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ABSTRACT

Interlaboratory Comparison 10/2019

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 in October 2019 (IAVOC 10/2019). 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 ten participants took part in the comparison. In total 77 % of the results reported by the participants were satisfactory when deviation of 20–40 % 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 mainly the mean of the results of the homogeneity measurements and the test results of the expert laboratory was used as the assigned value. The performance evaluation was based on the z scores.
Warm thanks to all the participants in this interlaboratory comparison!

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

TIIVISTELMÄ

Laboratorioiden välinen vertailumittaus 10/2019

Proftest SYKE järjesti yhteistyössä Työterveyslaitoksen (TTL) kanssa vertailumittauksen sisäilman VOC-määrityksiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille lokakuussa 2019 (IAVOC 10/2019). 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 10 laboratoriota. Koko tulosaineistossa hyväksyttäviä tuloksia oli 77 %, kun vertailuarvosta sallittiin 20–40 % poikkeama 95 % luottamusvälillä. Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella raportoiduille tuloksille. Muille testisuureille ja näytteille käytettiin vertailuarvona pääosin asiantuntijalaboratorion homogeenisuusmääritysten ja kierrosaikaisen tulosten 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 10/2019

Proftest SYKE genomförde tillsammans med Arbetshälsoinstitutet (TTL) i oktober 2019 en interkalibrering (IAVOC 10/2019) som 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 10 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 och testresultat. Resultaten värderades med hjälp av z värden. I interkalibrering var 77 % av alla resultaten acceptabla, när en total deviation på 20–40 % 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 in October 2019 (IAVOC 10/2019). 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 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 has been carried out under the scope of the SYKE reference laboratory and it 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 standard ISO/IEC 17043 [1] and applying ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE is accredited by the Finnish Accreditation Service 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
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The responsibilities in organizing the interlabotory comparison

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

Co-operation partner and analytical expert

Hanna Hovi, Finnish Institute of Occupational Health (FIOH), firstname.lastname@ttl.fi

Subcontracting

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

2.2 Participants

In total ten participants took part in this interlaboratory comparison. Eight of these were from Finland and two from abroad (Appendix 1).

Nine 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 5 in the result tables.

2.3 Samples and delivery

Participants received following samples:

- Synthetic sample (IA1)
- Blank sample (IA2)
- Two native indoor air samples (IA3_B1 or IA3_B2) 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 (IA4)

The synthetic sample was prepared gravimetrically in the laboratory of the FIOH. The concentrations of measurands in the synthetic sample were set considering 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 detail in the Appendix 2.

The samples were delivered on 1 October 2019 and they arrived to the participants at the latest on 3 October 2019.

The results were requested to be reported latest on 21 October 2019 and participants mainly reported their results accordingly. One participant reported their results one day later due to the transportation problem of the additional sample. The preliminary result report was delivered to the participants on 28 October 2019. As agreed, one participant reported their results only after the delivery of the preliminary results report. This participant did not get the preliminary results report. The results of this participant were not included in the calculations of the assigned values and, thus, the assigned values were not changed after the delivery of the preliminary results report.

The participants were requested to return the Tenax TA thermodesorption tubes to the provider latest on 12 November 2019. All participants returned the tubes to the provider within the given timetable. The provider warmly thanks all participants for the promptly returned sample tubes.

2.4 Homogeneity and stability studies

Homogeneity of the synthetic sample IA1 was tested by measuring the reference compound response factors (RCRF) for all the tested measurands from six to seven subsamples (Appendix 3). Homogeneity of IA3 samples (IA3_B1 or IA3_B2) was tested by measuring TVOC as toluene equivalent (TE) from four to eight samples. In the calculations the samples collected from the same duct adapter were treated as parallel samples making four (IA3_B1) or two (IA3_B2) 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 samples, with the exception of alpha-pinene, 2-butoxyethanol, $2EH_{TE}$ and $TXIB_{TE}$ in the sample IA1 and $TVOC_{Lab}$-Chamber blank in the sample IA3_B2. 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 mainly dealt with the sample delivery activity. The comments from the provider are mainly focused to the following the provider's instructions. All the feedback from the interlaboratory comparison 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 test before calculating the mean. The results, which differed from the data more than $5 \times s_{rob}$ or 50 % from the robust mean, were rejected before the statistical results handling.

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 (IA1, RCRF). For the other measurands and samples the mean of the results of the homogeneity measurements and the test results of the expert laboratory were used as the assigned value, with exception of measurands $2EH_{TE}$ and $TXIB_{TE}$ in the sample IA1 and $TVOC_{Lab}$-Chamber blank in the sample IA3_B2. For those the mean of the homogeneity measurements was used as the assigned values.

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 the standard deviations within and between sub samples [4].

For the calculated assigned values in the synthetic samples the expanded uncertainties were between 2.0 % and 2.7 % for the results based on compound specific responses (RCRF) and between 0.9 % and 6.7 % for the results based on toluene equivalent (TE). For the samples collected from the chamber, IA3_B1 and IA3_B2, for TVOC measurements, the expanded uncertainties of the assigned were 6.8 % and 16 %, respectively (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 scores

The results of this interlaboratory comparison were evaluated with the z score. The standard deviation for proficiency assessment was estimated basis of the measurand concentration, the results of homogeneity tests, the uncertainty of the assigned value, and the standard deviation values used in the earlier similar comparisons. The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 20–30 % for the measurands in the synthetic sample and for TVOC in the chamber samples to 30–40 %. **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

The reliability of the assigned value (except the assigned values of the synthetic sample as compound specific responses) 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]. When testing the reliability of the assigned value the criterion was mainly fulfilled in the every case and the assigned values were considered reliable.

In the following case, the criterion for the reliability of the assigned value was not met and, therefore, the evaluation of the performance is weakened in this interlaboratory comparison:

Sample	Measurand
IA3_B2	$TVOC_{Lab}$-Chamber blank

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.

The result of the individual measurand analysed from the synthetic sample (IA1) was subtracted with the result of the tube blank (IA2) and reported as measurands own response (RCRF, Reference Compound Response Factor) and as toluene equivalent (TE).

Two TVOC samples, collected from the chamber, were delivered to the participants and the results were processed as parallel results. The participants reported their TVOC results of the chamber samples as toluene equivalents (TE) and as subtracted by the result of the chamber blank (IA4) using their own method of calculation ($TVOC_{Lab}$-Chamber blank).

The robust standard deviation or the standard deviation for the results of the synthetic sample (IA1) varied from 6.8 to 49 % and for the chamber samples (IA3) from 13 to 31 % (Table 1). The variation was in the same range than in the previous similar ILC IDA 09/2018 [7].

Table 1. The summary of the results in the interlaboratory comparison IAVOC 10/2019.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	s_{rob} / *s*	s_{rob} % / *s* %	2 x s_{pt} %	n_{all}	Acc z %
Alpha-Pinene$_{RCRF}$ (CAS No 80-568)	IA1	ng/sample	73.5	69.3	73.4	66.2	16.4	22.4	20.0	8	88
Alpha-Pinene$_{TE}$	IA1	ng/sample	79.4	78.6	78.6	78.7	10.7	13.6	20.0	10	100
1-Butanol$_{RCRF}$ (CAS No 71-26-3)	IA1	ng/sample	143	149	-	147	*31*	*20.7*	20.0	7	57
1-Butanol$_{TE}$	IA1	ng/sample	50.1	44.3	55.6	40.0	27.3	49.0	25.0	10	40
2-Butoxyethanol$_{RCRF}$ (CAS No 111-76-2)	IA1	ng/sample	163	157	152	149	42	27.8	20.0	8	50
2-Butoxyethanol$_{TE}$	IA1	ng/sample	76.3	70.8	70.8	72.0	12.8	18.0	20.0	10	60
2EH$_{RCRF}$ (CAS No 104-76-7)	IA1	ng/sample	79.1	80.5	84.0	77.5	16.6	19.8	20.0	9	67
2EH$_{TE}$	IA1	ng/sample	62.0	61.3	63.4	62.4	11.7	18.5	20.0	10	80
Naphthalene$_{RCRF}$ (CAS No 91-20-3)	IA1	ng/sample	161	168	167	163	11	6.8	20.0	8	88
Naphthalene$_{TE}$	IA1	ng/sample	254	237	237	224	54	22.9	25.0	10	90
Styrene$_{RCRF}$ (CAS No 100-42-5)	IA1	ng/sample	102	113	113	113	15	13.5	20.0	9	78
Styrene$_{TE}$	IA1	ng/sample	111	107	106	106	12	11.3	20.0	10	90
Tetrachloroethylene$_{RCRF}$ (CAS No 127-18-4)	IA1	ng/sample	127	135	-	133	*15*	*11.2*	20.0	7	86
Tetrachloroethylene$_{TE}$	IA1	ng/sample	100	102	102	103	9	9.0	20.0	10	80
Toluene$_{RCRF}$ (CAS No 108-88-3)	IA1	ng/sample	155	166	164	162	16	9.9	20.0	10	90
TXIB$_{RCRF}$ (CAS No 6846-50-0)	IA1	ng/sample	48.3	52.4	52.4	53.7	12.1	23.0	30.0	9	89
TXIB$_{TE}$	IA1	ng/sample	70.6	67.1	67.1	66.0	29.2	43.4	30.0	10	60
$TVOC_{Lab}$-Chamber blank	IA3_B1	µg/m3	181	229	-	237	*29*	*12.7*	35.0	6	83
	IA3_B2	µg/m3	51.8	37.3	-	34.9	*11.4*	*30.7*	40.0	5	80

Rob. mean: the robust mean, s_{rob}: the robust standard deviation, s_{rob} %: the robust standard deviation as percent, *s : the standard deviation, s % : the 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 number of the participants.

3.2 Analytical methods

The participants could use different analytical methods for the measurements in the ILC. A questionnaire related to the used analytical methods was carried out 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 Used analytical methods

In the background survey participants were asked to report some basic information of the used analytical methods (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.

The used analytical methods of the participants and results are shown in more detail in Appendix 12. Two participants used TD-GC-FID/MS while the rest used TD-GC-MS. Based on the visual estimation of the results no clear difference between the used analytical methods was observed.

3.2.2 Results as toluene equivalent and compound specific response

For measurements of the synthetic sample (IA) mainly TD-GC-MS instrument was used. Two participants used a TD-GC-FID/MS instrument for at least part of the results. The used analytical methods of the participants and results are shown in more detail in Appendix 12.

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. The ratio varied between: 0.79 and 2.35 for alpha-pinene, 1.53 and 3.90 for 1-butanol, 1.71 and 4.28 for 2-butoxyethanol, 1.24 and 1.63 for 2EH, 0.54 and 0.89 for naphthalene, 0.92 and 1.16 for styrene, 1.13 and 5.26 for tetrachloroethylene and between 0.53 and 1.66 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.

Table 2. Participant results for the synthetic sample (IA1) 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**			
1	61.8	76.6	**0.81**	1	106	33	**3.21**
3	66.8	64.1	**1.04**	3	151	94.1	**1.60**
4	75	81.5	**0.92**	5	128.8	52.6	**2.41**
5	58.9	74.9	**0.79**	6	143.8	36.9	**3.90**
6	65.6	78.7	**0.83**	8	186	55.8	**3.33**
8	87.6	86.7	**1.01**	9	181	118	**1.53**
9	155	66	**2.35**	11	130.7	67.49	**1.94**
11	86.29	78.56	**1.10**				
2-Butoxyethanol				**2EH (2-ethyl-1-hexanol)**			
1	155	56.2	**2.76**	1	77.2	54.7	**1.41**
3	182	81.7	**2.23**	3	82.2	66.5	**1.24**
4	149	74.3	**2.01**	4	77.5	57.5	**1.35**
5	123.3	72	**1.71**	5	60.8	46.3	**1.31**
6	131.9	69.2	**1.91**	6	77.4	58.2	**1.33**
8	105	75.7	**1.39**	7	95	67	**1.42**
9	254	59.3	**4.28**	8	93.2	68	**1.37**
11	206.9	55.78	**3.71**	9	169	104	**1.63**
				11	76.44	51.51	**1.48**
Naphthalene				**Styrene**			
1	174	207	**0.84**	1	103	101	**1.02**
4	157	293	**0.54**	3	122	109	**1.12**
5	158.9	223.5	**0.71**	4	129	114	**1.13**
6	163.1	316.4	**0.52**	5	92.8	100.6	**0.92**
7	194	273	**0.71**	6	100.4	105.8	**0.95**
8	159	236	**0.67**	7	129	131	**0.98**
9	172	193	**0.89**	8	112	114	**0.98**
11	182.9	246.5	**0.74**	9	114	98.4	**1.16**
				11	114.8	106	**1.08**
Tetrachloroethylene				**TXIB (2,2,4-trimethyl-1,3-pentanediol diisobutyrate)**			
1	132	88.6	**1.49**	1	68.9	94.4	**0.73**
4	138	107	**1.29**	3	51.5	36.1	**1.43**
5	113.5	100.7	**1.13**	4	55.8	108	**0.52**
6	134.8	102.9	**1.31**	5	35	55.1	**0.64**
8	160	107	**1.50**	6	46.8	88.5	**0.53**
9	130	24.7	**5.26**	7	61	66	**0.92**
11	142.6	105.2	**1.36**	8	43.4	52.7	**0.82**
				9	56.5	34	**1.66**
				11	54	60.53	**0.89**

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 3, 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. One participant used modelling approach for some measurands. For the estimation of uncertainties, the MUkit measurement uncertainty software is available, but none of the participant used it [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.

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

Measurand	U_i%, IA1 / IA3
Alpha-pinene$_{RCRF}$	7.02-40
Alpha-pinene$_{TE}$	6.26-40
1-Butanol$_{RCRF}$	18.3-30
1-Butanol$_{TE}$	6.26-40
2-Butoxyethanol$_{RCRF}$	15-40
2-Butoxyethanol$_{TE}$	6.26-40
2EH$_{RCRF}$	20-47
2EH$_{TE}$	6.26-**118**
Naphthalene$_{RCRF}$	20-40
Naphthalene$_{TE}$	6.26-**90**
Styrene$_{RCRF}$	6.96-45.5
Styrene$_{TE}$	6.26-66
Tetrachloroethylene$_{RCRF}$	10-38
Tetrachloroethylene$_{TE}$	6.26-40
Toluene$_{RCRF}$	6.26-40
TXIB$_{RCRF}$	12.5-43
TXIB$_{TE}$	6.26-60
TVOC$_{Lab}$-Chamber blank	B1: 20-35; B2: 22-40

The estimated uncertainties varied for the tested measurands and samples (Table 3). 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.

4 Evaluation of the results

The performance evaluation of the participants was based on the z scores, which were calculated using the assigned values and the standard deviation for the performance assessment (Appendix 7). The z scores 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, 77 % of the results evaluated based on z scores were satisfactory when accepted deviation from the assigned value was 20–40 % at the 95 % confidence level (Appendix 9). From the participants 90 % used the accredited methods for at least some of the measurands and 76 % of those results were satisfactory. In the previous similar ILC IDA 09/2018, the performance was satisfactory for 70 % of the all participants when accepted deviation from the assigned value was 20–30 % [7].

Table 4. Summary of the performance evaluation in the interlaboratory comparison IAVOC 10/2019.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value at 95 % confidence level (%)	Remarks
IA1, RCRF	77	20-30	• Difficulties in measurements for some of the participants; satisfactory results < 80 % for 1-butanol, 2-butoxyethanol, 2EH. • In the previous ILC IDA 09/2018 the performance was satisfactory for 76 % of the results when accepting the deviation of 20-25 % from the assigned value [7].
IA1, TE	75	20-30	• Difficulties in measurements for some of the participants; satisfactory results < 80 % for 1-butanol, 2-butoxyethanol, TXIB. • In the previous ILC IDA 09/2018 the performance was satisfactory for 61 % of the results when accepting the deviation of 20-25 % from the assigned value [7].
$TVOC_{Lab}$-Chamber blank IA3_B1 IA3_B2	 83 80	 35 40	• Somewhat uncertain estimation for IA3_B2. • In the previous ILC IDA 09/2018 the performance was satisfactory for 75 % of the results when accepting the deviation of 30 % from the assigned value [7].

