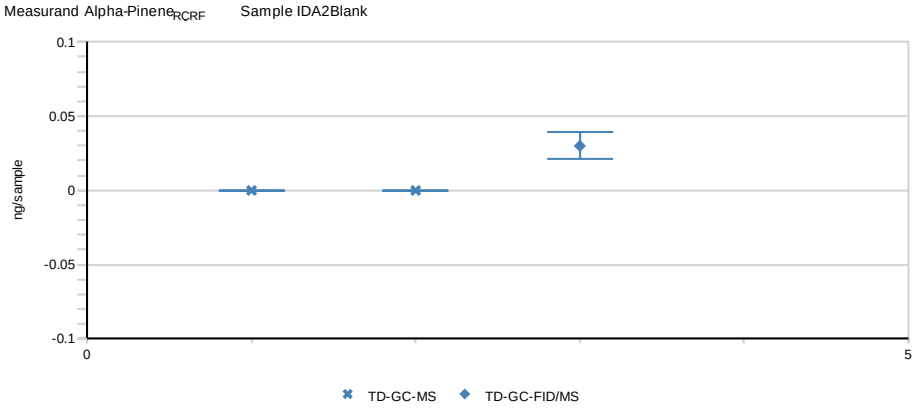
Measurand $2EH_{TE}$ Sample IDA1Synt

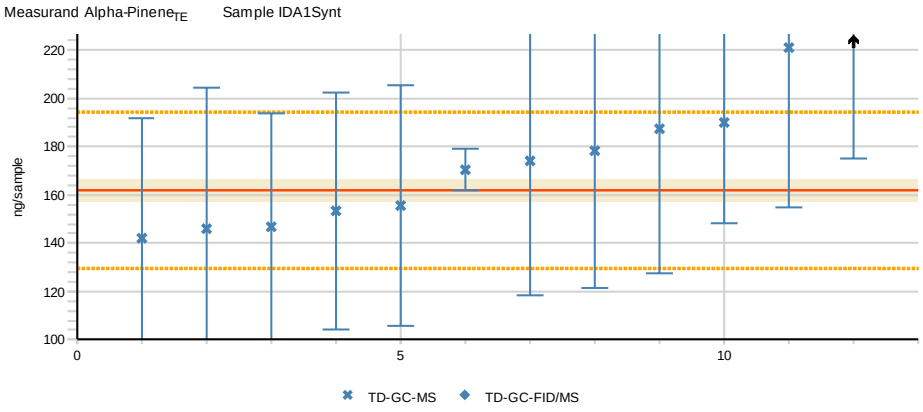


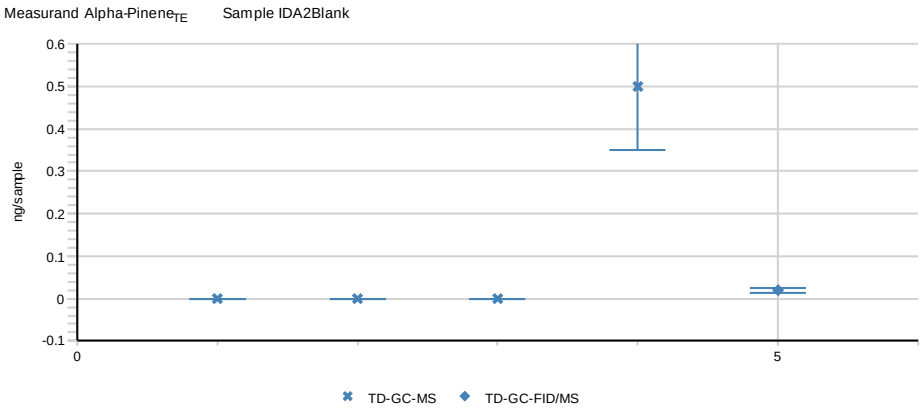
Measurand $2EH_{TE}$ Sample IDA2Blank

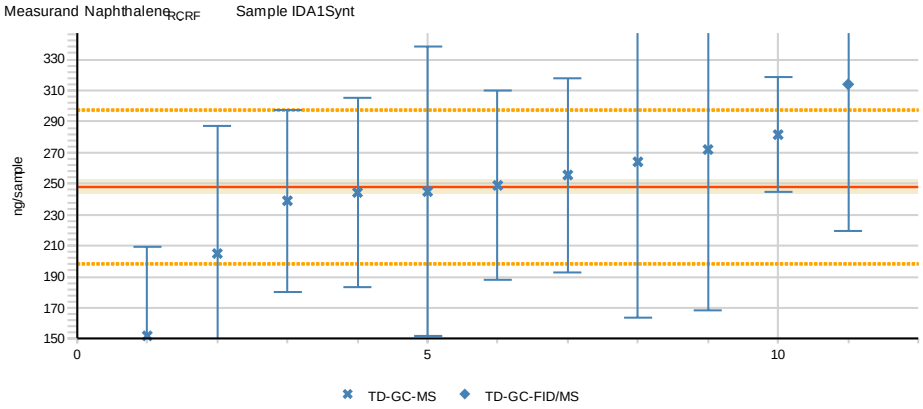


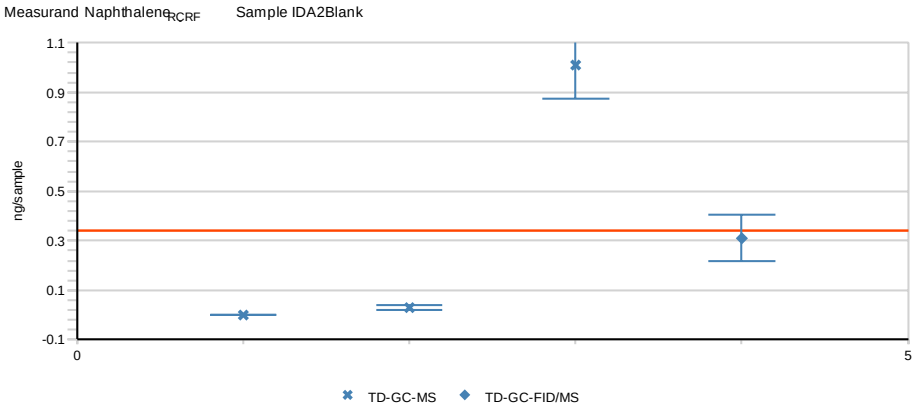

Measurand Alpha-Pinene RCRF
Sample IDA1Synt
ng/sample
210
190
170
150
130
110
90
0
5
TD-GC-MS
TD-GC-FID/MS

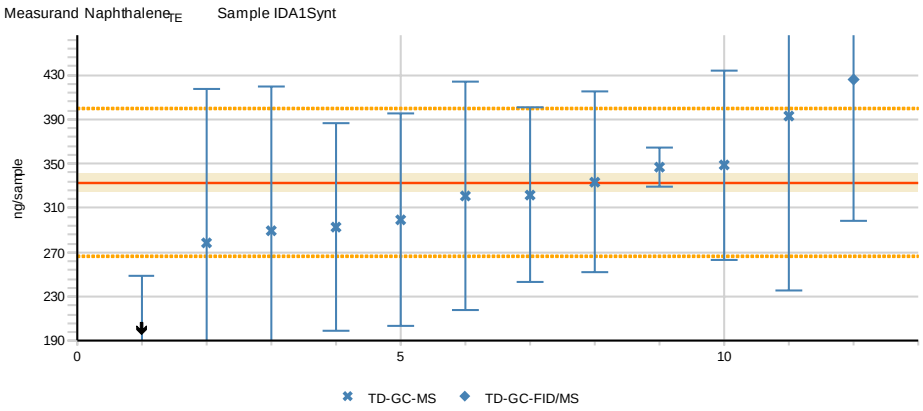

Measurand Alpha-Pinene RCRF
Sample IDA2Blank
ng/sample
0.1
0.05
0
-0.05
-0.1
0
5
TD-GC-MS
TD-GC-FID/MS

