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ABSTRACT

Interlaboratory Comparison 11/2020

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 September-October 2020 (IAVOC 11/2020). Further, the measurements of alpha-pinene, 1-butanol, 2-butoxyethanol, decane, ethylbenzene, 2EH (2-ethyl-1-hexanol), naphthalene, styrene, tetrachloroethylene, toluene, 1,2,4-trimethylbenzene, 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 71 % of the results reported by the participants were satisfactory when deviation of 15–35 % 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 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 sample comparisons

TIIVISTELMÄ

Laboratorioiden välinen vertailumittaus 11/2020

Proftest SYKE järjesti yhteistyössä Työterveyslaitoksen (TTL) kanssa vertailumittauksen sisäilman VOC-määrityksiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille syys-lokakuussa 2020 (IAVOC 11/2020). Vertailumittauksessa testattiin natiivinäytteistä kerättyjen TVOC-yhdisteiden määritysten vertailtavuutta Tenax TA-termodesorptioputkista sekä synteettisen näytteen alfa-pineeni, 1-butanoli, 2-butoksietanoli, dekaani, etyylibentseeni, 2EH (2-etyyli-1-heksanoli), naftaleeni, styreeni, tetrakloorietyleeni, tolueeni, 1,2,4-trimetyylibentseeni ja TXIB (2,2,4-trimetyyli-1,3-pentaanidiolidi-isobutyraatti) määritysten vertailtavuutta. Vertailumittaukseen osallistui yhteensä 8 laboratoriota. Koko tulosaineistossa hyväksyttäviä tuloksia oli 71 %, kun vertailuarvosta sallittiin 15–35 % poikkeama. Laskennallista pitoisuutta käytettiin vertailuarvona synteettisen näytteen omalla vasteella raportoiduille tuloksille. Muille testisuureille ja näytteille käytettiin vertailuarvona asiantuntijalaboratorion homogeenisuusmääritysten ja kierrosaikaisen tuloksen keskiarvoa. Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla.
Kiitos vertailumittauksen osallistujille!

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

SAMMANDRAG

Interkalibrering 11/2020

Proftest SYKE genomförde tillsammans med Arbetshälsoinstitutet (TTL) i september-oktober 2020 en interkalibrering (IAVOC 11/2020) 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, dekan, etylbensen, 2EH (2-etyl-1-hexanol), naftalen, styren, tetrakloroetylen, toluen, 1,2,4-trimetylbensen 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 och testresultat. Resultaten värderades med hjälp av z värden. I interkalibrering var 71 % av alla resultaten acceptabla, när en total deviation på 15–35 % från referensvärdet tillåts.
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 Finnish Institute of Occupational Health (FIOH) for VOC thermodesorption measurements (ISO 16000-6 [1]) from native indoor air samples in Tenax TA thermodesorption tubes (IAVOC 11/2020) in September-October 2020. Further, the measurements of alpha-pinene, 1-butanol, 2-butoxyethanol, decane, ethylbenzene, 2EH (2-ethyl-1-hexanol), naphthalene, styrene, tetrachloroethylene, toluene, 1,2,4-trimethylbenzene, 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 provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international standard ISO/IEC 17043 [2] and applying ISO 13528 [3] and IUPAC Technical report [4]. Proftest SYKE is accredited by 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 Proftest SYKE. The comparison follows the procedures of accredited schemes.

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 FIOH, accredited by FINAS, T013, www.finas.fi/sites/en)

2.2 Participants

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

Six 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 8 in this comparison.

2.3 Samples and delivery

Participants received following samples:

- Synthetic sample (sample code IA1)
- Blank sample (IA2)
- Two native indoor air samples (IA3) 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 by 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 28 September 2020 and they arrived to the participants at the latest on 30 September 2020.