The summary of the performance evaluation is shown in Table 4. The percentage of the satisfactory results varied between 75 % and 83 % for the tested sample types. The overall performance for the synthetic sample (IA1) and the chamber sample (IA3) was somewhat better than in the previous similar ILC IDA 09/2018, where the percentage of the satisfactory results varied between 61 and 72 % for the tested sample types [7].

Based on the results of this ILC as well as on the results of the previous similar ILC, IDA 09/2018 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) from native indoor air samples in Tenax TA thermodesorption tubes in October 2019 (IAVOC 10/2019). 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 ten participants took part in the interlaboratory comparison.

The calculated value was used as the assigned value for the measurands of the synthetic sample (IA1) for which the results were reported as compound specific responses (RCRF). Mainly for the other measurands and samples the mean of the homogeneity measurements and the test results of the expert laboratory was used as the assigned value. The mean of the homogeneity measurements of the expert laboratory was used as the assigned values of measurands $2EH_{TE}$ and $TXIB_{TE}$ in the sample IA1 and $TVOC_{Lab}$-Chamber blank in the sample IA3_B2.

For the calculated assigned values, the expanded uncertainties were between 2.0 % and 2.7 % for the results based on compound responses and between 0.9 % and 6.7 % for the results based on toluene equivalent (TE). For the chamber samples, IA3_B1 and IA3_B2, the expanded uncertainties of the assigned values were 6.8 % and 16 %, respectively.

The evaluation of the performance was based on the z scores. In this interlaboratory comparison 77 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value from 20 to 40 % at 95 % confidence level. 90 % of the participants used accredited methods and 76 % 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 2019 (IAVOC 10/2019). 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 10 laboratoriota.

Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella (RCRF) raportoiduille tuloksille. Pääosin muille testisuureille ja näytteille käytettiin vertailuarvona asiantuntijalaboratorion homogeenisuusmääritysten ja kierroksen tulosten keskiarvoa. Asiantuntijalaboratorion homogeenisuusmäärityksen tulosten keskiarvoa käytettiin vertailuarvona synteettisen näytteen (IA1) $2EH_{TE}$ ja $TXIB_{TE}$ testisuureille sekä kammionäytteen IA3_B2 $TVOC_{Lab}$-Chamber blank testisuureelle.

Synteettisen näytteen vertailuarvon laajennettu epävarmuus vaihteli välillä 2,0–2,7 % omalla vasteella raportoiduille tuloksille ja välillä 0,9–6,7 % tolueeniekvivalenttina (TE) raportoiduille tuloksille. Kammionäytteen IA3_B1 vertailuarvojen laajennettu epävarmuus oli 6.8 % ja IA3_B2 näytteen 16 %.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa hyväksyttäviä tuloksia oli 77 %, kun vertailuarvosta sallittiin 20–40 % poikkeama 95 % luottamusvälillä. 90 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 76 %. 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 interlaboratory comparison

Country	Participant
Denmark	Eurofins Product Testing Denmark A/S
Finland	Eurofins Environment Testing Finland Oy, Lahti
	Eurofins Expert Services Oy
	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 Quality

APPENDIX 2: Sample preparation

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 IA1.

Measurand/Solvent	Name, Producer, Code, Purity
Alpha-Pinene	Sigma Aldrich 80599, ≥99.0 %
1-Butanol	Sigma Aldrich 19422, ≥99.9 %
2-Butoxyethanol	Sigma Aldrich 53071, ≥99.5 %
2-ethyl-1-hexanol, 2EH	Sigma Aldrich 08607, ≥99.5 %
Methanol	20864.290 HiPerSolv Chromanorm, 100 %
Naphthalene	Sigma Aldrich analytical standard 84679, ≥99.7%
Styrene	Merck 8.07679.0100 for synthesis, ≥99.9 %
Tetrachloroethylene	VWR 83950.290 for spectroscopie, ≥99.9 %
Toluene	Merck 1.88325.100 ACS EMSURE, ≥99.9 %
2,2,4-trimethyl-1,3-pentanediol diisobutyrate, TXIB	Sigma Aldrich 41601, ≥98.5 %

Table 2. Weighing results for the preparation of synthetic sample IA1.

Measurand/Solvent	Mass (g)	Concentration (ng/ml)	Addition of 2 µl to each termodesorption tube, (ng/sample)	Assigned value RCRF (ng/sample)
Alpha-Pinene	0.00741	37.05	74.1	73.5
1-Butanol	0.01428	71.45	142.9	143
2-Butoxyethanol	0.01631	81.55	163.1	163
2EH	0.00793	39.65	79.3	79.1
Methanol	15.674	-	-	-
Naphthalene	0.01616	80.8	161.6	161
Styrene	0.01017	50.85	101.7	102
Tetrachloroethylene	0.01275	63.75	127.5	127
Toluene	0.01555	77.75	155.5	155
TXIB	0.00487	24.35	48.7	48.3

Preparation of the Chamber samples

The native samples were prepared using a controllable chamber at the laboratory of FIOH as in the previous similar ILC IDA 09/2018 [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 IA3_B1 started on 5 September 2019 and the samples were collected to Tenax TA tubes. First the blank samples (IA 4) were collected and selected tubes were tested before the native samples (IA3_B1) 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 (IA3_B1) collection started 24 hours after the chamber was closed, on 6 September 2019.

The collection of the samples IA3_B2 started on 17 September 2019 and the samples were collected to Tenax TA tubes. The blank samples were collected first, and selected tubes were tested before the native samples (IA3_B2) 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 (IA3_B1) collection started 24 hours after the chamber was closed, on 18 September 2019.

APPENDIX 3: Homogeneity of the samples

The samples collected from the chamber (IA3_B1 or IA3_B2) were homogeneity tested by measuring TVOC as toluene equivalents (TE) from four to eight samples. In the calculations the samples collected from the same duct adapter were treated as parallel samples making two to four parallel measurements (Table 1). Homogeneity of the synthetic sample IA1 was tested by measuring the tested substances (RCRF, Reference Compound Response Factor) from six or seven subsamples (Table 2).

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 for the samples collected from the chamber.

Sample/Measurand	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	$s_{sam}^2<c$?
IA3_B1/ $TVOC_{Lab}$-Chamber Blank	181	4	17.5	31.7	13.3	0.44	Yes	128	731	Yes
IA3_B2/ $TVOC_{Lab}$-Chamber Blank	51.8	2*	20	10.4	5.14	0.49	Yes	44.3	269	Yes

* Results from the homogeneity testing of the expert laboratory

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

Table 2. Results from the homogeneity testing for the synthetic sample.

IA1/Measurand	Concentration [RCRF, ng/sample]	n	s_{pt} %	s_{pt}	s_{sam}	s_{sam}/s_{pt}	$s_{sam}/s_{pt} < 0.5$?
Alpha-Pinene	82.7	6*	10	8.27	0.70	0.08	Yes
1-Butanol	135	7	10	13.5	3.79	0.28	Yes
2-butoxyethanol	143	6*	10	14.3	1.51	0.11	Yes
2EH	99.5	6*	10	9.94	4.66	0.47	Yes
naphthalene	156	7	10	15.6	1.60	0.10	Yes
Styrene	95.0	7	10	9.50	1.32	0.14	Yes
Tetrachloroethylene	115	7	10	11.5	1.48	0.13	Yes
Toluene	156	7	10	15.6	4.05	0.26	Yes
TXIB	47.5	6*	15	7.13	3.36	0.47	Yes

* Results from the homogeneity testing of the expert laboratory

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

APPENDIX 4: Feedback from the interlaboratory comparison

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical excecution	Action / Proftest SYKE
6	The provider distributed the samples to the former address of the participant.	The provider apologized the erroneous delivery and followed that the sample was finally delivered to correct address. The provider will follow more carefully the updates of the delivery addresses in the future rounds.
11	The participants informed from technical problems before the deadline of results delivery.	Due to the low number of participants the provider, exceptionally, accepted submission of the participant's results after the delivery of the preliminary report. Participant did not get the preliminary report and it was not downloaded to the ProftestWEB. The results of the participant were not included in the calculations of the assigned values and, thus, the assigned values were not changed after the delivery of the preliminary results report.
All	The sample arrival form was missing from the electronic client interface ProftestWEB.	The provider uploaded the form and apologized the situation. The provider will be more careful with the documents in the future rounds.

Participant	Comments to the results	Action / Proftest SYKE
2	As mentioned before, there are no guidelines, how many peaks should be analyzed in TVOC calculation. There is no clear quide for this in any standard. The number of peaks is normally between 50-70. This has quite a big effect on the results.	The provider thanks for the feedback. This ILC was carried out with the reference to the international standard ISO 16000-6 [1]. This standard does not describe clear guidelines for the number of peaks to be included in the TVOC calculation. The standard is currently under revision, and the provider will follow up if in the forthcoming version there will be some further guidelines for the TVOC calculation.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
2, 3, 11	The participants did not report their accreditation status for some of the measurands. It is recommended to follow up the data report instructions of the provider.

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}
1-Butanol$_{RCRF}$	IA1	ng/sample	143	3	2.0	Calculated value	0.10
1-Butanol$_{TE}$	IA1	ng/sample	50.1	1.0	2.0	Mean value of the expert laboratory	0.08
2-Butoxyethanol$_{RCRF}$	IA1	ng/sample	163	3	2.0	Calculated value	0.10
2-Butoxyethanol$_{TE}$	IA1	ng/sample	76.3	1.7	2.2	Mean value of the expert laboratory	0.11
2EH$_{RCRF}$	IA1	ng/sample	79.1	1.7	2.2	Calculated value	0.11
2EH$_{TE}$	IA1	ng/sample	62.0	2.0	3.2	Mean value of the homogeneity testing data	0.16
Alpha-Pinene$_{RCRF}$	IA1	ng/sample	73.5	1.7	2.3	Calculated value	0.12
Alpha-Pinene$_{TE}$	IA1	ng/sample	79.4	3.2	4.0	Mean value of the expert laboratory	0.20
Naphthalene$_{RCRF}$	IA1	ng/sample	161	3	2.0	Calculated value	0.10
Naphthalene$_{TE}$	IA1	ng/sample	254	10	4.1	Mean value of the expert laboratory	0.16
Styrene$_{RCRF}$	IA1	ng/sample	102	2	2.0	Calculated value	0.10
Styrene$_{TE}$	IA1	ng/sample	111	4	3.2	Mean of the expert laboratory	0.16
Tetrachloroethylene$_{RCRF}$	IA1	ng/sample	127	3	2.0	Calculated value	0.10
Tetrachloroethylene$_{TE}$	IA1	ng/sample	100	1	0.9	Mean of the expert laboratory	0.05
Toluene$_{RCRF}$	IA1	ng/sample	155	3	2.0	Calculated value	0.10
TVOC$_{Lab}$-Chamber blank	IA3_B1	µg/m3	181	12	6.8	Mean of the expert laboratory	0.19
	IA3_B2	µg/m3	51.8	8.3	16.0	Mean of the homogeneity testing data	0.40
TXIB$_{RCRF}$	IA1	ng/sample	48.3	1.3	2.7	Calculated value	0.09
TXIB$_{TE}$	IA1	ng/sample	70.6	4.7	6.7	Mean value of the homogeneity testing data	0.22

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
Participant'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 ($i = 1, 2, \ldots, p$)
s^* = 1.483 × median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

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 1												
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	IA1		-2.59	143	20	106	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		-2.73	50.1	25	33.0	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-0.49	163	20	155	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-2.63	76.3	20	56.2	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		-0.24	79.1	20	77.2	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		-1.18	62.0	20	54.7	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		-1.59	73.5	20	61.8	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		-0.35	79.4	20	76.6	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		0.81	161	20	174	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		-1.48	254	25	207	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		0.10	102	20	103	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		-0.90	111	20	101	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.39	127	20	132	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		-1.14	100	20	89	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		0.00	155	20	155	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B1		2.67	181	35	266	237	229	29	12.7	5
TXIB$_{RCRF}$	ng/sample	IA1		2.84	48.3	30	68.9	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		2.25	70.6	30	94.4	66.0	67.1	25.7	38.3	9

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	IA1		-2.11	50.1	25	36.9	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-2.28	76.3	20	58.9	72.0	70.8	11.3	15.9	9
2EH$_{TE}$	ng/sample	IA1		1.58	62.0	20	71.8	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{TE}$	ng/sample	IA1		0.92	79.4	20	86.7	78.7	78.6	9.4	12.0	9
Naphthalene$_{TE}$	ng/sample	IA1		-1.22	254	25	215	224	237	48	20.2	9
Styrene$_{TE}$	ng/sample	IA1		-2.22	111	20	86	106	107	13	11.7	9
Tetrachloroethylene$_{TE}$	ng/sample	IA1		-0.44	100	20	96	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		0.02	155	20	155	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B2		-0.78	51.8	40	43.7	34.9	37.3	11.4	30.7	5
TXIB$_{TE}$	ng/sample	IA1		-0.10	70.6	30	69.5	66.0	67.1	25.7	38.3	9

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	IA1		0.56	143	20	151	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		7.03	50.1	25	94.1	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		1.17	163	20	182	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		0.71	76.3	20	81.7	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		0.39	79.1	20	82.2	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		0.73	62.0	20	66.5	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		-0.91	73.5	20	66.8	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		-1.93	79.4	20	64.1	78.7	78.6	9.4	12.0	9
Naphthalene$_{TE}$	ng/sample	IA1		-2.55	254	25	173	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		1.96	102	20	122	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		-0.18	111	20	109	106	107	13	11.7	9
Tetrachloroethylene$_{TE}$	ng/sample	IA1		-7.46	100	20	25	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		1.55	155	20	179	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B2		-1.63	51.8	40	34.9	34.9	37.3	11.4	30.7	5
TXIB$_{RCRF}$	ng/sample	IA1		0.44	48.3	30	51.5	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		-3.26	70.6	30	36.1	66.0	67.1	25.7	38.3	9

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	IA1		-1.61	50.1	25	40.0	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-0.86	163	20	149	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-0.26	76.3	20	74.3	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		-0.20	79.1	20	77.5	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		-0.73	62.0	20	57.5	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		0.20	73.5	20	75.0	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		0.26	79.4	20	81.5	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		-0.25	161	20	157	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		1.23	254	25	293	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		2.65	102	20	129	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		0.27	111	20	114	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.87	127	20	138	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		0.70	100	20	107	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		0.52	155	20	163	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B2		0.12	51.8	40	53.0	34.9	37.3	11.4	30.7	5
TXIB$_{RCRF}$	ng/sample	IA1		1.04	48.3	30	55.8	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		3.53	70.6	30	108.0	66.0	67.1	25.7	38.3	9

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	IA1		-1.13	143	20	127	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		0.40	50.1	25	52.6	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-2.44	163	20	123	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-0.56	76.3	20	72.0	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		-2.31	79.1	20	60.8	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		-2.53	62.0	20	46.3	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		-1.99	73.5	20	58.9	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		-0.57	79.4	20	74.9	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		-0.13	161	20	159	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		-0.96	254	25	224	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		-0.90	102	20	93	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		-0.94	111	20	101	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		-1.06	127	20	114	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		0.07	100	20	101	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		-0.49	155	20	147	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B1		0.62	181	35	201	237	229	29	12.7	5
	µg/m3	IA3_B2		-1.96	51.8	40	31.5	34.9	37.3	11.4	30.7	5
TXIB$_{RCRF}$	ng/sample	IA1		-1.84	48.3	30	35.0	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		-1.46	70.6	30	55.1	66.0	67.1	25.7	38.3	9