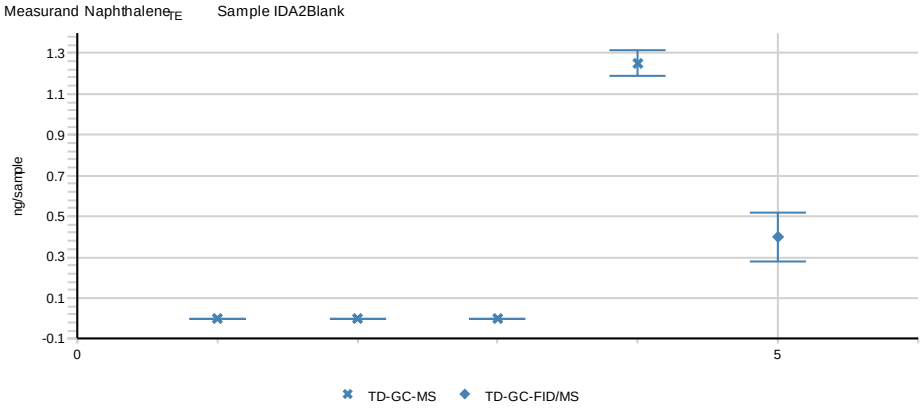

Measurand Alpha-Pinene TE
Sample IDA1Synt
ng/sample
220
200
180
160
140
120
100
0
5
10
TD-GC-MS
TD-GC-FID/MS

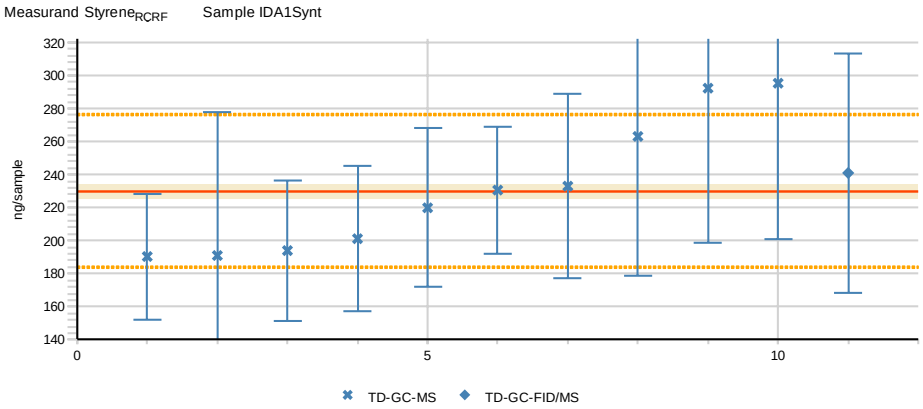

Measurand Alpha-Pinene_TE
Sample IDA2Blank
ng/sample
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Naphthalene_RCRF
Sample IDA1Synt
ng/sample
330
310
290
270
250
230
210
190
170
150
0
5
10
TD-GC-MS
TD-GC-FID/MS

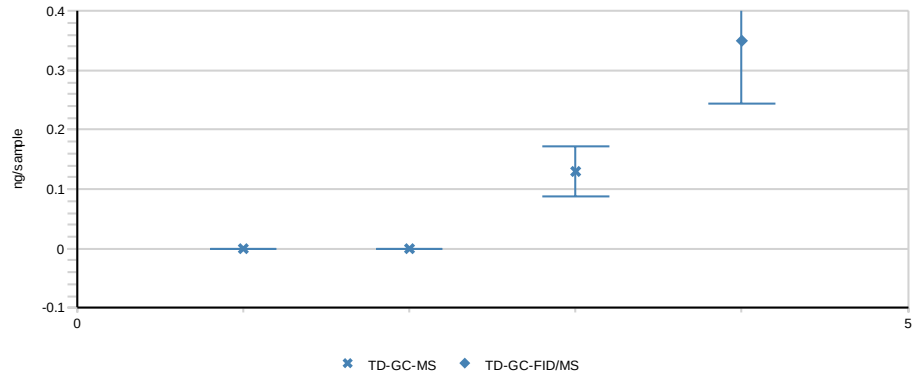

Measurand Naphthalene_RCRF
Sample IDA2Blank
ng/sample
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Naphthalene_TE
Sample IDA1Synt
ng/sample
430
390
350
310
270
230
190
0
5
10
TD-GC-MS
TD-GC-FID/MS

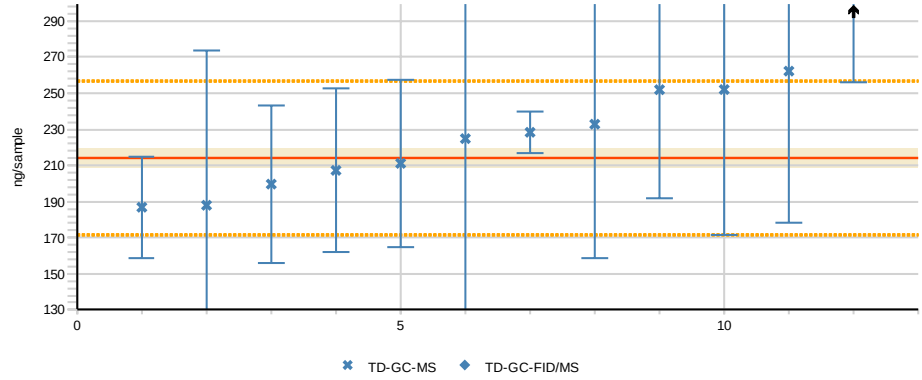

Measurand Naphthalene_TE
Sample IDA2Blank
ng/sample
1.3
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Styrene_RCRF
Sample IDA1Synt
ng/sample
320
300
280
260
240
220
200
180
160
140
0
5
10
TD-GC-MS
TD-GC-FID/MS

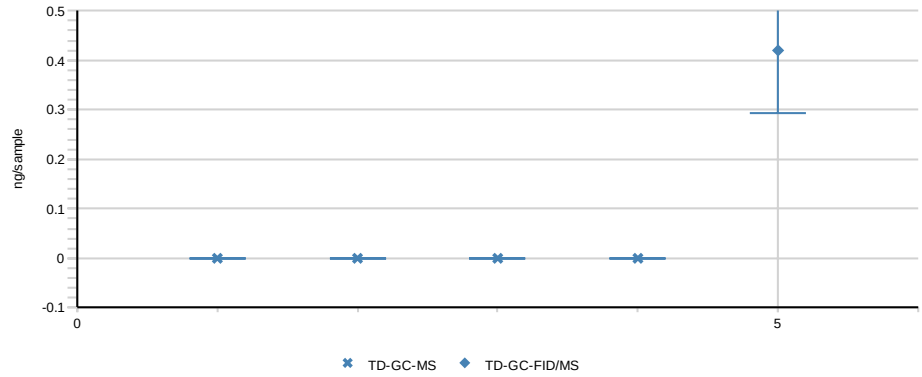
Measurand $Styrene_{RCRF}$ Sample IDA2Blank