All participants reported their results as requested, at the latest on 19 October 2020. The preliminary result report was delivered to the participants on 26 October 2020. The participants were requested to return the Tenax TA thermodesorption tubes to the provider latest on 6 November 2020. All participants returned the tubes to the provider. 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 five to six subsamples (Appendix 3). Homogeneity of IA3 samples was tested by measuring TVOC as toluene equivalent (TE) from four samples. In the calculations the samples collected from the same duct adapter were treated as parallel samples making four parallel measurements (Appendix 3). As the samples are known

to be stable, some of the reported test results of the expert laboratory were added to the homogeneity testing calculations as well as for the final evaluation of the homogeneity and stability of the synthetic samples (Appendix 3). 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 5. The comment from the participant focused to some measurement problems. The comments from the provider are mainly focused to the lacking conversancy to the given information with the results. 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

To test the normality of the data the Kolmogorov-Smirnov test was applied. The outliers were rejected according to the Grubbs or Hampel 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. If the result has been reported as below detection limit, it has not been included in the statistical 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 (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 was used as the assigned value. The evaluation of the results reported as toluene equivalents (TE, semiquantitative) turned out to be challenging in the current ILC. Due to the high difference between the homogeneity test results (131 ng/sample) and the median of the reported participant results (184 ng/sample), the assigned value was not set for the results of alpha-pinene$_{TE}$ in the synthetic sample (IA1).

For the calculated assigned values, the expanded uncertainties were 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 [6].

For the calculated assigned values, the expanded uncertainties were between 2.0 % and 2.8 % for the results based on compound specific responses (RCRF) and between 1.5 % and 14 % 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 $TVOC_{Lab}$-Chamber blank, the expanded uncertainty of the assigned was 6 % (Appendix 5). **After reporting the preliminary results no changes have been done for the assigned values.**

2.6.3 Proficiency assessment procedure

The standard deviation for proficiency assessment was estimated on the 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 results of this interlaboratory comparison were evaluated with the z scores (Appendix 2). The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 15–35 %. **After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.**

The reliability of the assigned value for the other test items than the synthetic sample as 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 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
IA1	1,2,4-Trimethylbenzene$_{TE}$, Naphthalene$_{TE}$, Styrene$_{TE}$,

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 as subtracted by the result of the chamber blank ($TVOC_{Lab}$-Chamber blank).

Table 1. The summary of the results in the proficiency test IAVOC 11/2020.

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$_{RCRF}$	IA1	ng/sample	150	161	-	166	*18*	*10.9*	20.0	6	83
Alpha-Pinene$_{TE}$	IA1	ng/sample	-	189	189	184	41	21.6	-	8	-
Decane$_{RCRF}$	IA1	ng/sample	105	111	-	114	*10*	*9.0*	20.0	4	75
Decane$_{TE}$	IA1	ng/sample	96.9	112.3	112.3	117.0	28.7	25.6	35.0	8	63
1-Butanol$_{RCRF}$	IA1	ng/sample	186	172	-	171	*11*	*6.2*	20.0	5	100
1-Butanol$_{TE}$	IA1	ng/sample	60.5	63.4	63.3	62.0	13.3	21.0	25.0	8	75
2-Butoxyethanol$_{RCRF}$	IA1	ng/sample	154	133	-	132	*11*	*8.1*	20.0	5	60
2-Butoxyethanol$_{TE}$	IA1	ng/sample	58.3	64.3	64.5	65.0	16.1	25.0	30.0	8	50
Ethylbenzene$_{RCRF}$	IA1	ng/sample	67.4	66.7	-	67.2	*4,2*	*6.2*	15.0	6	100
Ethylbenzene$_{TE}$	IA1	ng/sample	66.1	81.1	80.8	79.7	15.1	18.7	35.0	8	75
2EH$_{RCRF}$	IA1	ng/sample	107	107	-	103	*12*	*11.5*	20.0	7	86
2EH$_{TE}$	IA1	ng/sample	74.1	90.0	-	90.9	*17.9*	*19.9*	30.0	8	50
Naphthalene$_{RCRF}$	IA1	ng/sample	81.3	84.3	82.9	83.9	8.1	9.7	20.0	7	86
Naphthalene$_{TE}$	IA1	ng/sample	107	125	125	129	30	24.0	30.0	8	63
Styrene$_{RCRF}$	IA1	ng/sample	180	201	201	187	35	17.4	20.0	7	57
Styrene$_{TE}$	IA1	ng/sample	161	197	197	203	36	18.1	30.0	8	63
Tetrachloroethylene$_{RCRF}$	IA1	ng/sample	64.5	65.8	-	67.5	*4,1*	*6.2*	15.0	6	100
Tetrachloroethylene$_{TE}$	IA1	ng/sample	40.3	49.0	48.7	49.7	20.5	42.2	30.0	8	50
Toluene$_{RCRF}$	IA1	ng/sample	109	106	104	101	14	13.5	20.0	8	88
1,2,4-Trimethylbenzene$_{RCRF}$	IA1	ng/sample	63.5	65.9	-	66.3	*5.9*	*9.0*	15.0	5	100
1,2,4-Trimethylbenzene$_{TE}$	IA1	ng/sample	69.2	78.5	-	84.1	*13.6*	*17.3*	35.0	8	75
TXIB$_{RCRF}$	IA1	ng/sample	74.0	73.1	-	74.2	*14.9*	*20.4*	20.0	7	43
TXIB$_{TE}$	IA1	ng/sample	81.7	96.7	95.4	97.1	33.7	35.3	30.0	8	50
TVOC$_{Lab}$-Chamber blank	IA3	µg/m^3	228	258	258	271	84	32.7	35.0	8	75