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	IA1		0.06	143	20	144	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		-2.11	50.1	25	36.9	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-1.91	163	20	132	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-0.93	76.3	20	69.2	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		-0.21	79.1	20	77.4	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		-0.61	62.0	20	58.2	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		-1.07	73.5	20	65.6	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		-0.09	79.4	20	78.7	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		0.13	161	20	163	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		1.97	254	25	316	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		-0.16	102	20	100	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		-0.47	111	20	106	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.61	127	20	135	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		0.29	100	20	103	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		0.44	155	20	162	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B1		1.96	181	35	243	237	229	29	12.7	5
TXIB$_{RCRF}$	ng/sample	IA1		-0.21	48.3	30	46.8	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		1.69	70.6	30	88.5	66.0	67.1	25.7	38.3	9

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$_{TE}$	ng/sample	IA1		0.78	50.1	25	55.0	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		1.80	76.3	20	90.0	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		2.01	79.1	20	95.0	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		0.81	62.0	20	67.0	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{TE}$	ng/sample	IA1		1.59	79.4	20	92.0	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		2.05	161	20	194	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		0.60	254	25	273	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		2.65	102	20	129	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		1.80	111	20	131	106	107	13	11.7	9
Tetrachloroethylene$_{TE}$	ng/sample	IA1		1.30	100	20	113	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		3.23	155	20	205	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B1		1.75	181	35	237	237	229	29	12.7	5
TXIB$_{RCRF}$	ng/sample	IA1		1.75	48.3	30	61.0	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		-0.43	70.6	30	66.0	66.0	67.1	25.7	38.3	9

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	IA1		3.01	143	20	186	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		0.91	50.1	25	55.8	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-3.56	163	20	105	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-0.08	76.3	20	75.7	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		1.78	79.1	20	93.2	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		0.97	62.0	20	68.0	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		1.92	73.5	20	87.6	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		0.92	79.4	20	86.7	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		-0.12	161	20	159	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		-0.57	254	25	236	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		0.98	102	20	112	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		0.27	111	20	114	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		2.60	127	20	160	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		0.70	100	20	107	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		1.48	155	20	178	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B1		0.54	181	35	198	237	229	29	12.7	5
TXIB$_{RCRF}$	ng/sample	IA1		-0.68	48.3	30	43.4	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		-1.69	70.6	30	52.7	66.0	67.1	25.7	38.3	9

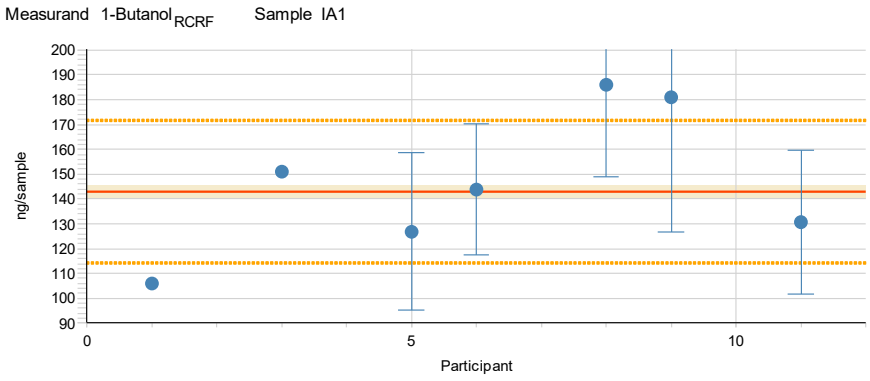
Participant 9												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1-Butanol$_{RCRF}$	ng/sample	IA1		2.66	143	20	181	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		10.84	50.1	25	118.0	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		5.58	163	20	254	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-2.23	76.3	20	59.3	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		11.37	79.1	20	169.0	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		6.77	62.0	20	104.0	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		11.09	73.5	20	155.0	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		-1.69	79.4	20	66.0	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		0.68	161	20	172	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		-1.92	254	25	193	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		1.18	102	20	114	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		-1.14	111	20	98	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.24	127	20	130	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		-7.53	100	20	25	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		-0.26	155	20	151	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B2		-2.76	51.8	40	23.3	34.9	37.3	11.4	30.7	5
TXIB$_{RCRF}$	ng/sample	IA1		1.13	48.3	30	56.5	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		-3.46	70.6	30	34.0	66.0	67.1	25.7	38.3	9

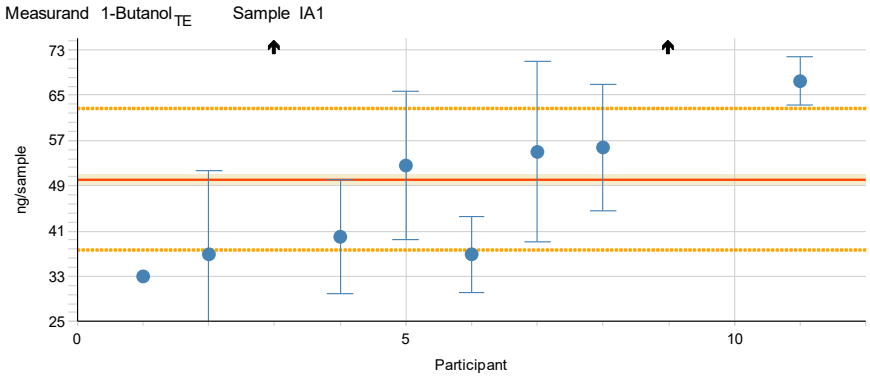
Participant 11												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1-Butanol$_{RCRF}$	ng/sample	IA1		-0.86	143	20	131	147	149	31	20.7	6
1-Butanol$_{TE}$	ng/sample	IA1		2.78	50.1	25	67.5	40.0	44.3	9.8	22.0	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		2.69	163	20	207	149	157	49	31.4	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-2.69	76.3	20	55.8	72.0	70.8	11.3	15.9	9
2EH$_{RCRF}$	ng/sample	IA1		-0.34	79.1	20	76.4	77.5	80.5	11.5	14.3	7
2EH$_{TE}$	ng/sample	IA1		-1.69	62.0	20	51.5	62.4	61.3	8.5	13.9	8
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		1.74	73.5	20	86.3	66.2	69.3	10.5	15.2	6
Alpha-Pinene$_{TE}$	ng/sample	IA1		-0.11	79.4	20	78.6	78.7	78.6	9.4	12.0	9
Naphthalene$_{RCRF}$	ng/sample	IA1		1.36	161	20	183	163	168	13	7.8	7
Naphthalene$_{TE}$	ng/sample	IA1		-0.24	254	25	247	224	237	48	20.2	9
Styrene$_{RCRF}$	ng/sample	IA1		1.25	102	20	115	113	113	13	11.9	8
Styrene$_{TE}$	ng/sample	IA1		-0.45	111	20	106	106	107	13	11.7	9
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		1.23	127	20	143	133	135	15	11.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		0.52	100	20	105	103	102	8	7.9	7
Toluene$_{RCRF}$	ng/sample	IA1		1.57	155	20	179	162	166	18	11.0	9
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3_B1		1.78	181	35	238	237	229	29	12.7	5
TXIB$_{RCRF}$	ng/sample	IA1		0.79	48.3	30	54.0	53.7	52.4	10.6	20.3	8
TXIB$_{TE}$	ng/sample	IA1		-0.95	70.6	30	60.5	66.0	67.1	25.7	38.3	9

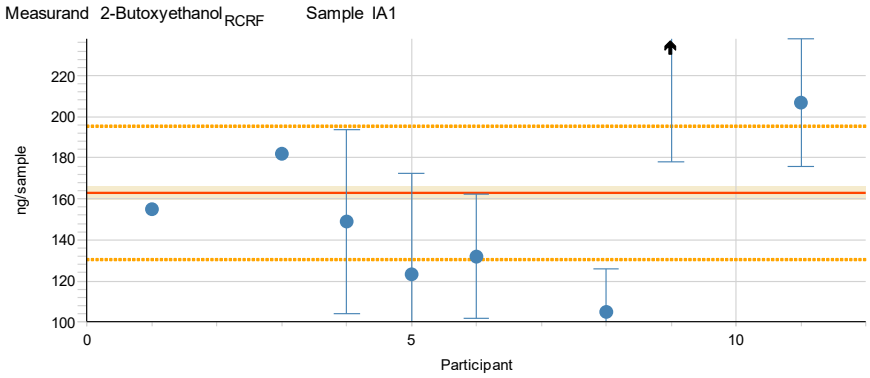
APPENDIX 8: Results of participants and their uncertainties

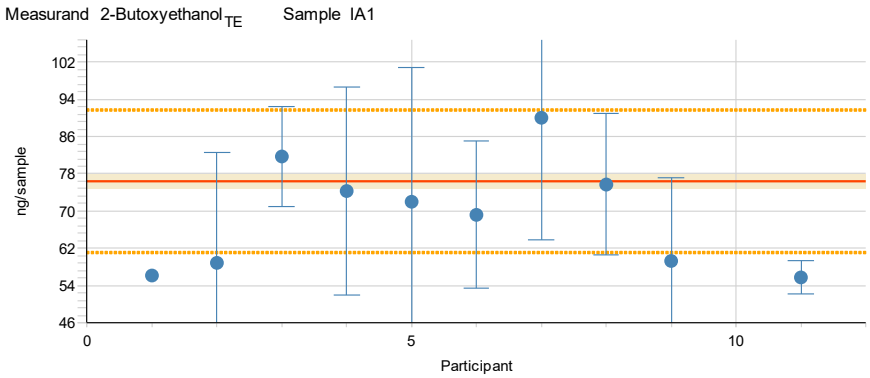
In figures:

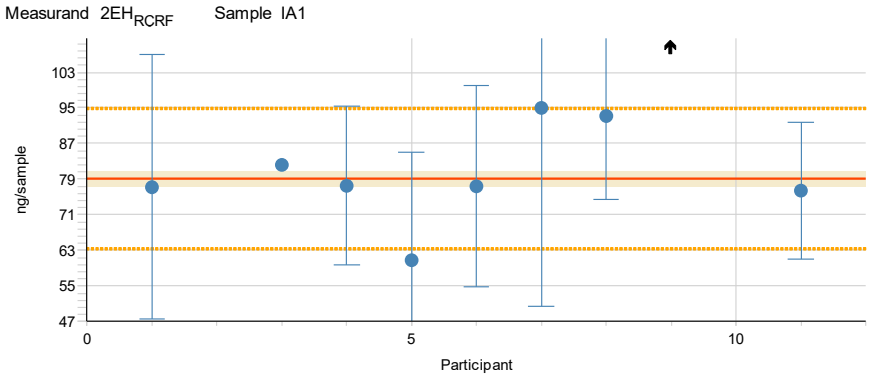
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded uncertainty of the assigned value, and the arrow describes the value outside the scale.

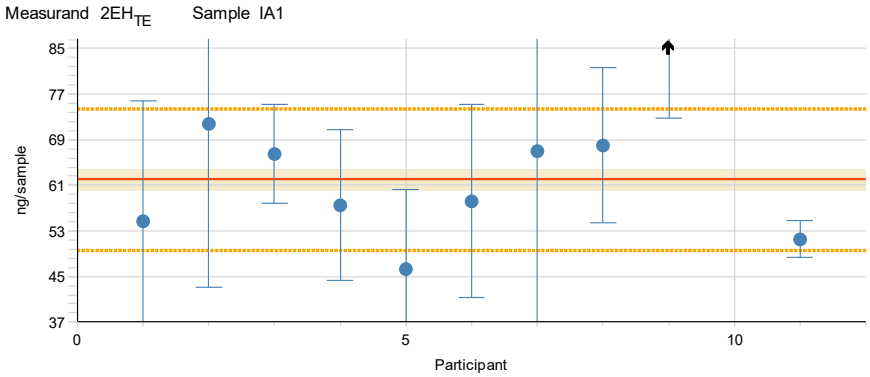


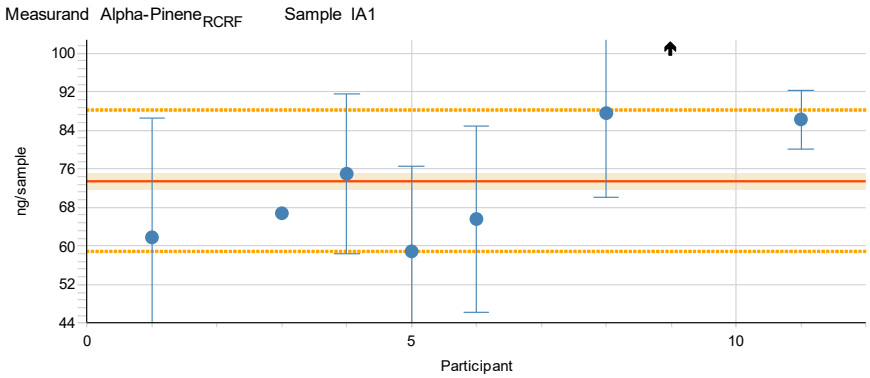


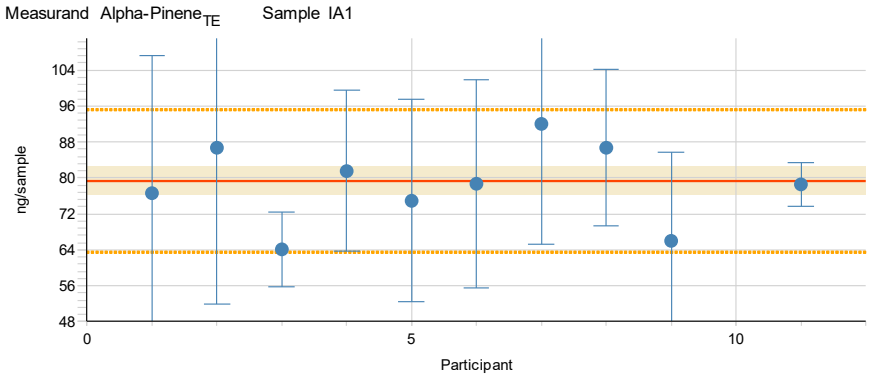


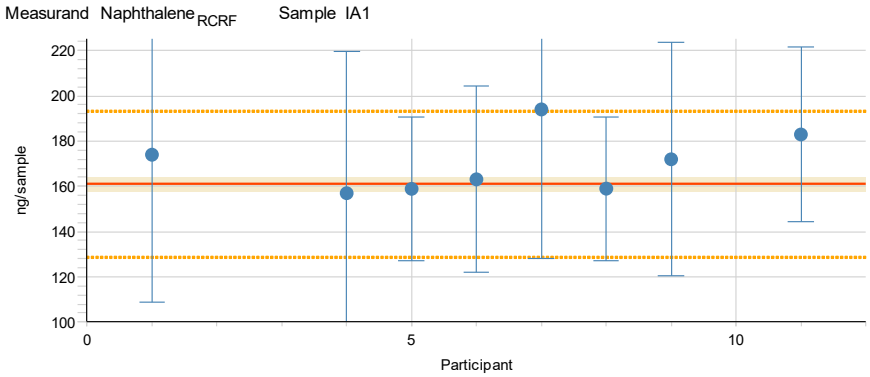

Measurand 2-Butoxyethanol TE
Sample IA1
ng/sample
102
94
86
78
70
62
54
46
0
5
10
Participant