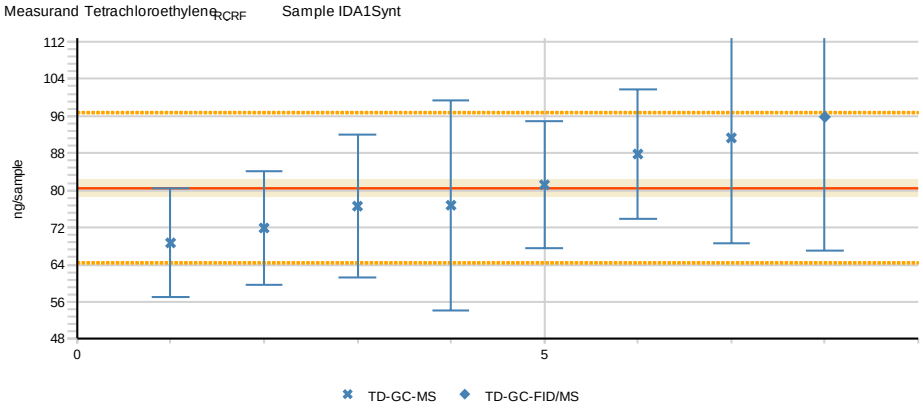


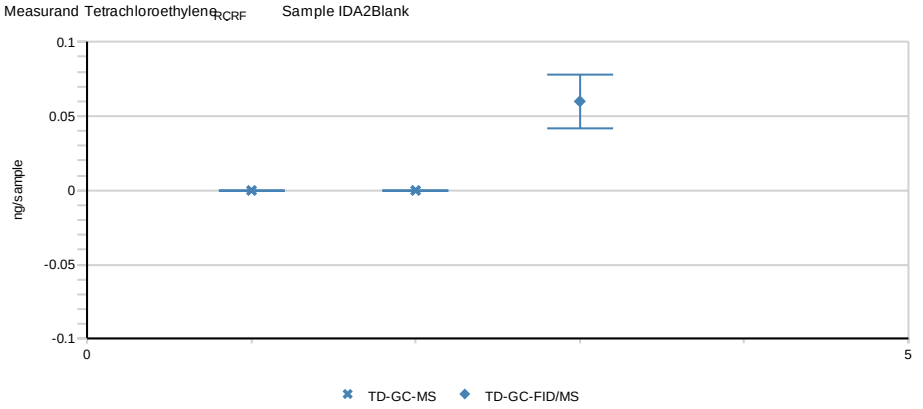
Measurand $Styrene_{TE}$ Sample IDA1Synt

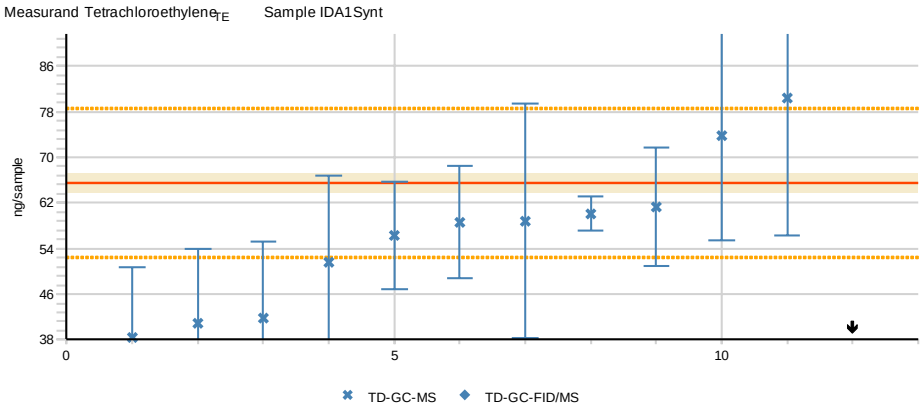


Measurand $Styrene_{TE}$ Sample IDA2Blank

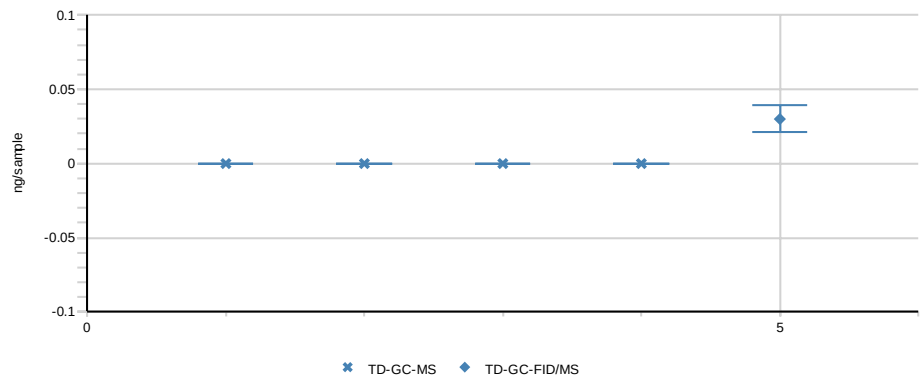



Measurand Tetrachloroethylene RCRF
Sample IDA1Synt
ng/sample
112
104
96
88
80
72
64
56
48
0
5
TD-GC-MS
TD-GC-FID/MS

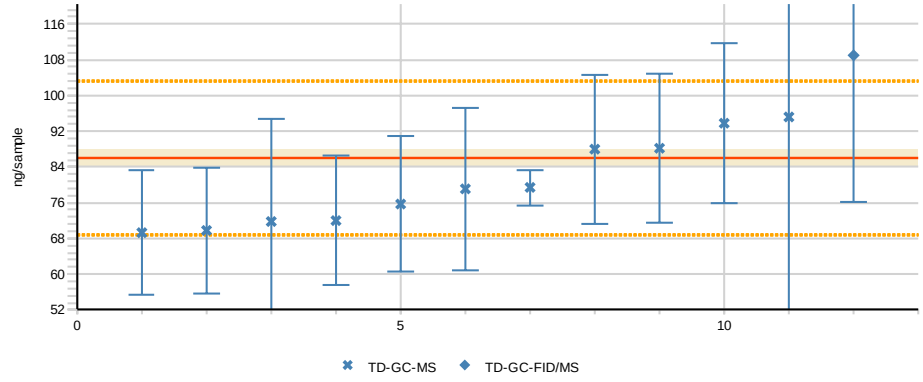

Measurand Tetrachloroethylene RCRF
Sample IDA2Blank
ng/sample
0.1
0.05
0
-0.05
-0.1
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Tetrachloroethylene TE
Sample IDA1Synt
ng/sample
86
78
70
62
54
46
38
0
5
10
TD-GC-MS
TD-GC-FID/MS