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

The results of the individual measurands analysed from the synthetic sample (IA1) minus the tube blank (IA2) were reported both as compound specific responses (RCRF, Reference Compound Response Factor) and as toluene equivalents (TE).

The robust standard deviation or the standard deviation for the results of the synthetic sample (IA1) and the chamber sample (IA3) varied from 6.8 to 42 % (Table 1). The variation was in the same range than in the previous similar ILC IAVOC 10/2019 [7].

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the ILC. A survey 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 Used analytical methods

In the background survey participants were asked to report some basic information of the used analytical methods (Appendix 11). Five of eight participants answered to the survey. 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. One participant used TD-GC-FID/MS while the rest used TD-GC-MS.

3.2.2 Results as toluene equivalent and compound specific response

In the ILC the participants were requested to report the results for the synthetic sample both based on the compound specific response (RCRF) and the toluene equivalent (TE). One participant reported only the results based on the toluene equivalent (Appendices 7, 8, 12).

In this ILC the variation of the results reported based on the toluene equivalent was higher than in the previous ILC IAVOC 10/2019 [7]. Therefore, for one measurand (alpha-pinene$_{TE}$) it was not possible to evaluate the results, and in some cases the standard deviation for proficiency assessment was higher than before.

In this ILC a similar kind of difference between the compound specific response results and the toluene equivalent results was noticed as in the previous similar kind of ILCs, e.g. IAVOC 10/2019 [7]. The results based on the toluene equivalent are semiquantitative [1]. Figure 1 illustrates that semiquantitative nature of toluene equivalent results. For example, with the same measurement response, the result for 2-butoxyethanol is 200 ng/sample as toluene equivalent (TE) and 440 ng/sample as compound specific response (RCRF). Further, the results for TXIB are 200 ng/sample (TE) and 160 ng/sample (RCRF) (Fig. 1). It is evident, that it is not possible to estimate one single conversion factor to convert the result from compound specific response to toluene equivalent or vice versa for different measurands. The information of desorption of toluene (i.e. toluene equivalent response) is not adequate to estimate the desorption of other compounds even in similar conditions. Thus, it is recommended to use the compound specific responses instead of the semiquantitative toluene equivalent results. The international standard ISO 16000-6 supports this recommendation [1].