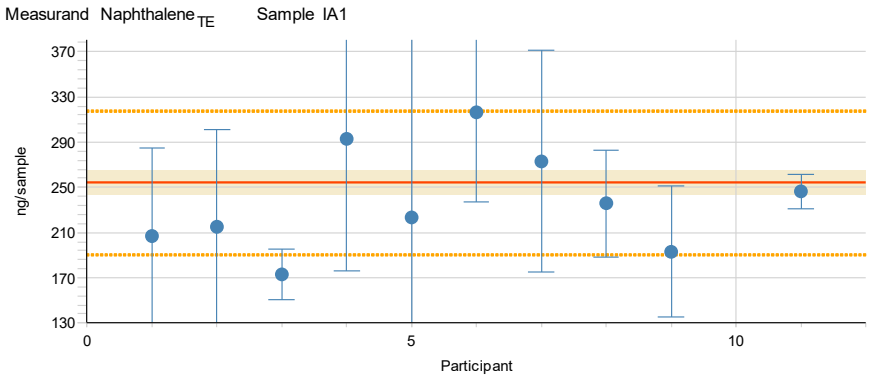

Measurand 2EH RCRF
Sample IA1
ng/sample
103
95
87
79
71
63
55
47
0
5
10
Participant

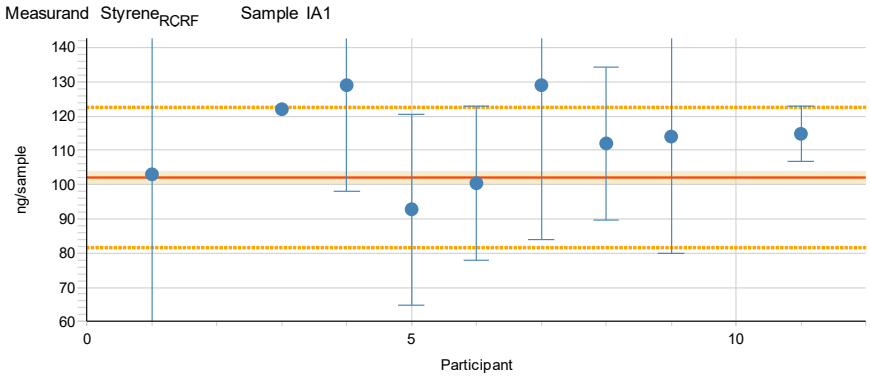

Measurand 2EH TE
Sample IA1
ng/sample
85
77
69
61
53
45
37
0
5
10
Participant

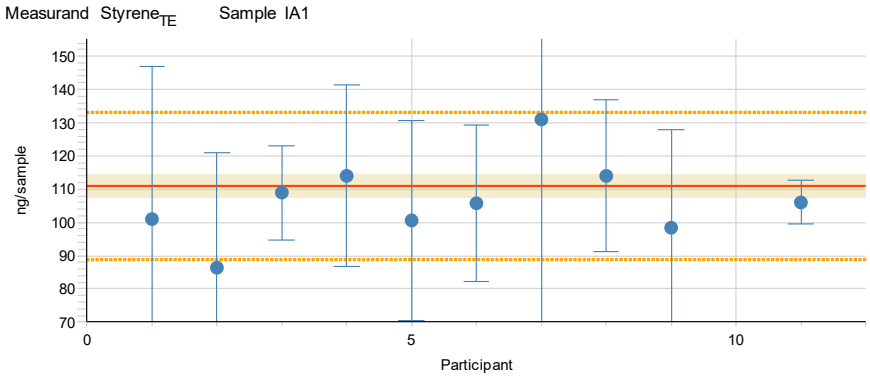

Measurand Alpha-Pinene RCRF
Sample IA1
ng/sample
100
92
84
76
68
60
52
44
0
5
10
Participant

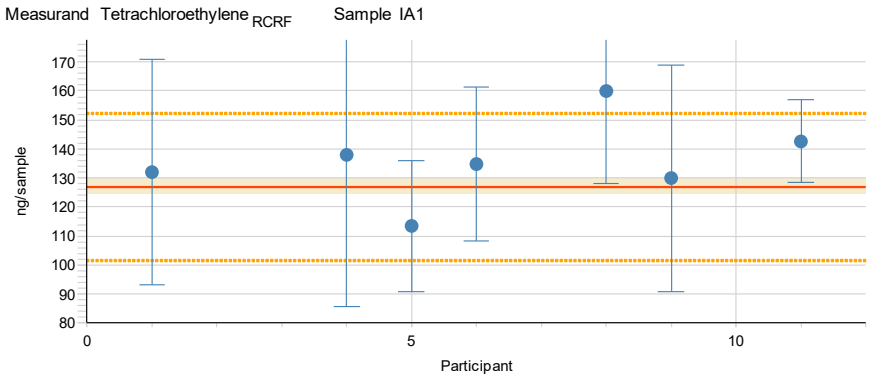

Measurand Alpha-Pinene TE
Sample IA1
ng/sample
104
96
88
80
72
64
56
48
0
5
10
Participant

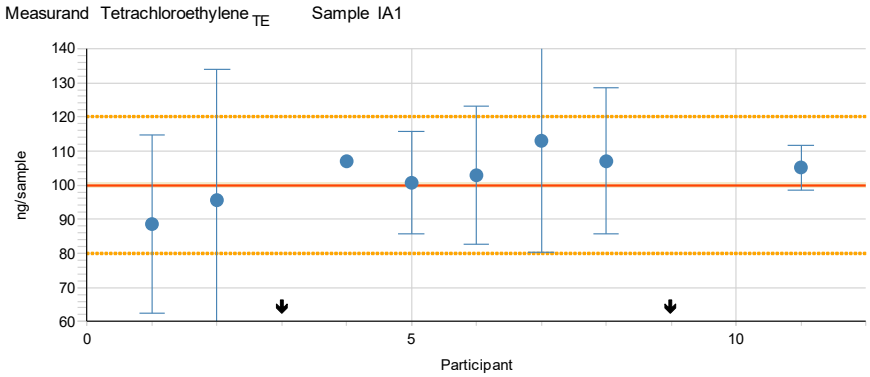

Measurand Naphthalene RCRF
Sample IA1
ng/sample
220
200
180
160
140
120
100
0
5
10
Participant

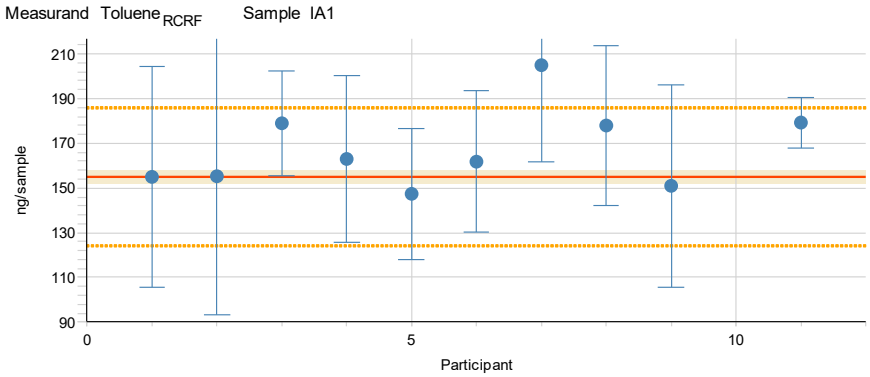

Measurand Naphthalene TE
Sample IA1
ng/sample
370
330
290
250
210
170
130
0
5
10
Participant

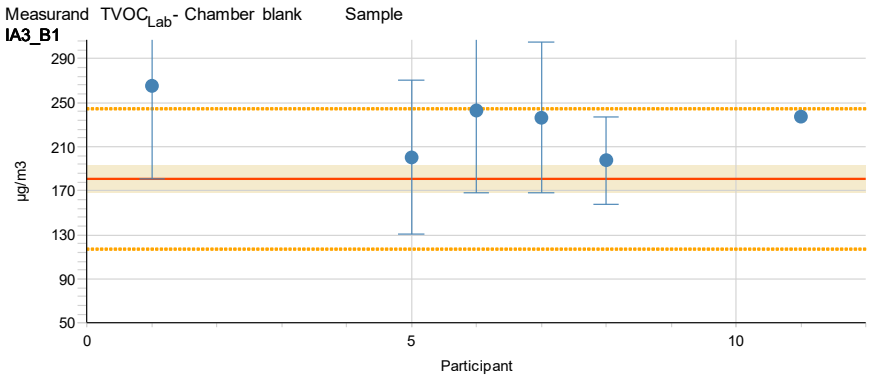

Measurand Styrene RCRF
Sample IA1
ng/sample
140
130
120
110
100
90
80
70
60
0
5
10
Participant

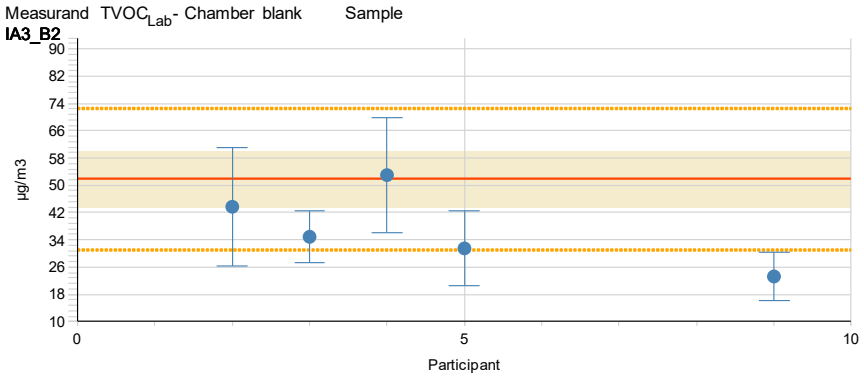

Measurand Styrene TE
Sample IA1
ng/sample
150
140
130
120
110
100
90
80
70
0
5
10
Participant

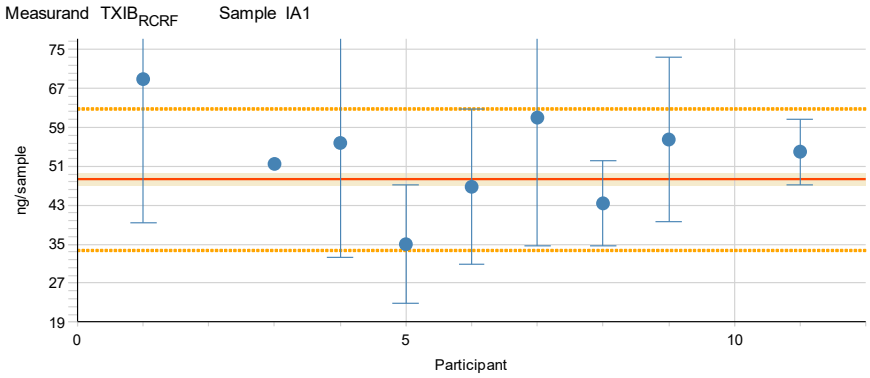

Measurand Tetrachloroethylene RCRF
Sample IA1
ng/sample
170
160
150
140
130
120
110
100
90
80
0
5
10
Participant

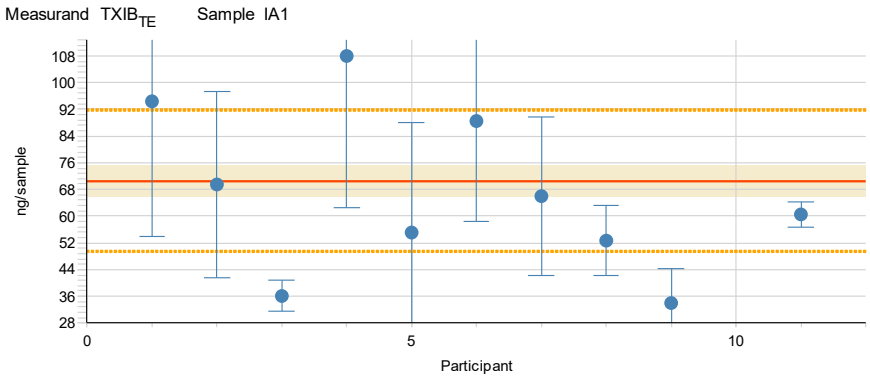

Measurand Tetrachloroethylene TE
Sample IA1
ng/sample
140
130
120
110
100
90
80
70
60
0
5
10
Participant


Measurand Toluene RCRF
Sample IA1
ng/sample
210
190
170
150
130
110
90
0
5
10
Participant


Measurand TVOC$_{Lab}$- Chamber blank Sample
IA3_B1
µg/m3
290
250
210
170
130
90
50
0
5
10
Participant


Measurand TVOC$_{Lab}$- Chamber blank Sample
IA3_B2
µg/m3
90
82
74
66
58
50
42
34
26
18
10
0
5
10
Participant


Measurand TXIB$_{RCRF}$ Sample IA1
ng/sample
75
67
59
51
43
35
27
19
0
5
10
Participant


Measurand TXIB$_{TE}$
Sample IA1
ng/sample
108
100
92
84
76
68
60
52
44
36
28
0
5
10
Participant

APPENDIX 9: Summary of the z scores

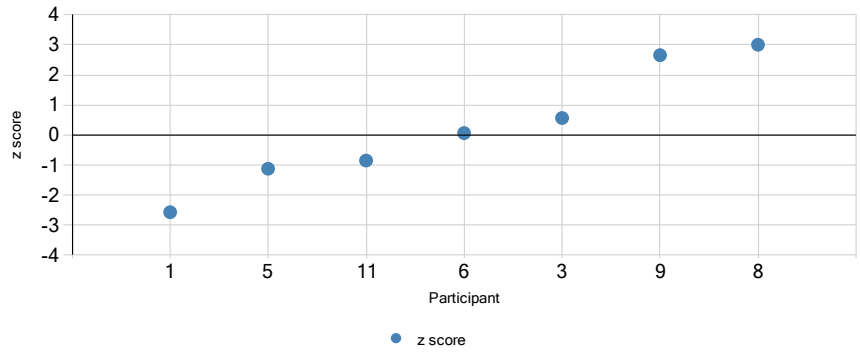
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
1-Butanol$_{RCRF}$	IA1	*q*	.	*S*	.	**S**	**S**	.	**U**	**Q**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	57.1
1-Butanol$_{TE}$	IA1	*q*	**q**	**U**	**S**	**S**	**q**	**S**	*S*	**U**	.	*Q*	.	.	.	.	.	.	.	.	.	.	.	.	40.0
2-Butoxyethanol$_{RCRF}$	IA1	*S*	.	*S*	**S**	**q**	**S**	.	*u*	**U**	.	*Q*	.	.	.	.	.	.	.	.	.	.	.	.	50.0
2-Butoxyethanol$_{TE}$	IA1	*q*	q	**S**	**S**	**S**	**S**	**S**	*S*	**q**	.	*q*	.	.	.	.	.	.	.	.	.	.	.	.	60.0
2EH$_{RCRF}$	IA1	**S**	.	*S*	**S**	**q**	**S**	**Q**	**S**	**U**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	66.7
2EH$_{TE}$	IA1	**S**	S	**S**	**S**	**q**	**S**	**S**	*S*	**U**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	80.0
Alpha-Pinene$_{RCRF}$	IA1	**S**	.	*S*	**S**	**S**	**S**	.	*S*	**U**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	87.5
Alpha-Pinene$_{TE}$	IA1	**S**	S	**S**	**S**	**S**	**S**	**S**	*S*	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	100
Naphthalene$_{RCRF}$	IA1	**S**	.	.	**S**	**S**	**S**	**Q**	**S**	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	87.5
Naphthalene$_{TE}$	IA1	**S**	S	q	**S**	**S**	**S**	**S**	*S*	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	90.0
Styrene$_{RCRF}$	IA1	**S**	.	*S*	**Q**	**S**	**S**	**Q**	**S**	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	77.8
Styrene$_{TE}$	IA1	**S**	q	**S**	**S**	**S**	**S**	**S**	*S*	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	90.0
Tetrachloroethylene$_{RCRF}$	IA1	**S**	.	.	**S**	**S**	**S**	.	*Q*	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	85.7
Tetrachloroethylene$_{TE}$	IA1	**S**	S	**u**	**S**	**S**	**S**	**S**	*S*	**u**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	80.0
Toluene$_{RCRF}$	IA1	**S**	S	**S**	**S**	**S**	**S**	**U**	**S**	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	90.0
TVOC$_{Lab}$-Chamber blank	IA3_B1	**Q**	.	.	.	**S**	**S**	**S**	*S*	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	83.3
	IA3_B2	.	S	**S**	**S**	**S**	.	.	.	**q**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	80.0
TXIB$_{RCRF}$	IA1	**Q**	.	*S*	**S**	**S**	**S**	**S**	*S*	**S**	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	88.9
TXIB$_{TE}$	IA1	**Q**	S	**u**	**U**	**S**	**S**	**S**	*S*	**u**	.	S	.	.	.	.	.	.	.	.	.	.	.	.	60.0
%		67	70	75	88	84	94	71	83	44		83													
accredited		14	1	9	17	19	18	14	5	18															