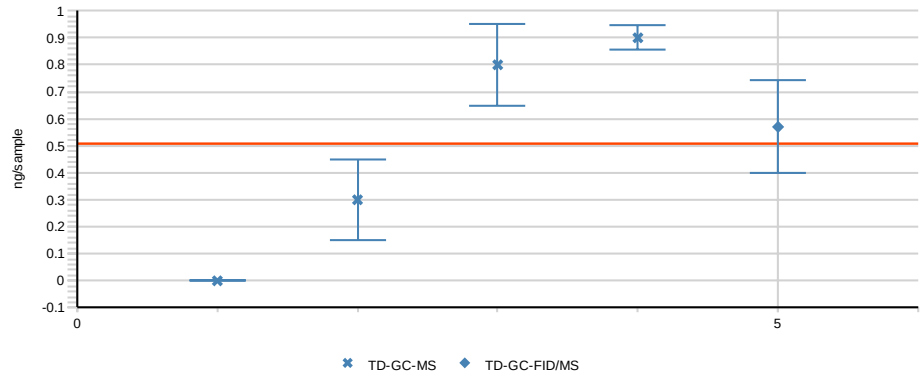
Measurand Tetrachloroethylene$_{TE}$ Sample IDA2Blank

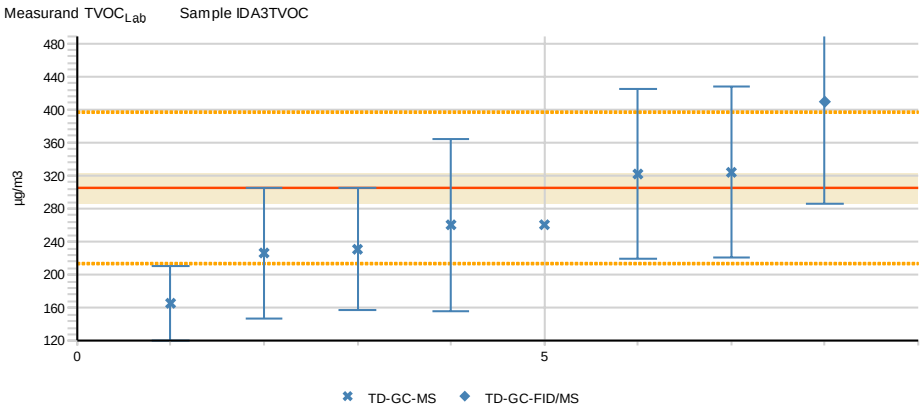


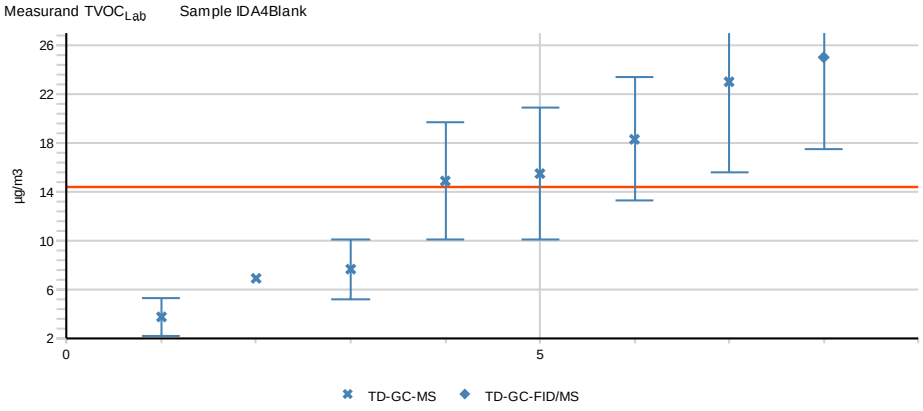
Measurand Toluene$_{RCRF}$ Sample IDA1Synt

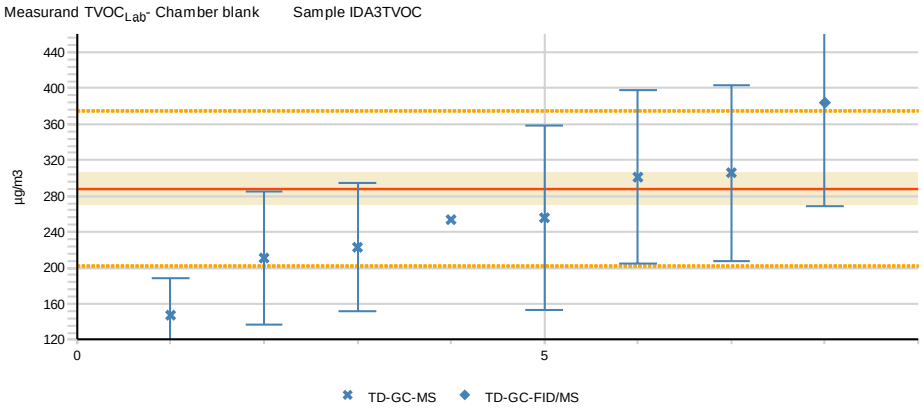


Measurand Toluene$_{RCRF}$ Sample IDA2Blank

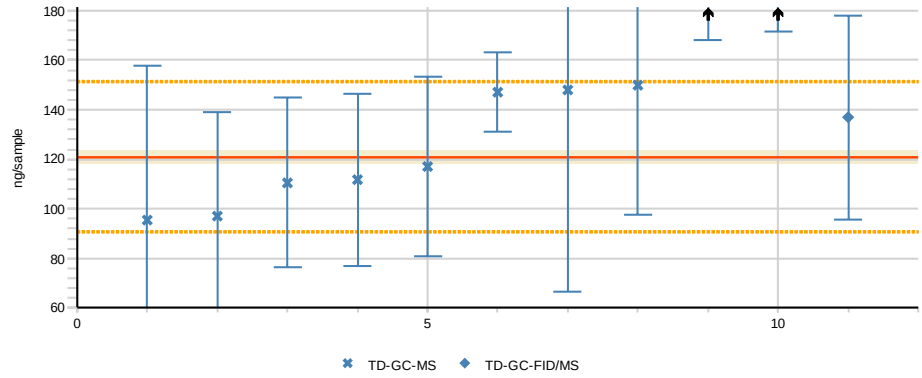



Measurand TVOC$_{Lab}$
Sample IDA3TVOC
µg/m3
480
440
400
360
320
280
240
200
160
120
0
5
TD-GC-MS
TD-GC-FID/MS

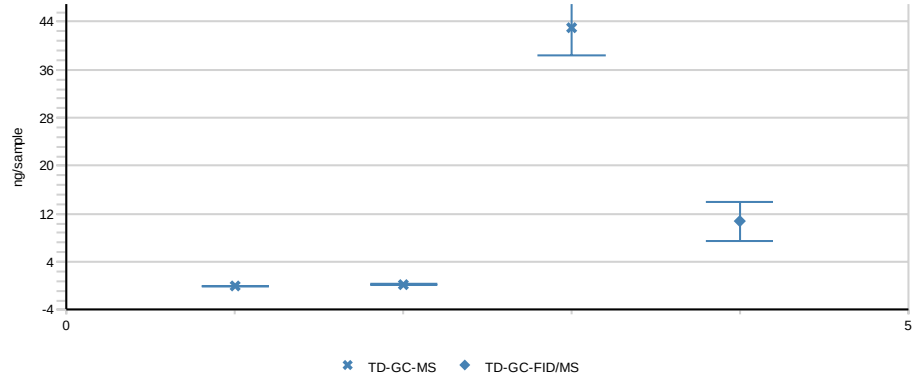

Measurand TVOC$_{Lab}$
Sample IDA4Blank
µg/m3
26
22
18
14
10
6
2
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand TVOC$_{Lab}$- Chamber blank
Sample IDA3TVOC
µg/m3
440
400
360
320
280
240
200
160
120
0
5
TD-GC-MS
TD-GC-FID/MS