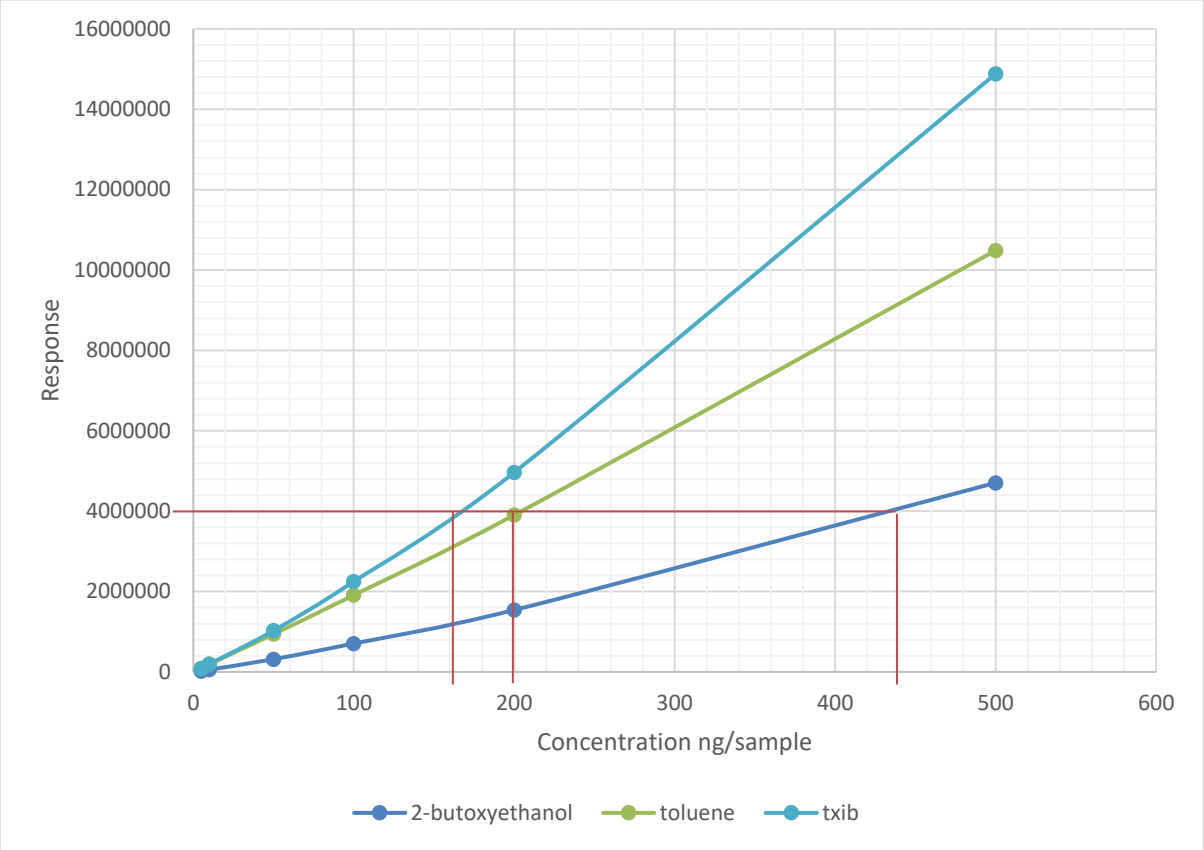


Figure 1. Graphical example of the differences between the compound specific response (RCRF) and toluene equivalent (TE) results. The lines are the compound specific calibration curves for toluene (green line), 2-butoxyethanol (dark blue) and TXIB (light blue). The red line shows an example of measurement response (4000000). Data from FIOH (not from the samples in this ILC).

3.3 Uncertainties of the results

Almost all participants reported the expanded measurement uncertainties (k=2) with at least some of their results (Table 2, Appendix 13). Three 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 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 participants used it [8, 9]. 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 2. The range of the reported expanded measurement uncertainties (k=2, U_i%).

Alpha-pinene$_{RCRF}$	6.3-30	Naphthalene$_{RCRF}$	3.6-40
Alpha-pinene$_{TE}$	9-35	Naphthalene$_{TE}$	9-**90**
Decane$_{RCRF}$	7.9-35	Styrene$_{RCRF}$	7.6-30
Decane$_{TE}$	9-35	Styrene$_{TE}$	9-35
1-Butanol$_{RCRF}$	5.6-30	Tetrachloroethylene$_{RCRF}$	8.2-30
1-Butanol$_{TE}$	9-**80**	Tetrachloroethylene$_{TE}$	9-35
2-Butoxyethanol$_{RCRF}$	6.9-40	1,2,4-Trimethylbenzene$_{RCRF}$	5.3-34
2-Butoxyethanol$_{RCRF}$	9-**70**	1,2,4-Trimethylbenzene$_{TE}$	9-**60**
Ethylbenzene$_{RCRF}$	8-30	Toluene$_{RCRF}$	9-35
Ethylbenzene$_{TE}$	9-35	TXIB$_{RCRF}$	4.6-**50**
2EH$_{RCRF}$	4.4-40	TXIB$_{TE}$	9-**60**
2EH$_{TE}$	95-3	TVOC$_{Lab}$-Chamber blank	22-35

The estimated measurements uncertainties varied for the tested measurands and samples (Table 2). 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.