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, normal - unknown
% - percentage of satisfactory results

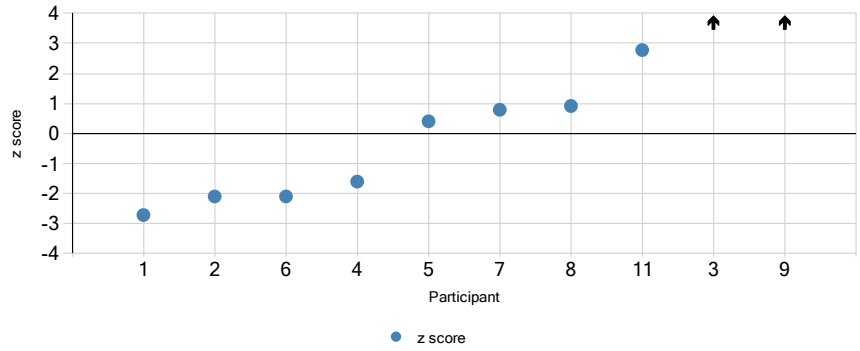
Totally satisfactory, % in all: 77 % in accredited: 76 % in non-accredited: 79

APPENDIX 10: z scores in ascending order

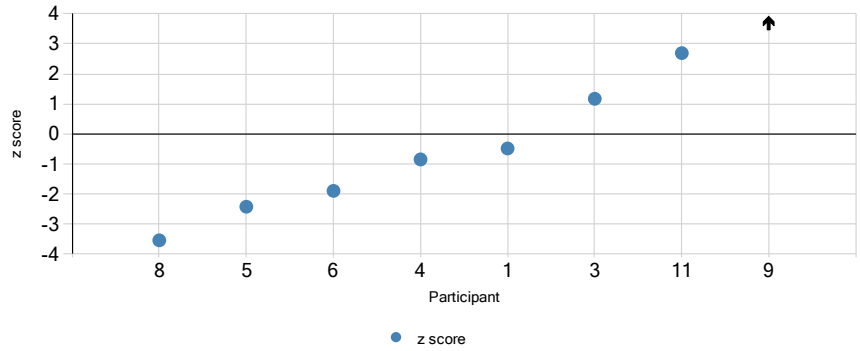
Measurand 1-Butanol$_{RCRF}$ Sample IA1

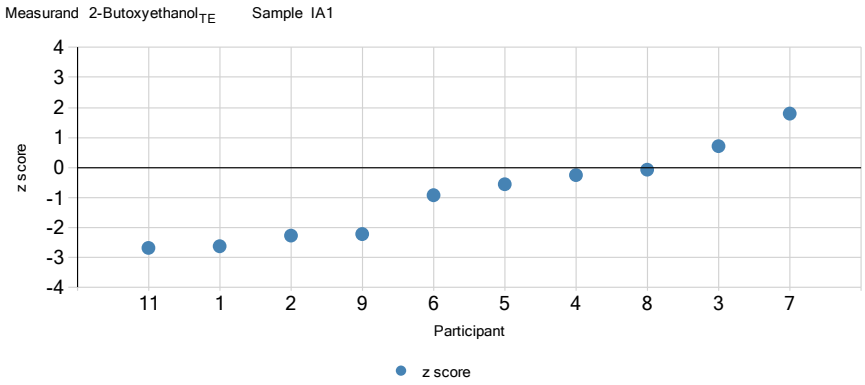


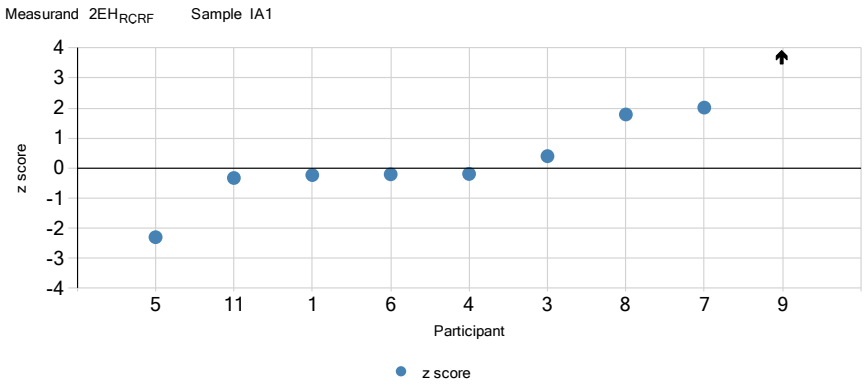
Measurand 1-Butanol$_{TE}$ Sample IA1

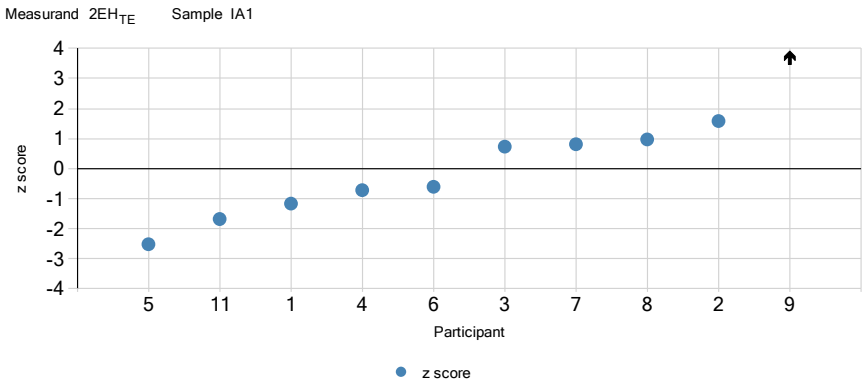


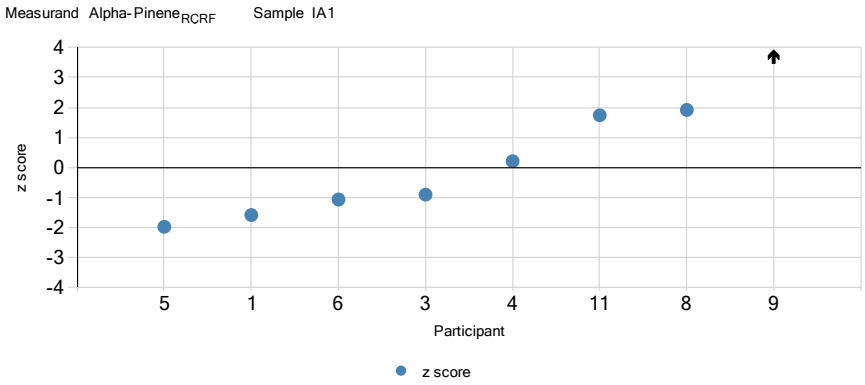
Measurand 2-Butoxyethanol$_{RCRF}$ Sample IA1

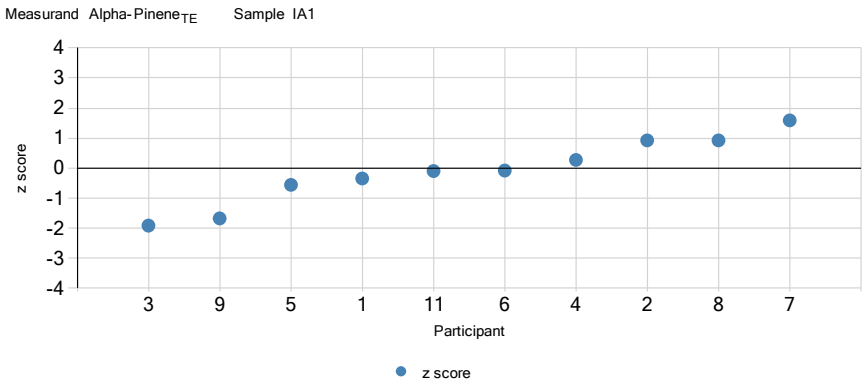


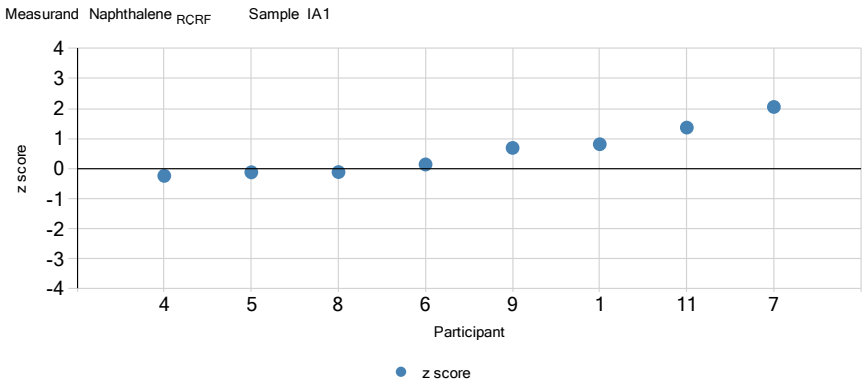

Measurand 2-Butoxyethanol$_{TE}$ Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
11 1 2 9 6 5 4 8 3 7
Participant
z score

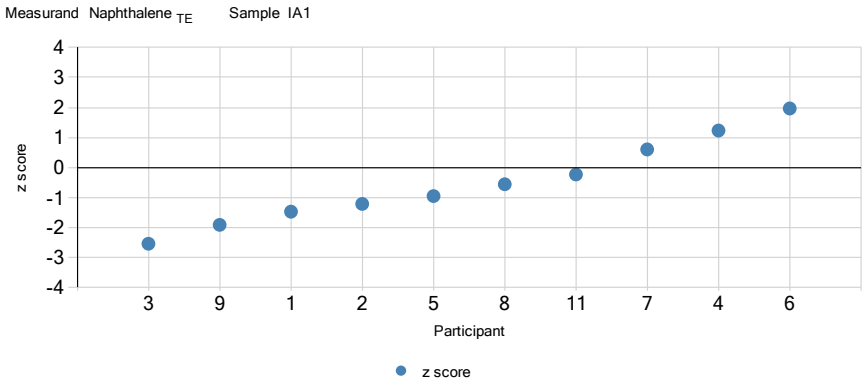

Measurand 2EH$_{RCRF}$ Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5 11 1 6 4 3 8 7 9
Participant
z score

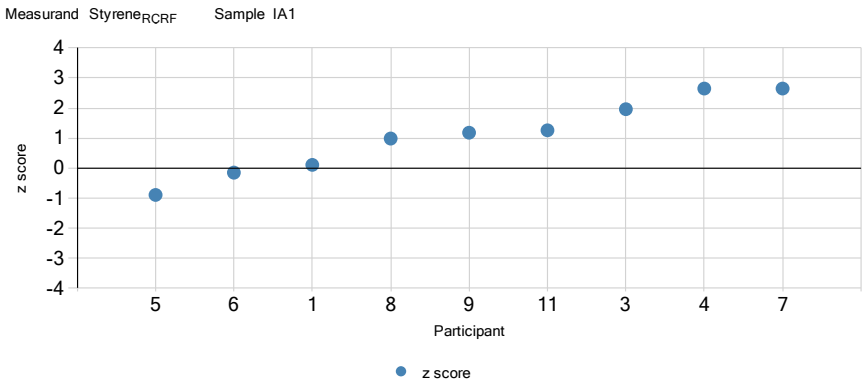

Measurand 2EH$_{TE}$ Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5 11 1 4 6 3 7 8 2 9
Participant
z score

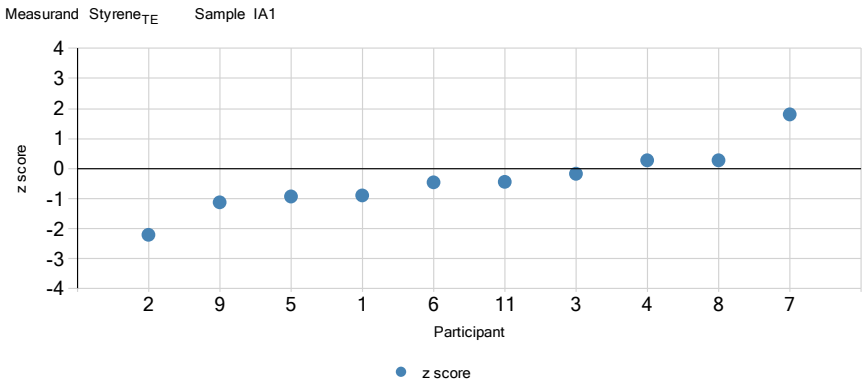

Measurand Alpha-Pinene RCRF
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5
1
6
3
4
11
8
9
Participant
z score

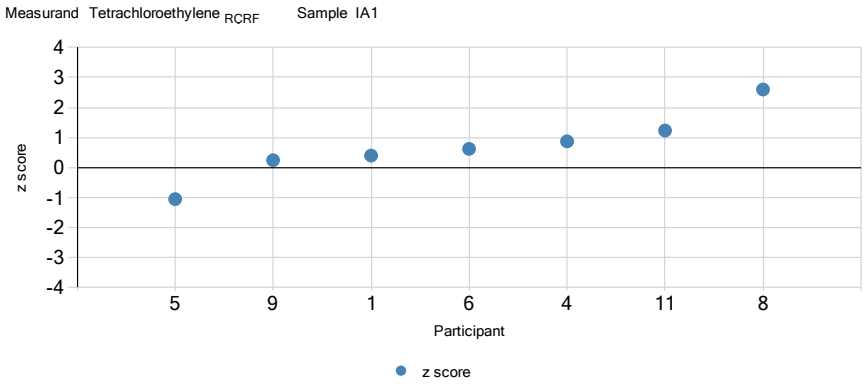

Measurand Alpha-Pinene TE
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
3
9
5
1
11
6
4
2
8
7
Participant
z score

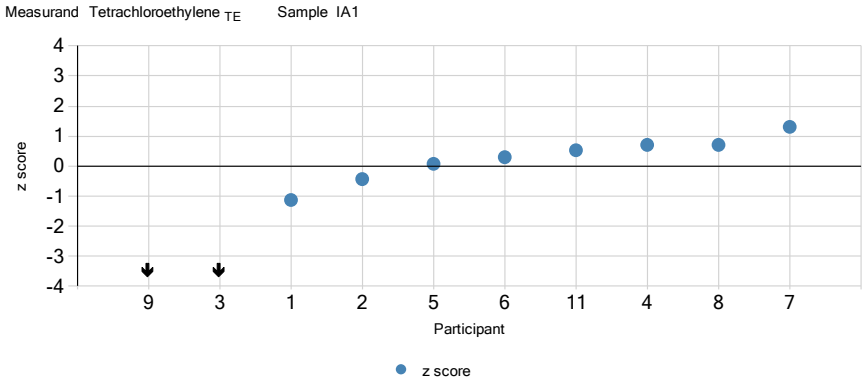

Measurand Naphthalene RCRF
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
4
5
8
6
9
1
11
7
Participant
z score