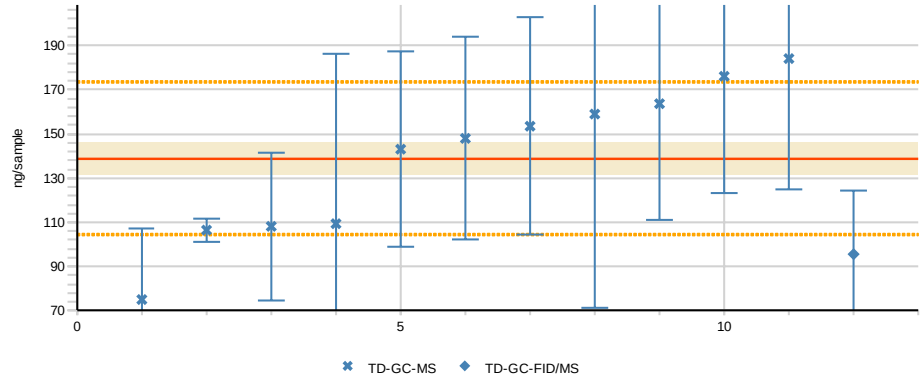
Measurand $TXIB_{RCRF}$ Sample IDA1Synt

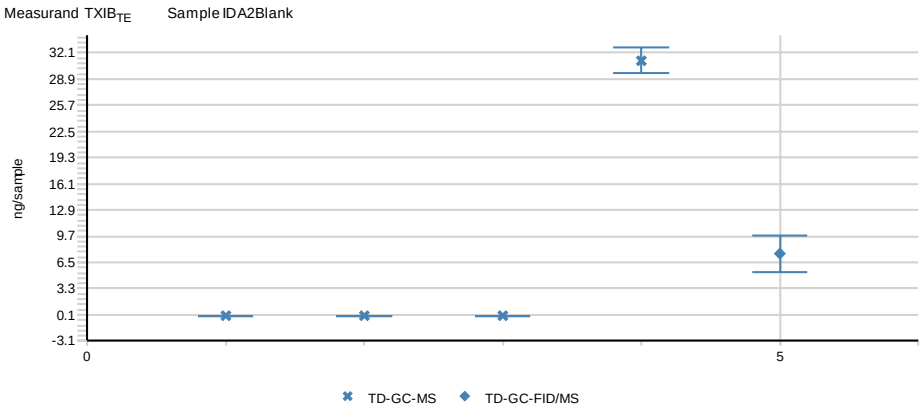


Measurand $TXIB_{RCRF}$ Sample IDA2Blank



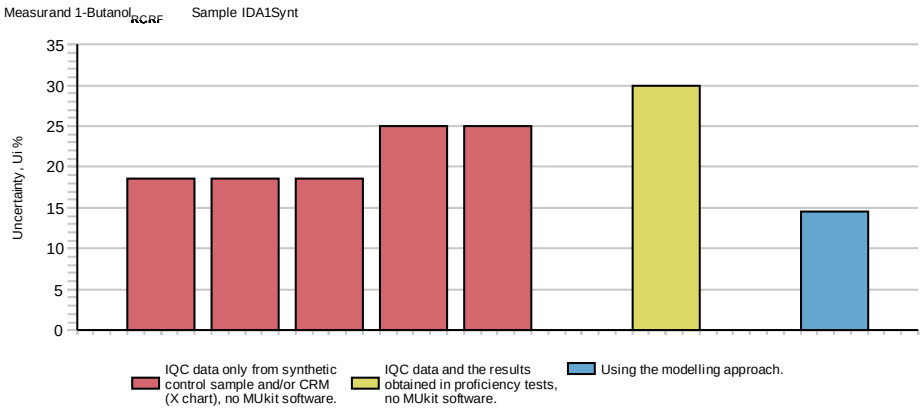
Measurand $TXIB_{TE}$ Sample IDA1Synt

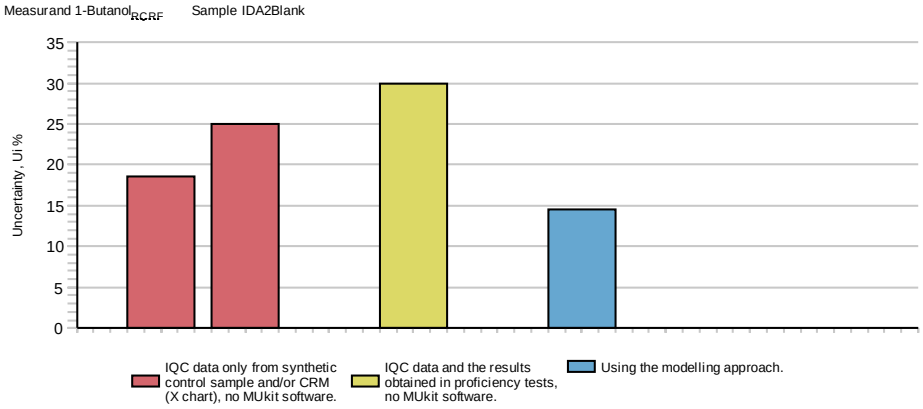


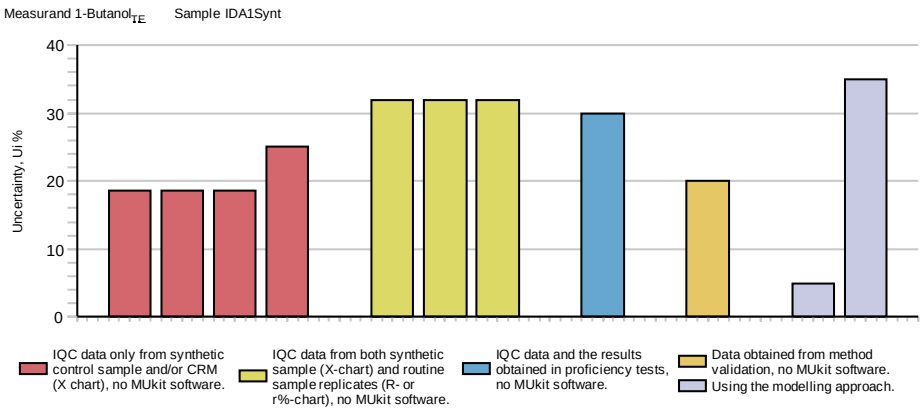

Measurand TXIB$_{TE}$
Sample IDA2Blank
32.1
28.9
25.7
22.5
19.3
16.1
12.9
9.7
6.5
3.3
0.1
-3.1
ng/sample
0
5
TD-GC-MS
TD-GC-FID/MS