For some measurands uncertainties exceed 50 % (bold in Table 2). 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, 71 % of the results evaluated based on z scores were satisfactory when accepted deviation from the assigned value was 15–35 % at the 95 % confidence level (Appendix 9). Six of eight participant used the accredited methods for at least some of the measurands and 68 % of those results were satisfactory. In the previous ILC IAVOC 10/2019, the performance was satisfactory for 77 % of the all participants when accepted deviation from the assigned value was 20–40 % [7].

The summary of the performance evaluation is shown in Table 3. The percentage of the satisfactory results varied between 61 % and 81 % for the tested sample types. The overall performance for the synthetic sample (IA) was clearly better, 81 %, for the results based on the compounds own response (RCRF) than for the results based on toluene equivalents (TE), 61 %

(Table 3). In the previous similar ILC IAVOC 10/2019 the percentage of the satisfactory results varied between 75–83 % for the tested sample types [7]. The performance for the synthetic sample IA1 results based on RCRF was somewhat better, while the performance of the synthetic sample IA1 results based on TE was clearly lower than in the previous ILC IAVOC 10/2019 (Table 3).

Based on the results of this ILC as well as on the results of the previous similar ILC IAVOC 10/2019 and ISO 16000-6, it is further recommended to increase the number of the pure compounds in calibrations [1, 7]. The values based on toluene equivalents are only semiquantitative results.

Table 3. Summary of the performance evaluation in the interlaboratory comparison IAVOC 11/2020.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value at 95 % confidence level (%)	Remarks
IA1, RCRF	81	15-20	• Difficulties in measurements for some of the participants; satisfactory results < 80 % for 2-butoxyethanol and decane. • In the previous ILC IAVOC 10/2019 the performance was satisfactory for 77 % of the results when accepting the deviation of 20-30 % from the assigned value [7].
IA1, TE	61	25-35	• The participants have difficulties in measurements; satisfactory results **< 80 % for all measurands.** • Somewhat uncertain estimation for 1,2,4-trimethylbenzene, naphthalene and styrene. • In the previous ILC IAVOC 10/2019 the performance was satisfactory for 75 % of the results when accepting the deviation of 20-30 % from the assigned value [7].
$IA3_{Lab}$-Chamber blank	75	35	• In the previous ILC IAVOC 10/2019 the performance was satisfactory for 83/80% % of the results when accepting the deviation of 35/40 % from the assigned value [7].

5 Summary

Proftest SYKE carried out the interlaboratory comparison (ILC) in cooperation with Finnish Institute of Occupational Health (FIOH) for VOC thermodesorption measurements (ISO 16000-6 [1]) from native indoor air samples in Tenax TA thermodesorption tubes (IAVOC 11/2020) in September-October 2020. Further, the measurements of alpha-pinene, 1-butanol, 2-butoxyethanol, decane, ethylbenzene, 2EH (2-ethyl-1-hexanol), naphthalene, styrene, tetrachloroethylene, toluene, 1,2,4-trimethylbenzene, 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 and the test results of the expert laboratory was used as the assigned value. For the calculated assigned values, the expanded uncertainties were between 2.0 % and 2.8 % for the results based on compound specific responses (RCRF) and between 1.5 % and 14 % 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 $TVOC_{Lab}$-Chamber blank, the expanded uncertainty of the assigned values was 6 %.

The evaluation of the performance was based on the z scores. In this interlaboratory comparison 71 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value from 15 to 35 % at 95 % confidence level. Six of eight participant used the accredited methods for at least some of the measurands and 68 % of those results were satisfactory. In this ILC the participants were requested to report the results for the synthetic sample both based on the compound specific response and toluene equivalent. Based on the results it is not possible to have a conversion factor to convert the result from compound response to toluene equivalent or vice versa. The information of desorption of toluene (i.e. toluene equivalent response) is not adequate to estimate the desorption of other compounds even in similar conditions. Thus, it is recommended to use the compound specific responses instead of semiquantitative toluene equivalents.