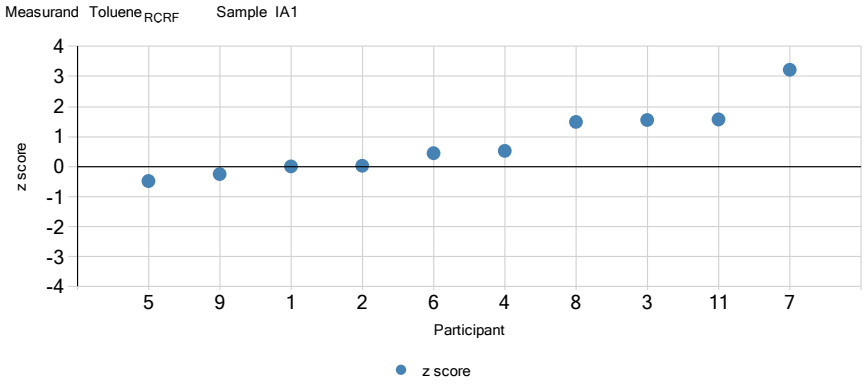

Measurand Naphthalene TE
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
3 9 1 2 5 8 11 7 4 6
Participant
z score

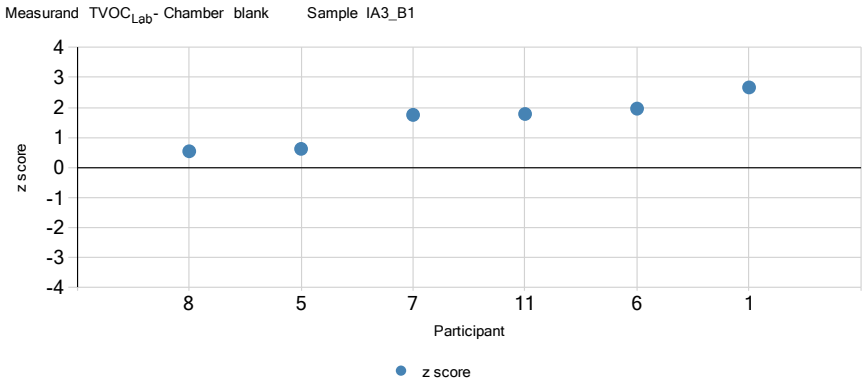

Measurand Styrene RCRF
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5 6 1 8 9 11 3 4 7
Participant
z score

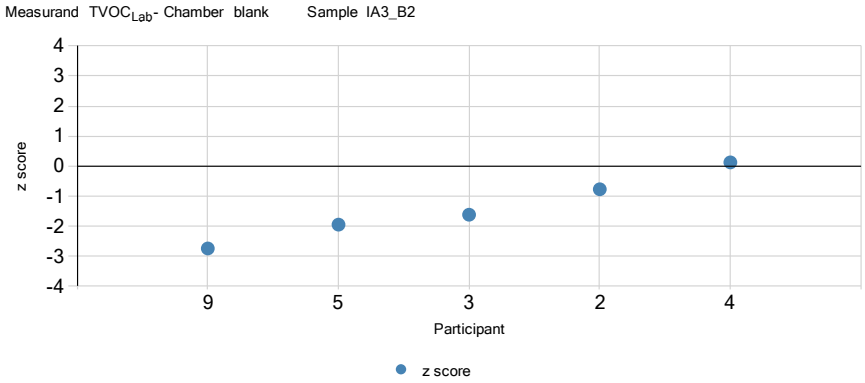

Measurand Styrene TE
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
2 9 5 1 6 11 3 4 8 7
Participant
z score

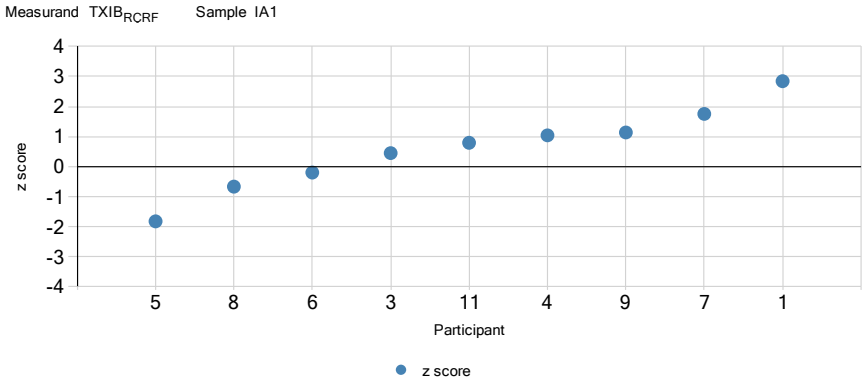

Measurand Tetrachloroethylene RCRF
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5
9
1
6
4
11
8
Participant
z score

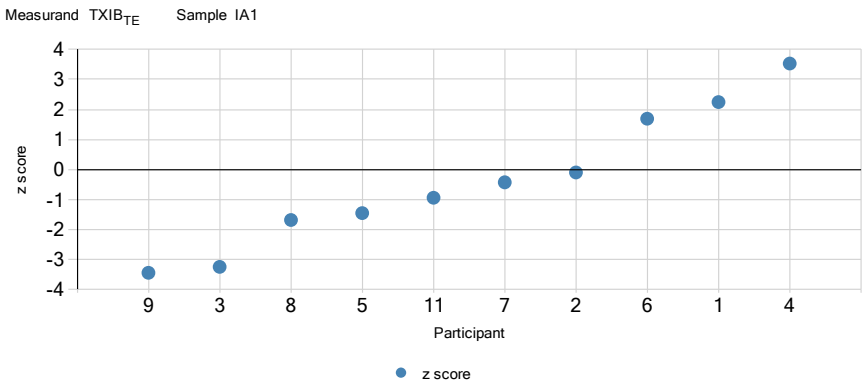

Measurand Tetrachloroethylene TE
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
9
3
1
2
5
6
11
4
8
7
Participant
z score


Measurand Toluene RCRF
Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5
9
1
2
6
4
8
3
11
7
Participant
z score


Measurand TVOC$_{Lab}$- Chamber blank Sample IA3_B1
z score
4
3
2
1
0
-1
-2
-3
-4
8
5
7
11
6
1
Participant
z score


Measurand TVOC$_{Lab}$- Chamber blank Sample IA3_B2
z score
4
3
2
1
0
-1
-2
-3
-4
9
5
3
2
4
Participant
z score


Measurand TXIB$_{RCRF}$ Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
5
8
6
3
11
4
9
7
1
Participant
z score

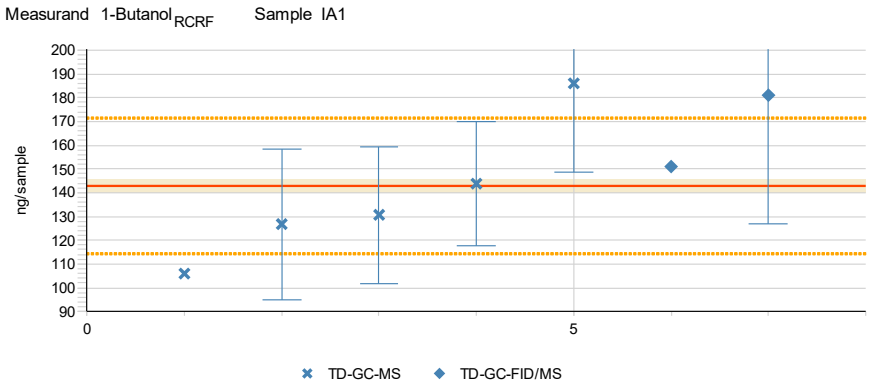

Measurand TXIB$_{TE}$ Sample IA1
z score
4
3
2
1
0
-1
-2
-3
-4
9
3
8
5
11
7
2
6
1
4
Participant
z score

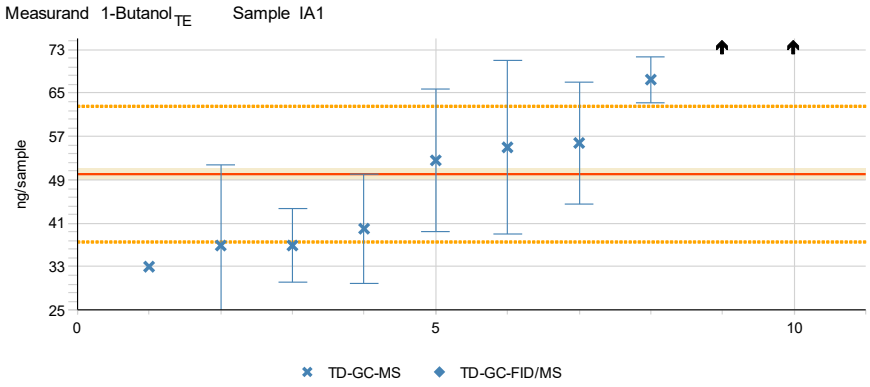
APPENDIX 11: Analytical methods

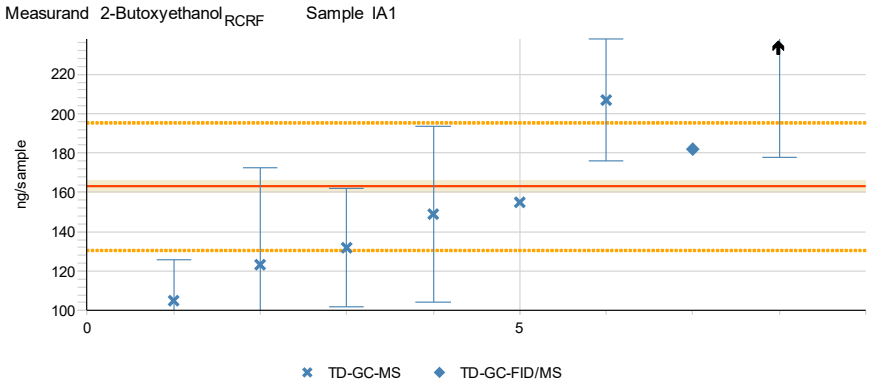
Participant	1	3	2	4	5	6	7	8	9	11
What kind of thermodesorption system/instrument was used?	Markes TD	Markes TD-100	Markes TD100	Markes TD	Markes TD100, Agilent GC-MSD	TD-100 Markes GC 7890 Agilent MSD 5977A Agilent	Markes TD100-xr /Agilent GC/MS	Markes TD-100.	Markes TD 100	Perkin Elmer TurboMatrix 350 ATD
What desorption temperature was used, in (°C)?		260 °C	280	270	280	320	300	300	300	260
What desorption flow was the used, in ml/min?		50 ml/min	50	30	50	50	50	40	20	30
How long was desorption time, in minutes?		6 min	5	10	10	Tube desorption 8 min and cold trap desorption 5 min	5	7	8	10
What was the temperature of the cryo cold trap and the heating temperature, in °C?		TD cold trap heating temperature 280 °C	0 and 300 (trap high)	-10, 300	-20 => 300	15 and 320	-20, 300	10C of the cold trap. Trap high = 300C	310	cryo temperature=-30ºC; heating temperature=300ºC
What was flow rate of carrier gas, in ml/min?		1 ml/min	20	2	1	1,2 ml/min and split 20 ml/min	0,8		20	0.6
Which type of analytical column was used?		HP-5MS (50 m, 0.200 mm, 0.33 µm)	Agilent HP5-MS	HP-5MS	HP-5MS	HP-5ms (50 m x 0,2 mm x 0.33 µm)	ZB-5MSPlus, 30m*0.25mm*0.5um	30 m HP-5 column, Id. 0.25 mm, coating 0.25 µm	HP5-MSUI, 30x0.25x0.25	HP5 (50m, 0.2mm, 0.50um)
What kind of detector(s) was used?	MSD	FID and MSD	Agilent MSD 5975C	MSD	MSD	MSD	MS	Agilent Mass spectrometer	MSD/FID	MSD 5973
Did your results include the recovery rate?	no	no	no	no	no	no		no	yes	no
Other comments?		Only FID results reported								
Do you have suggestions for substances for the next intercomparison?							Different kinds of alcohols C8-C10 in plastic mats		Some alcane hydrocarbon, decane and tetradecane for eaxmple.	Ethylbenzene; limonene; 1,2,4-trimethylbenzene

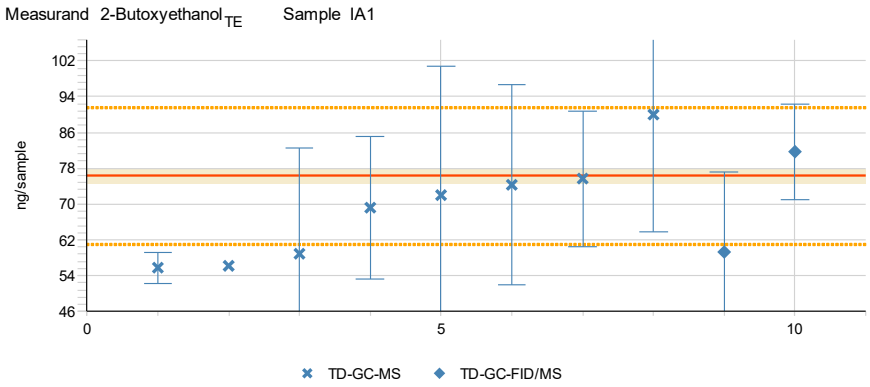
APPENDIX 12: Results grouped according to the methods

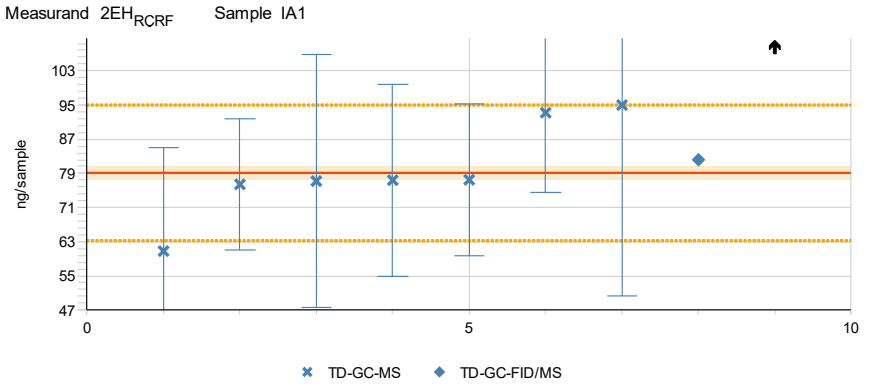
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.