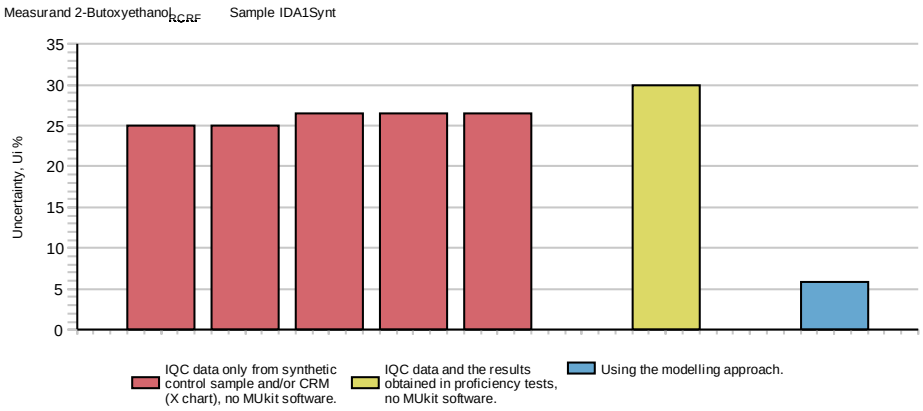
APPENDIX 13: Examples of measurement uncertainties reported by the participants

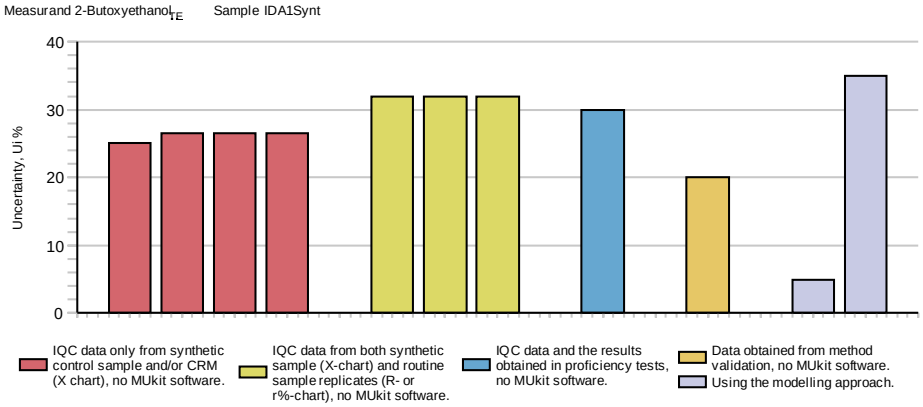
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [8, 9] or using a modelling approach based [10, 11].

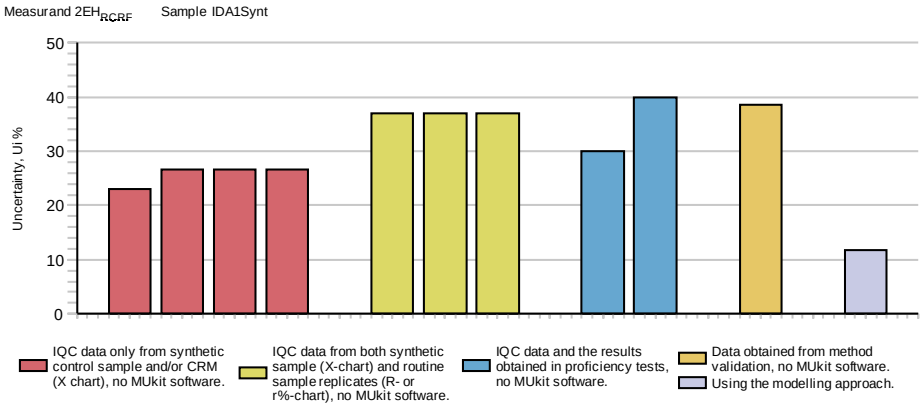




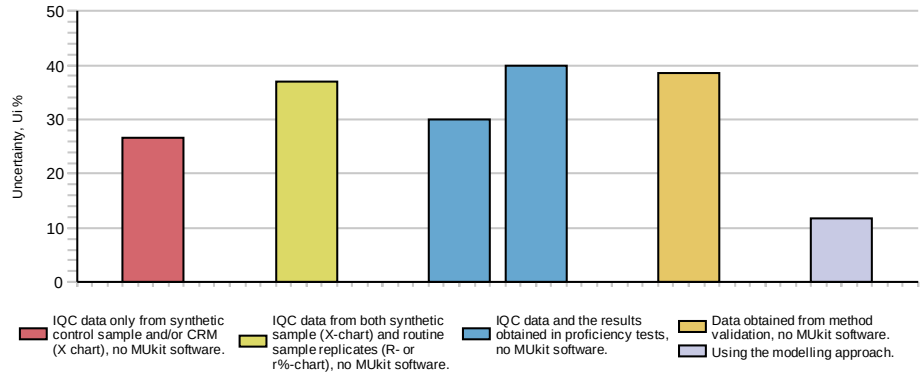



Measurand 2-Butoxyethanol$_{RCRF}$ Sample IDA1Synt
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Using the modelling approach.

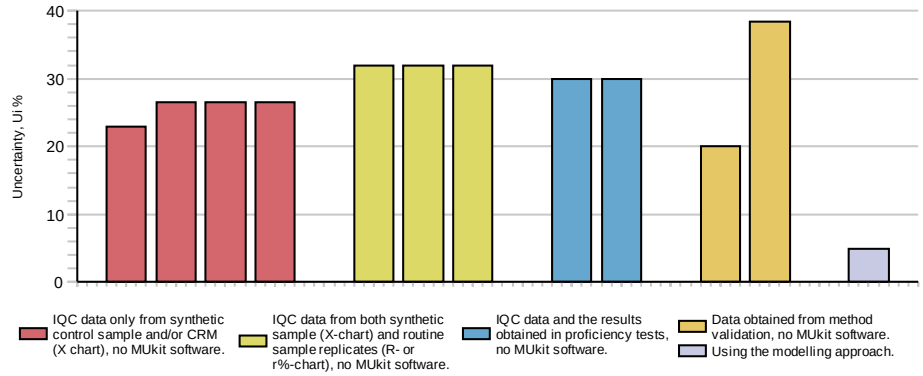

Measurand 2-Butoxyethanol$_{TE}$ Sample IDA1Synt
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand 2EH$_{RCRF}$ Sample IDA1Synt
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