6 Summary in Finnish

Proftest SYKE järjesti vertailumittauksen yhteistyössä Työterveyslaitoksen (TTL) kanssa sisäilman VOC-määrityksiä (ISO 16000-6) Tenax TA-termodesorptioputkista tekeville laboratorioille syys-lokakuussa 2020 (IAVOC 11/2020). Vertailumittauksessa testattiin natiivinäytteistä kerättyjen TVOC-yhdisteiden määritysten vertailtavuutta Tenax TA-termodesorptioputkista sekä synteettisen näytteen alfa-pineeni, 1-butanoli, 2-butoksietanoli, dekaani, etyylibentseeni, 2EH (2-etyyli-1-heksanoli), naftaleeni, styreeni, tetrakloorietyleeni, tolueeni, 1,2,4-trimetyylibentseeni 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 homogeenisuustestitulosten ja kierrosaikaisten tulosten keskiarvoa.

Synteettisen näytteen vertailuarvon laajennettu epävarmuus vaihteli välillä 2,0–2,8 % omalla vasteella raportoiduille tuloksille ja välillä 1,5–14 % tolueeniekvivalenttina (TE) raportoiduille tuloksille. Kammionäytteen vertailuarvon laajennettu epävarmuus oli 6 %.

Osallistujien pätevyyden arviointi tehtiin z-arvojen avulla. Koko tulosaineistossa hyväksyttäviä tuloksia oli 71 %, kun vertailuarvosta sallittiin 15–35 % poikkeama 95 % luottamusvälillä. Kuusi osallistujaa kahdeksasta ilmoitti käyttäneensä akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 68 %. 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 tolueeniekvivalentiksi tai päinvastoin. Tolueenin desorptiokäyttäytymisestä (ts. tolueenin ekvivalenttivaste) ei saada riittävästi tietoa muiden yhdisteiden desorptiokäyttäytymisen arvioimiseksi edes samanlaisissa olosuhteissa. Siksi on suositeltavaa käyttää yhdistekohtaisia vasteita semikvantitatiivisten tolueeniekvivalenttien sijaan.

REFERENCES

1. ISO 16000-6, 2011. Indoor air- Part 6: Determination of volatile organic compounds in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS or MS-FID.

2. SFS-EN ISO 17043, 2010. Conformity assessment – General requirements for Proficiency Testing.

3. ISO 13528, 2015. Statistical methods for use in proficiency testing by interlaboratory comparisons.

4. Thompson, M., Ellison, S. L. R., Wood, R., 2006. The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry laboratories (IUPAC Technical report).

5. Ministry of Social Affairs and Health 2015. Decree of the Ministry of Social Affairs and Health on Health-related Conditions of Housing and Other Residential Buildings and Qualification Requirements for Third-party Experts 545/2015. https://www.finlex.fi/en/laki/kaannokset/2015/en20150545.pdf (in English), https://www.finlex.fi/fi/laki/alkup/2015/20150545 (in Finnish)

6. Proftest SYKE Guide for laboratories: www.syke.fi/proftest/en → Running proficiency test (www.syke.fi/download/noname/%7B3FFB2F05-9363-4208-9265-1E2CE936D48C%7D/39886).

7. Leivuori, M., Hovi, H., Koivikko, R., Tervonen, K., Lanteri, S. and Ilmakunnas M., 2020. Interlaboratory comparison 10/2019. VOC measurements from indoor air samples. Reports of the Finnish Environment Institute 3 (2020). 57 pp. https://helda.helsinki.fi/handle/10138/310385.

8. Näykki, T., Virtanen, A. and Leito, I., 2012. Software support for the Nordtest method of measurement uncertainty evaluation. Accred. Qual. Assur. 17: 603-612. *MUkit website: www.syke.fi/envical.*

9. Magnusson B., Näykki T., Hovind H., Krysell M., Sahlin E., 2017. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories. Nordtest Report TR 537 (ed. 4). www.nordtest.info.