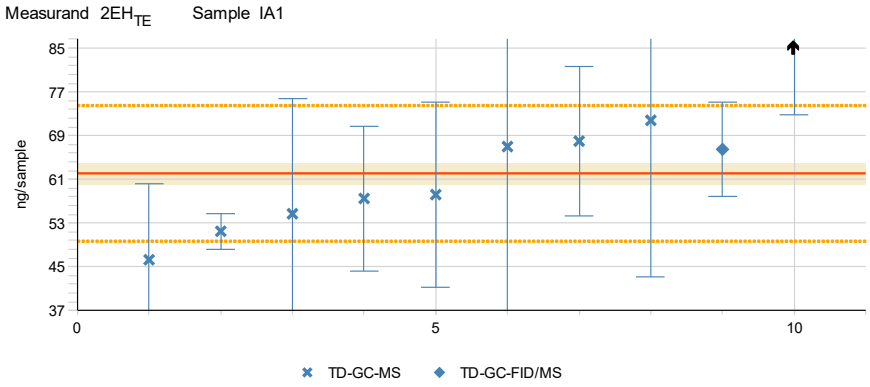


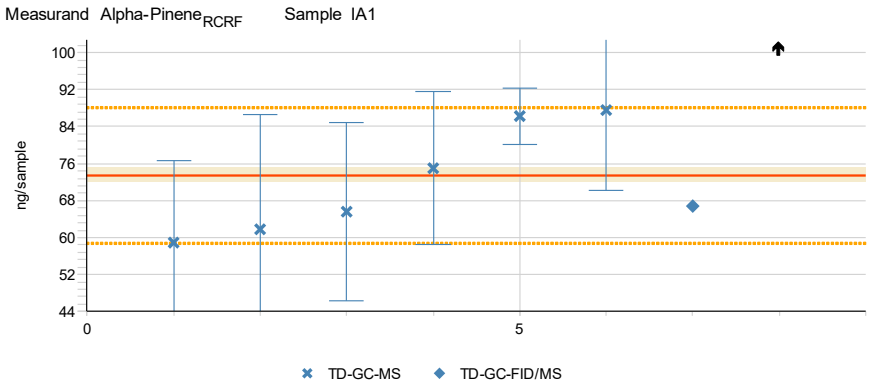


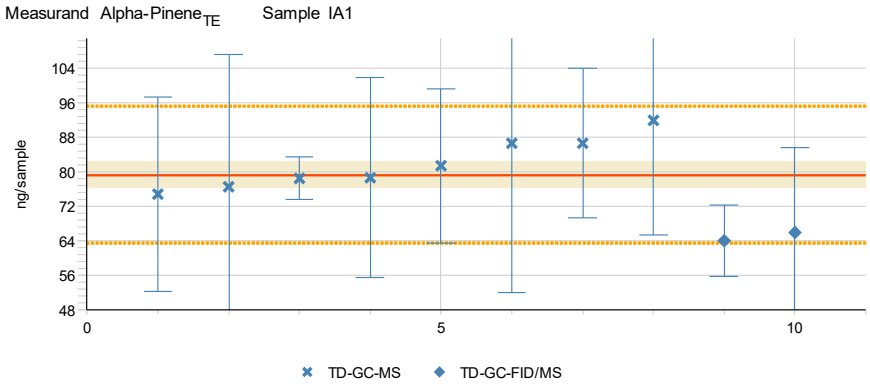


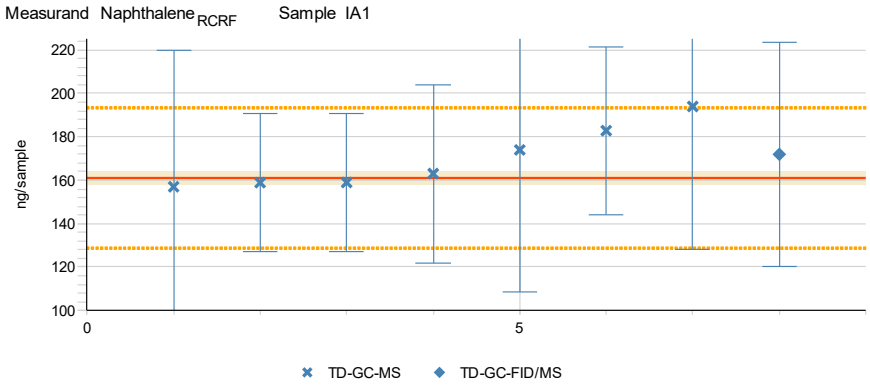

Measurand 2-Butoxyethanol TE
Sample IA1
ng/sample
102
94
86
78
70
62
54
46
0
5
10
TD-GC-MS
TD-GC-FID/MS

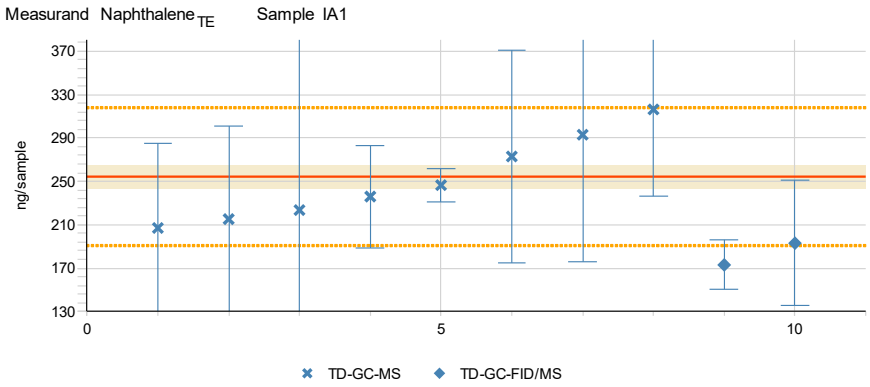

Measurand 2EH RCRF
Sample IA1
ng/sample
103
95
87
79
71
63
55
47
0
5
10
TD-GC-MS
TD-GC-FID/MS

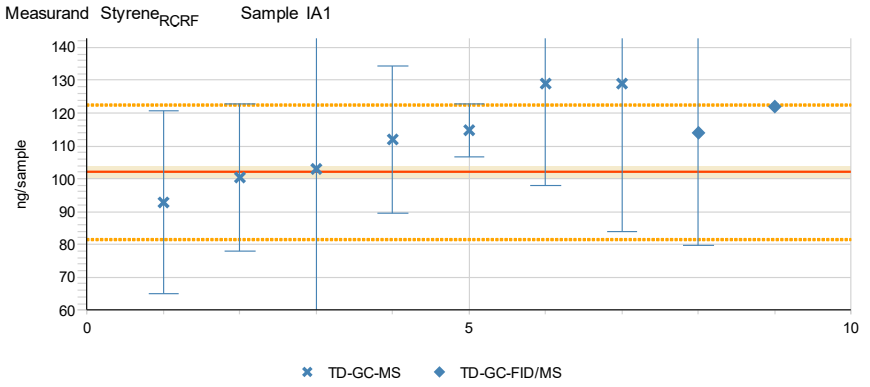

Measurand 2EH TE
Sample IA1
ng/sample
85
77
69
61
53
45
37
0
5
10
TD-GC-MS
TD-GC-FID/MS

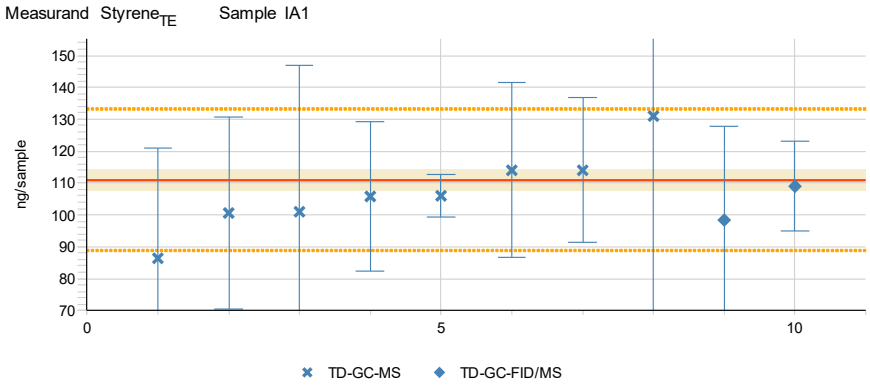

Measurand Alpha-Pinene RCRF
Sample IA1
ng/sample
100
92
84
76
68
60
52
44
0
5
TD-GC-MS
TD-GC-FID/MS

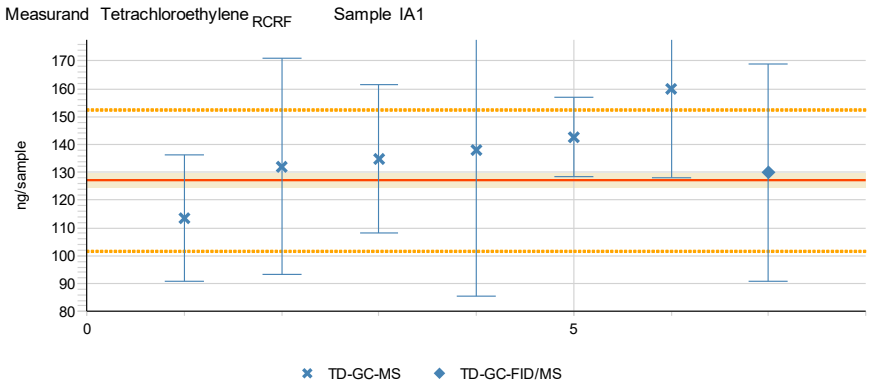

Measurand Alpha-Pinene TE
Sample IA1
ng/sample
104
96
88
80
72
64
56
48
0
5
10
TD-GC-MS
TD-GC-FID/MS

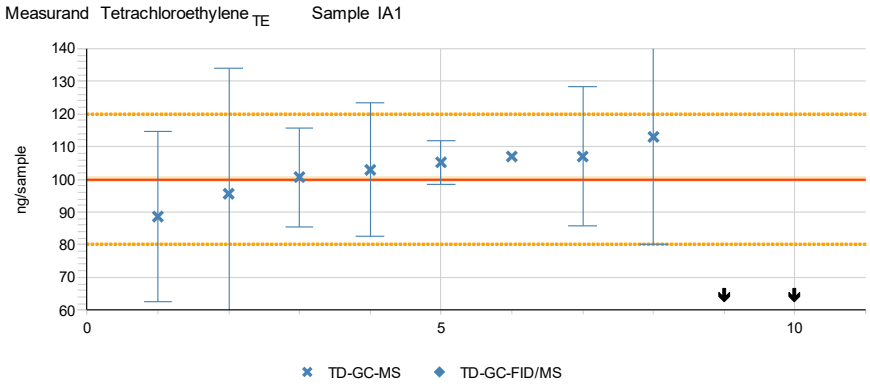

Measurand Naphthalene RCRF
Sample IA1
ng/sample
220
200
180
160
140
120
100
0
5
TD-GC-MS
TD-GC-FID/MS

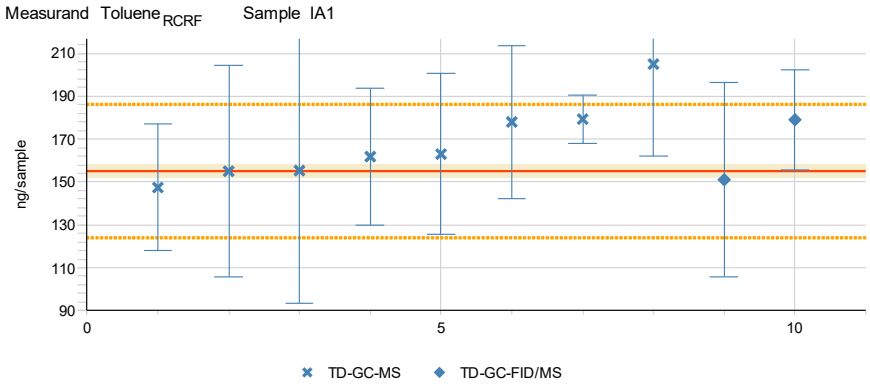

Measurand Naphthalene TE
Sample IA1
ng/sample
370
330
290
250
210
170
130
0
5
10
TD-GC-MS
TD-GC-FID/MS

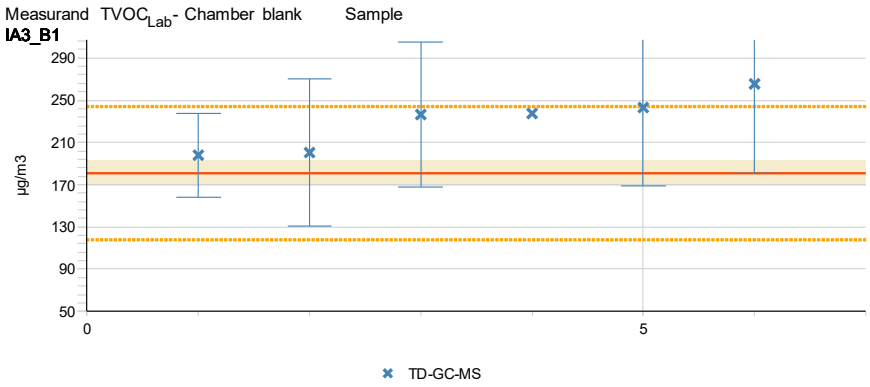

Measurand Styrene RCRF
Sample IA1
ng/sample
140
130
120
110
100
90
80
70
60
0
5
10
TD-GC-MS
TD-GC-FID/MS

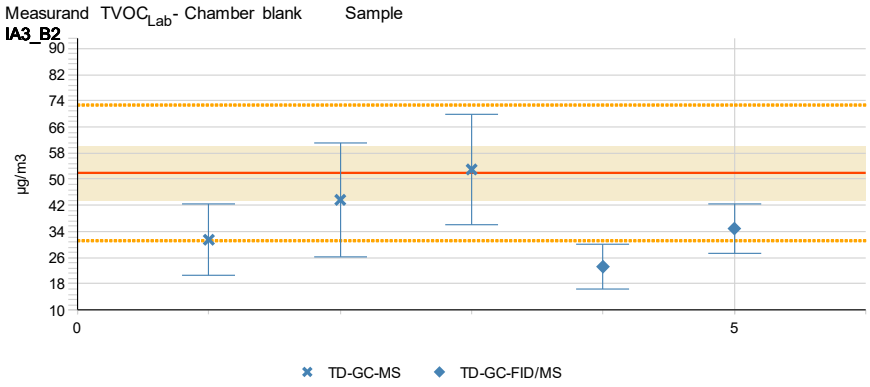

Measurand Styrene TE
Sample IA1
ng/sample
150
140
130
120
110
100
90
80
70
0
5
10
TD-GC-MS
TD-GC-FID/MS

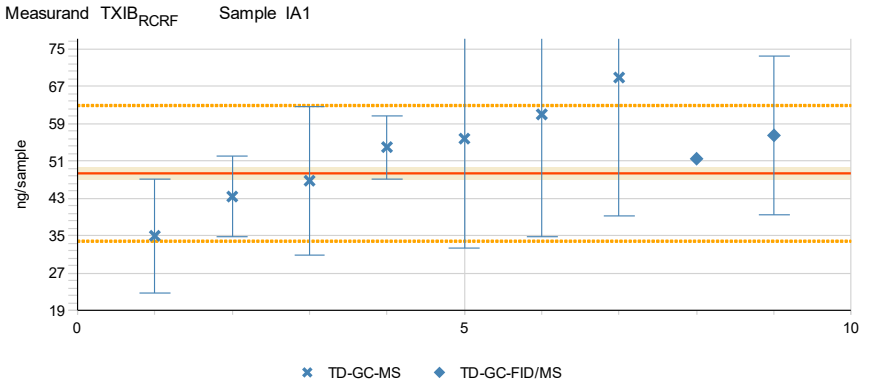

Measurand Tetrachloroethylene RCRF
Sample IA1
ng/sample
170
160
150
140
130
120
110
100
90
80
0
5
TD-GC-MS
TD-GC-FID/MS

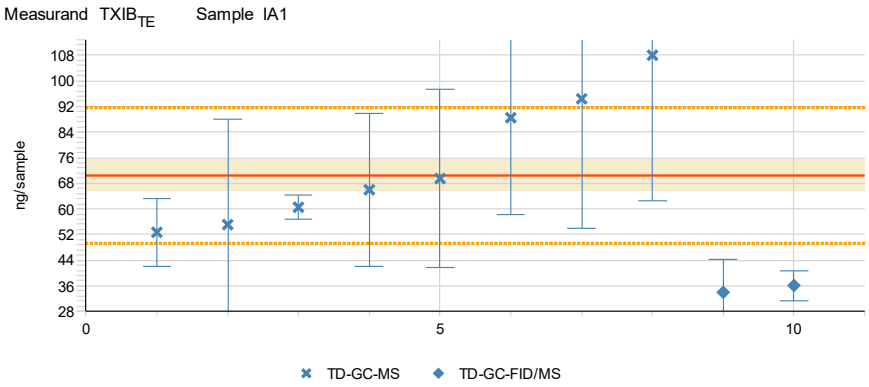

Measurand Tetrachloroethylene TE
Sample IA1
ng/sample
140
130
120
110
100
90
80
70
60
0
5
10
TD-GC-MS
TD-GC-FID/MS