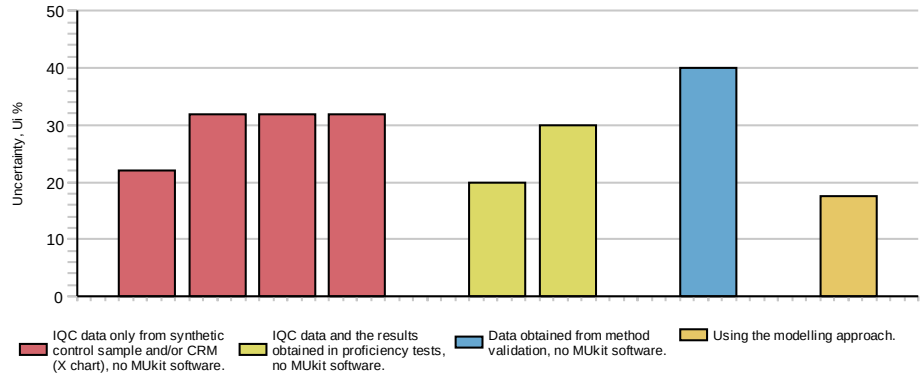
Measurand 2EH$_{RCRF}$ Sample IDA2Blank

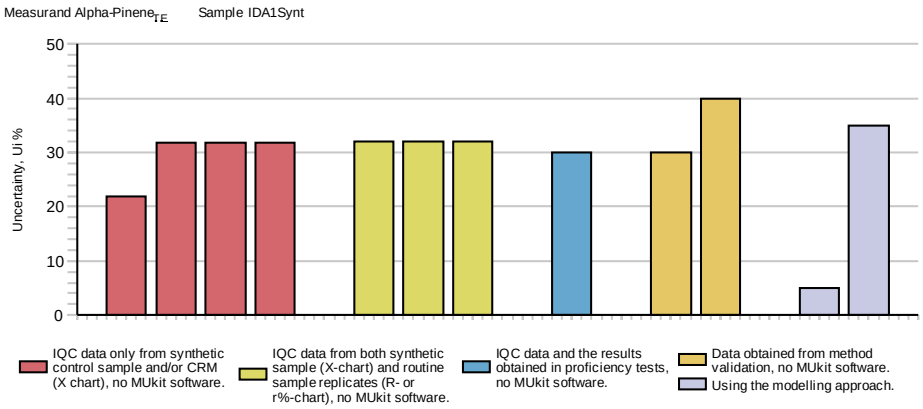


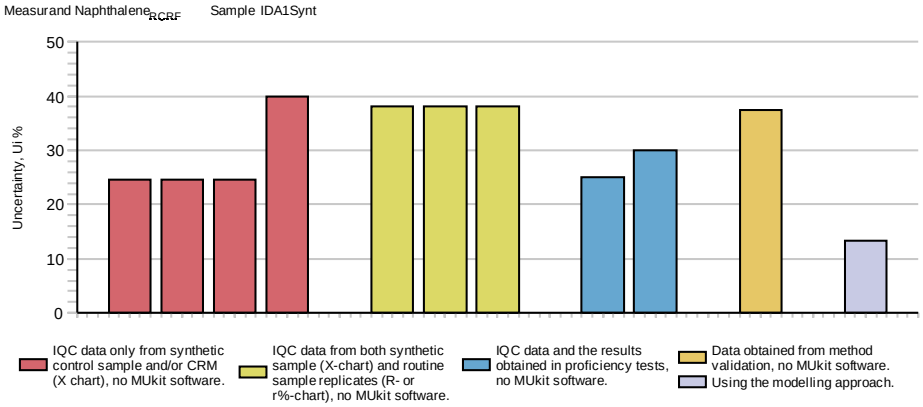
Measurand 2EH$_{TE}$ Sample IDA1Synt

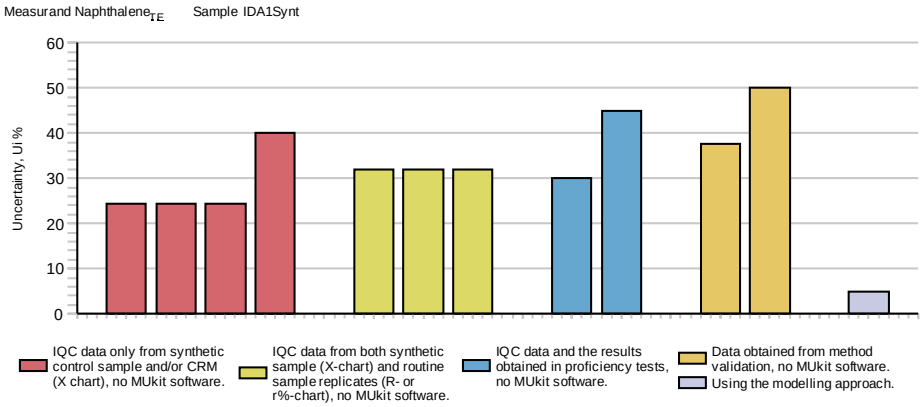


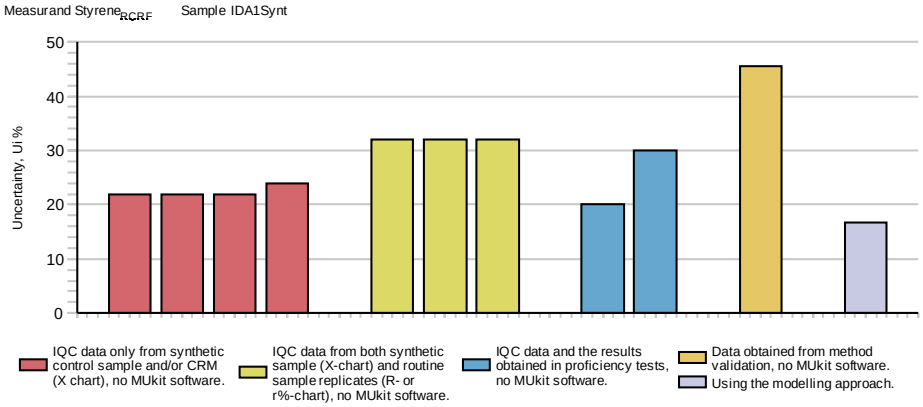
Measurand Alpha-Pinene$_{RCRF}$ Sample IDA1Synt

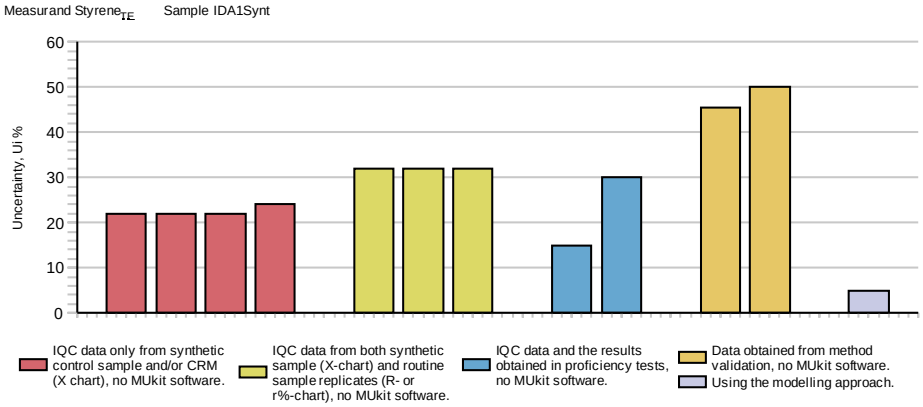


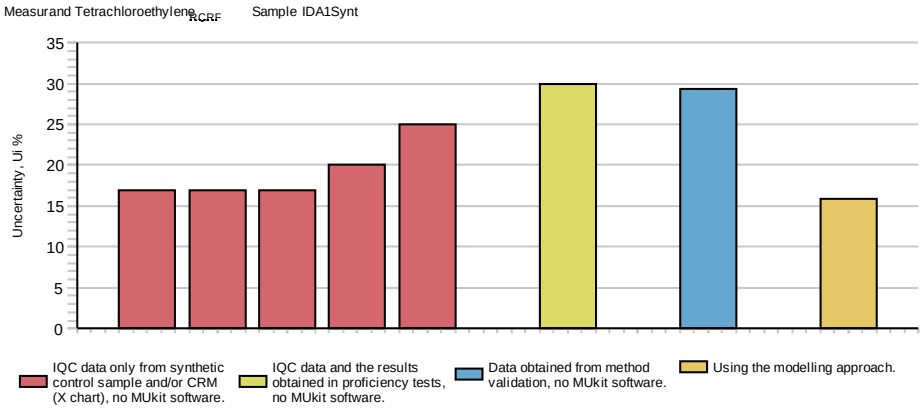

Measurand Alpha-Pinene$_{TE}$ Sample IDA1Synt
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