10. Ellison, S., L., R. and Williams, A. (Eds). (2012) Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, ISBN 978-0-948926-30-3.

11. ISO/IEC Guide 98-3:2008. Uncertainty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM: 1995).

APPENDIX 1: Participants in the proficiency test

Country	Participant
Finland	Finnish Institute of Occupational Health
	Kiwa Inspecta Oy, KiwaLab, Oulu
	MetropoliLab Oy
	Mikrobioni Oy
	Ositum Oy
	WSP Finland Oy, Sisäilmalaboratorio, Jyväskylä
Germany	ERGO Umweltinstitut GmbH
Portugal	INEGI - Institute of Science and Innovation in Mechanical and Industrial Engineering, Laboratory for Indoor Air

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 %
Decane	Sigma Aldrich 30540, ≥99.8 %
Ethylbenzene	Sigma Aldrich 03079, ≥99.5 %
2-Ethyl-1-hexanol, 2EH	Sigma Aldrich 08607, ≥99.5 %
Methanol	Merck 1.00837.0000 for GC MS SupraSolv, ≥99.8 %
Naphthalene	Sigma Aldrich 84679, ≥99.7 %
Styrene	Merck 8.07679.0100 for synthesis, ≥99.9 %
Tetrachloroethylene	VWR 83950.290 for spectroscopy, ≥99.9 %
Toluene	Sigma Aldrich 89680, ≥99.9 %
1,2,4-Trimethylbenzene	Sigma Aldrich T73601, ≥98.5 %
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	0.01501	75.05	150.1	150
1-Butanol	0.0186	93.0	186	186
Decane	0.01054	52.7	105.4	105
Ethylbenzene	0.00675	33.75	67.5	67.4
2-Butoxyethanol	0.01542	77.1	154.2	154
2EH	0.01070	53.5	107	107
Methanol	15.597	-	-	-
Naphthalene	0.00814	40.7	81.4	81.3
Styrene	0.01801	90.05	180.1	180
Tetrachloroethylene	0.00646	32.3	64.6	64.5
Toluene	0.01092	54.6	109.2	109
1,2,4-Trimethylbenzene	0.00645	32.25	64.5	63.5
TXIB	0.00747	37.35	74.7	74.0

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 IAVOC 10/2019 [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 IA started on 3 September 2020 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) 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) collection started 24 hours after the chamber was closed, on 4 September 2020.

APPENDIX 3: Homogeneity of the samples

The homogeneity of the samples collected from the chamber (IA3) was tested by measuring TVOC as toluene equivalents (TE) from four samples. In the calculations the samples collected from the same duct adapter were treated as parallel samples making four parallel measurements (Table 1). Homogeneity of the synthetic sample IA1 was tested by measuring the tested substances (RCRF, Reference Compound Response Factor) from five or six 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 [3, 4].

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/ $TVOC_{Lab}$-Chamber Blank	228	4*	17.5	40.0	17.6	0.44	Yes	943	1245	Yes

* Results from the homogeneity testing and the results of the round of the expert laboratory. Totally eight samples, from which parallel samples were from each duct adapter.

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.

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	170	6	10	17.0	3.62	0.21	Yes
1-Butanol	195	5*	10	19.5	3.86	0.20	Yes
2-Butoxyethanol	130	6	10	13.0	5.18	0.40	Yes
Decane	111	6	10	11.1	4.64	0.42	Yes
Ethylbenzene	68.6	6	7.5	5.14	1.66	0.32	Yes
2EH	110	6	10	11.0	2.21	0.20	Yes
Naphthalene	84,4	6	10	8.44	2.38	0.28	Yes
Styrene	181	6	10	18.1	2.93	0.17	Yes
Tetrachloroethylene	61.8	6	7.5	4.64	1.12	0.24	Yes
1,2,4-Trimethylbenzene	61.2	6	7.5	4.60	0.70	0.15	Yes
Toluene	102	6	10	10.2	1.21	0.12	Yes
TXIB	73.6	5*	10	7.36	1.34	0.18	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 proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments to the results	Action / Proftest SYKE
2	The participant informed, that their calibration responses changed during the measurements.	The provided acknowledged the information.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
5	The participant did not report the expanded measurement uncertainties for Ethylbenzene$_{TE}$ in the sample IA1. Participant reported that their method is accredited. The measurement uncertainty should be always reported for accredited measurements.
5, 6, 7	The participants did not report the status of their accreditation for some measurands. The provider recommended to follow up the given instructions of the requested background information.