Measurand Toluene RCRF
Sample IA1
ng/sample
210
190
170
150
130
110
90
0
5
10
TD-GC-MS
TD-GC-FID/MS


Measurand TVOC$_{Lab}$- Chamber blank Sample
IA3_B1
µg/m3
290
250
210
170
130
90
50
0
5
TD-GC-MS

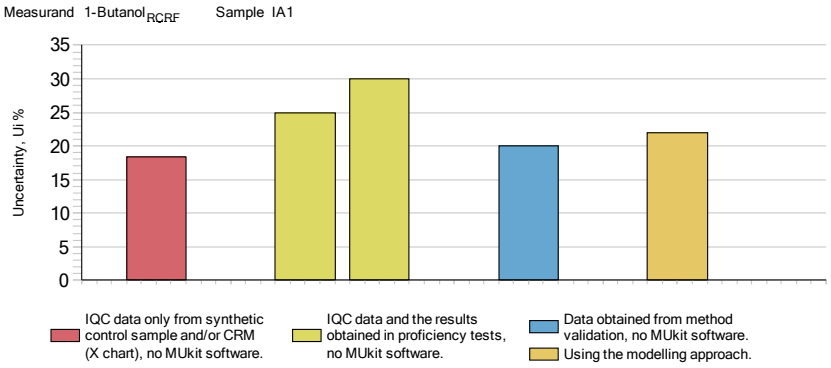

Measurand TVOC$_{Lab}$- Chamber blank Sample
IA3_B2
µg/m3
90
82
74
66
58
50
42
34
26
18
10
0
5
TD-GC-MS
TD-GC-FID/MS

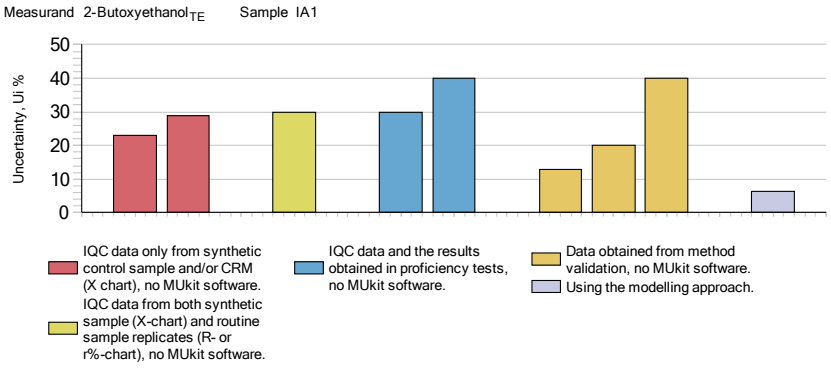

Measurand TXIB$_{RCRF}$ Sample IA1
ng/sample
75
67
59
51
43
35
27
19
0
5
10
TD-GC-MS
TD-GC-FID/MS

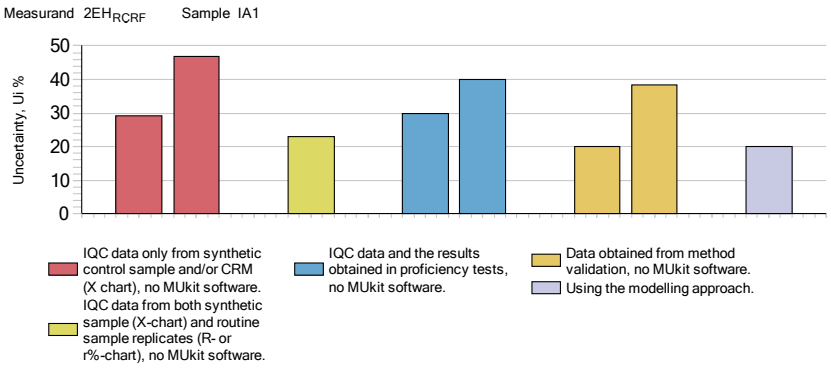

Measurand TXIB$_{TE}$
Sample IA1
ng/sample
108
100
92
84
76
68
60
52
44
36
28
0
5
10
TD-GC-MS
TD-GC-FID/MS

APPENDIX 13: Examples of measurement uncertainties reported by the participants

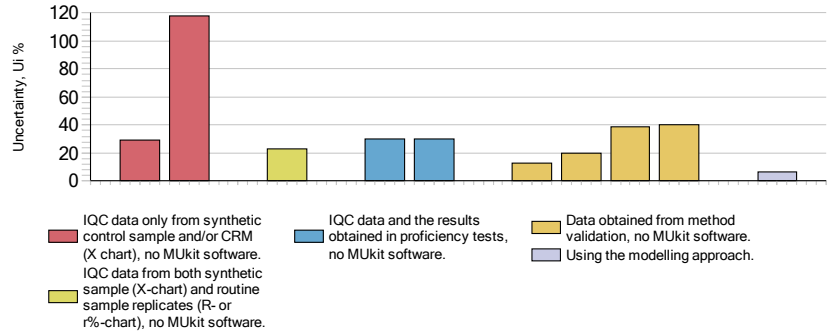
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g.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



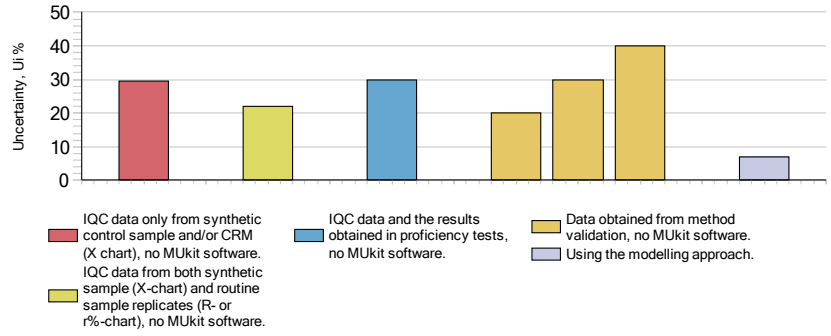




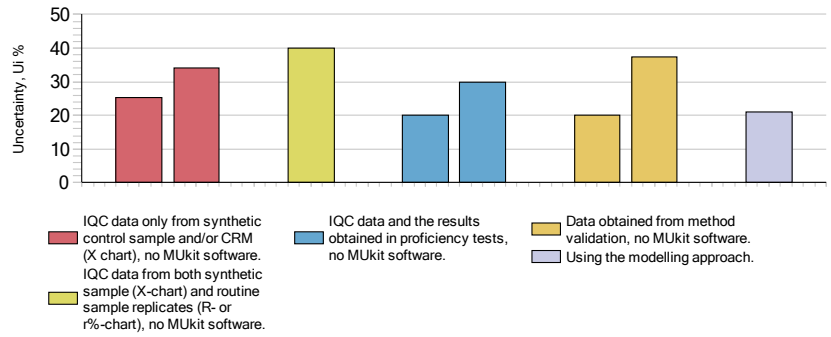
Measurand $2EH_{TE}$ Sample IA1



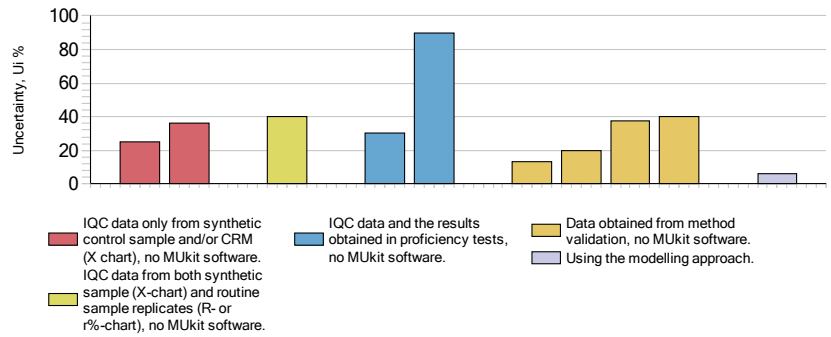
Measurand Alpha-$Pinene_{RCRF}$ Sample IA1

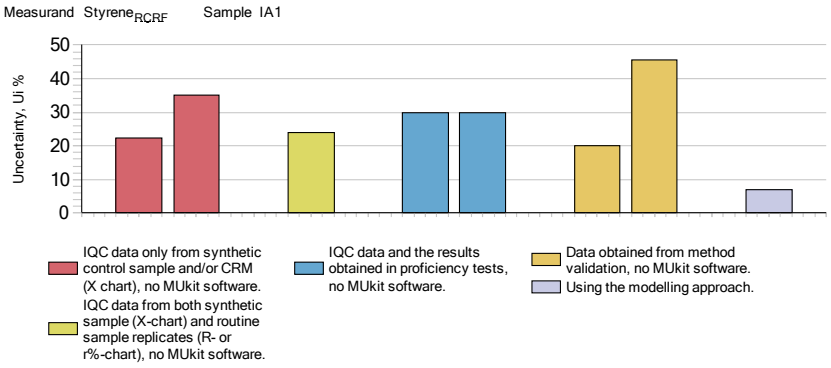


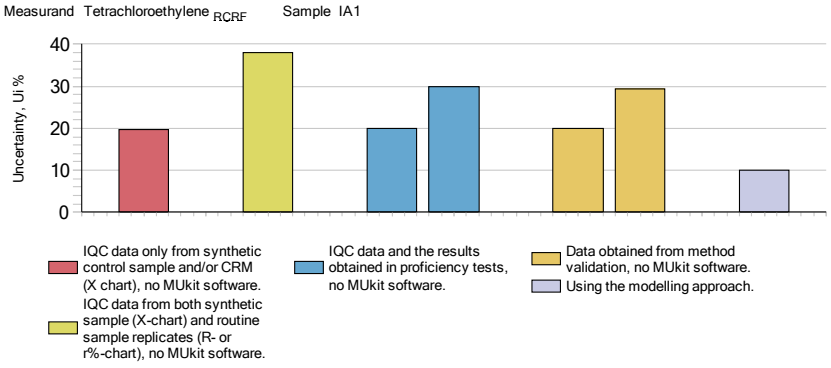
Measurand Naphthalene $_{RCRF}$ Sample IA1

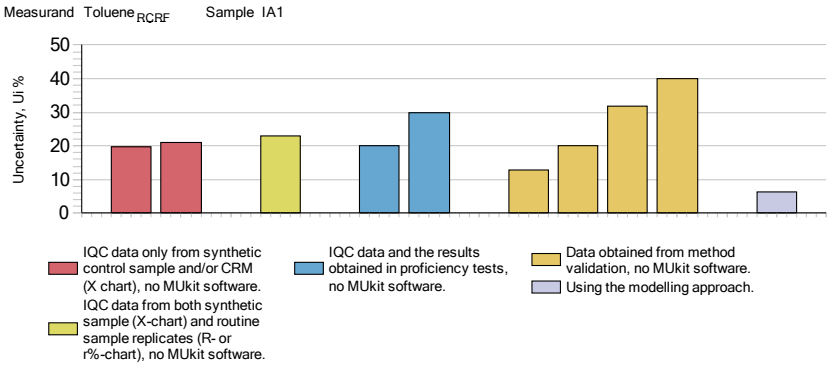


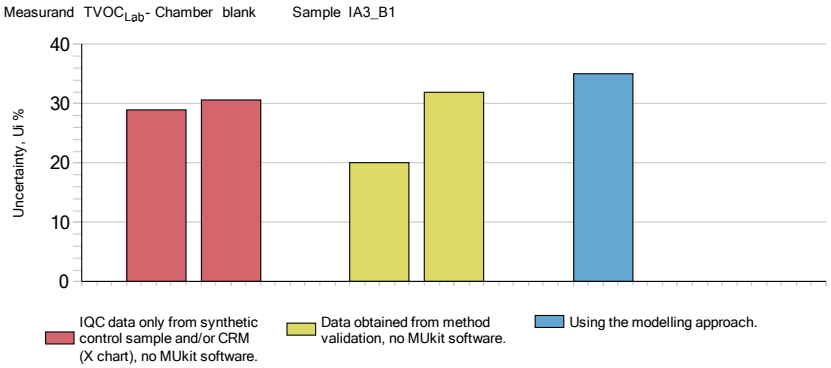
Measurand Naphthalene $_{TE}$ Sample IA1



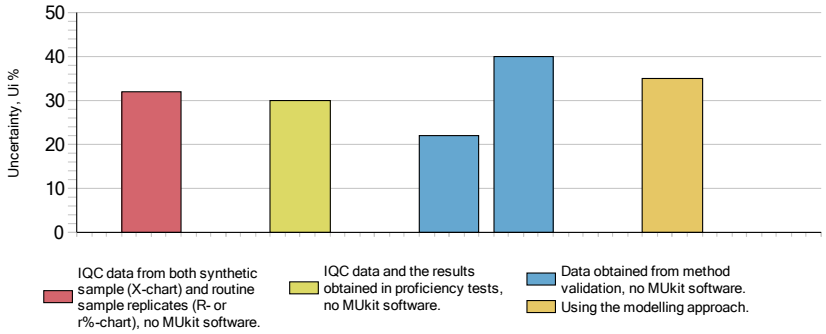

Measurand Styrene RCRF
Sample IA1
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.


Measurand Tetrachloroethylene RCRF
Sample IA1
Uncertainty, Ui %
40
30
20
10
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.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.

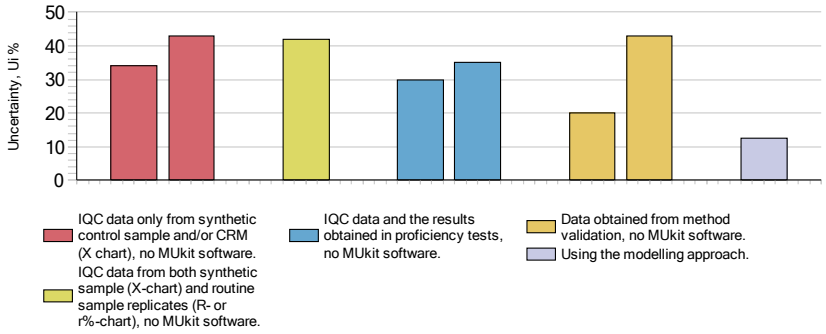

Measurand Toluene RCRF
Sample IA1
Uncertainty, Ui %
50
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.


Measurand TVOC Lab - Chamber blank
Sample IA3_B1
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

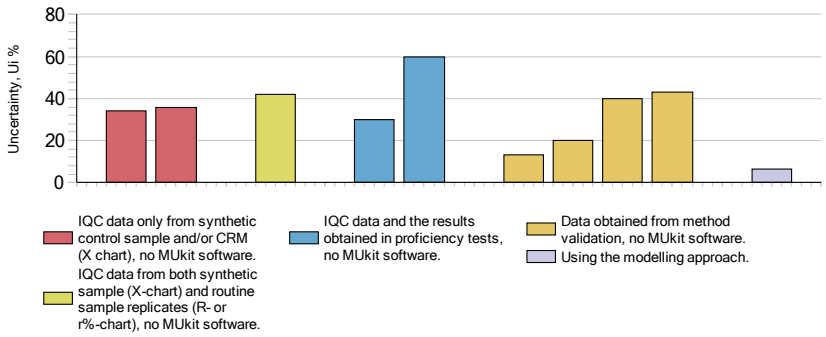
Measurand $TVOC_{Lab}$- Chamber blank Sample IA3_B2



Measurand $TXIB_{RCRF}$ Sample IA1



Measurand $TXIB_{TE}$ Sample IA1



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