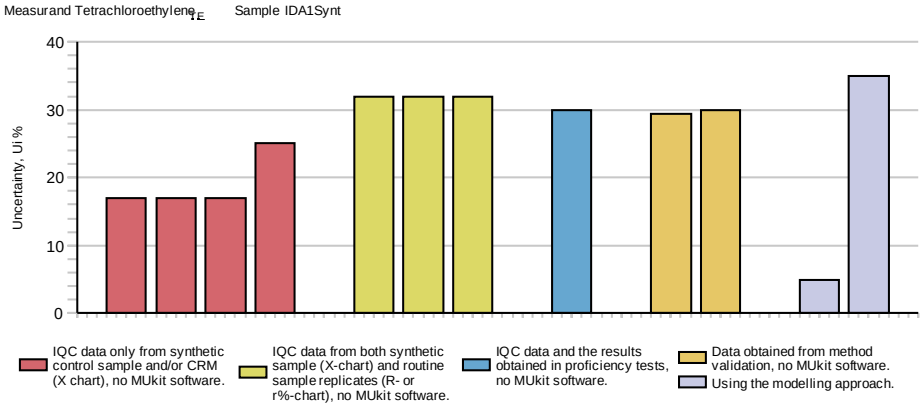

Measurand Naphthalene$_{RCRF}$ Sample IDA1Synt
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

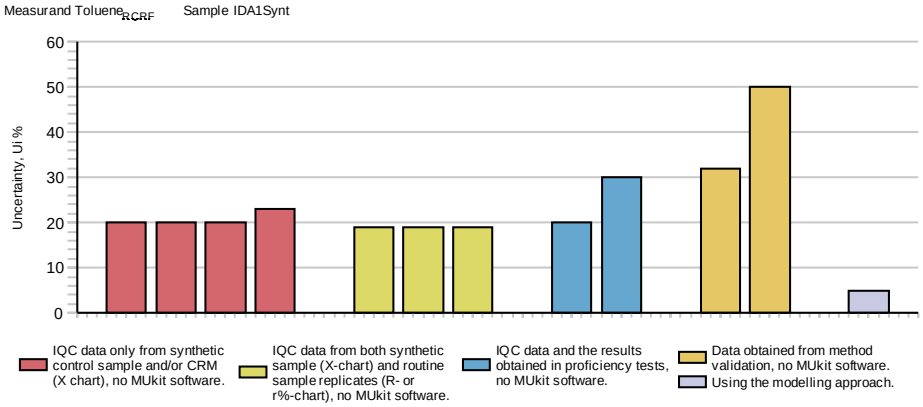

Measurand Naphthalene$_{TE}$ Sample IDA1Synt
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

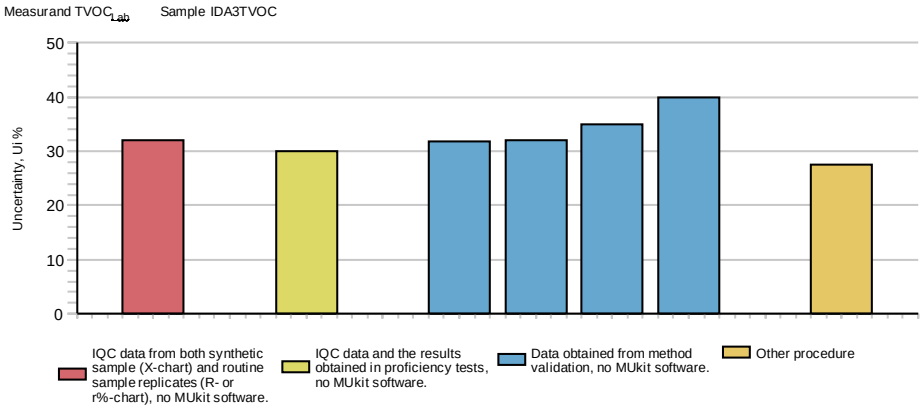

Measurand Styrene RCRF
Sample IDA1Synt
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

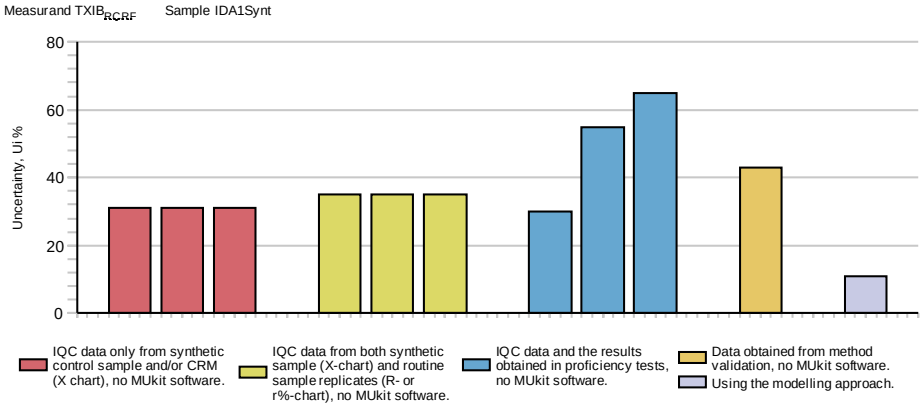

Measurand Styrene TE
Sample IDA1Synt
Uncertainty, Ui %
60
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

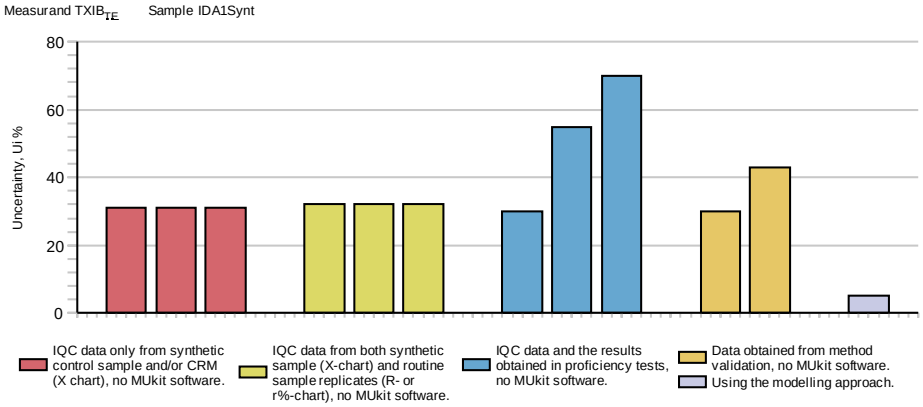

Measurand Tetrachloroethylene RCRF
Sample IDA1Synt
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand Tetrachloroethylene$_{TE}$ Sample IDA1Synt
Uncertainty, Ui %
0
10
20
30
40
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand Toluene$_{RCRF}$ Sample IDA1Synt
Uncertainty, Ui %
0
10
20
30
40
50
60
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand TVOC$_{Lab}$ Sample IDA3TVOC
Uncertainty, Ui %
0
10
20
30
40
50
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure


Measurand TXIB$_{RCRF}$
Sample IDA1Synt
Uncertainty, Ui %
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand TXIB$_{TE}$
Sample IDA1Synt
Uncertainty, Ui %
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

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