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}
1,2,4-Trimethylbenzene$_{RCRF}$	IA1	ng/sample	63.5	1.8	2.8	Calculated value	0.19
1,2,4-Trimethylbenzene$_{TE}$	IA1	ng/sample	69.2	9.0	13.0	Mean value of the expert laboratory	0.37
1-Butanol$_{RCRF}$	IA1	ng/sample	186	4	2.0	Calculated value	0.10
1-Butanol$_{TE}$	IA1	ng/sample	60.5	0.9	1.5	Mean value of the expert laboratory	0.06
2-Butoxyethanol$_{RCRF}$	IA1	ng/sample	154	3	2.0	Calculated value	0.10
2-Butoxyethanol$_{TE}$	IA1	ng/sample	58.3	2.9	4.9	Mean value of the expert laboratory	0.16
2EH$_{RCRF}$	IA1	ng/sample	107	2	2.1	Calculated value	0.11
2EH$_{TE}$	IA1	ng/sample	74.1	4.9	6.6	Mean value of the expert laboratory	0.22
Alpha-Pinene$_{RCRF}$	IA1	ng/sample	150	3	2.1	Calculated value	0.11
Alpha-Pinene$_{TE}$	IA1	ng/sample	-	-	-	-	-
Decane$_{RCRF}$	IA1	ng/sample	105	2	2.1	Calculated value	0.11
Decane$_{TE}$	IA1	ng/sample	96.9	11.6	12.0	Mean value of the expert laboratory	0.34
Ethylbentzene$_{RCRF}$	IA1	ng/sample	67.4	1.6	2.4	Calculated value	0.16
Ethylbenzene$_{TE}$	IA1	ng/sample	66.1	7.9	12.0	Mean value of the expert laboratory	0.34
Naphthalene$_{RCRF}$	IA1	ng/sample	81.3	1.9	2.3	Calculated value	0.12
Naphthalene$_{TE}$	IA1	ng/sample	107	15	14.0	Mean value of the expert laboratory	0.47
Styrene$_{RCRF}$	IA1	ng/sample	180	4	2.0	Calculated value	0.10
Styrene$_{TE}$	IA1	ng/sample	161	19	12.0	Mean value of the expert laboratory	0.40
Tetrachloroethylene$_{RCRF}$	IA1	ng/sample	64.5	1.5	2.4	Calculated value	0.16
Tetrachloroethylene$_{TE}$	IA1	ng/sample	40.3	4.0	10.0	Mean value of the expert laboratory	0.33
Toluene$_{RCRF}$	IA1	ng/sample	109	2	2.1	Calculated value	0.11
TVOC$_{Lab}$-Chamber blank	IA3	µg/m3	228	14	6.0	Mean of the expert laboratory	0.17
TXIB$_{RCRF}$	IA1	ng/sample	74.0	1.9	2.5	Calculated value	0.13
TXIB$_{TE}$	IA1	ng/sample	81.7	3.4	4.2	Mean value of the expert laboratory	0.14

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}**
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		-0.62	69.2	35	61.7	84.1	78.5	13.6	17.3	6
1-Butanol$_{RCRF}$	ng/sample	IA1		-1.51	186	20	158	171	172	11	6.2	5
1-Butanol$_{TE}$	ng/sample	IA1		0.36	60.5	25	63.2	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		0.22	58.3	30	60.2	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		-1.05	107	20	96	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		3.68	74.1	30	115.0	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		19.20	150	20	438	166	161	18	10.9	5
Alpha-Pinene$_{TE}$	ng/sample	IA1					395	184	189	36	19.1	7
Decane$_{TE}$	ng/sample	IA1		0.42	96.9	35	104.0	117.0	112.3	25.3	22.5	7
Ethylbentzene$_{RCRF}$	ng/sample	IA1		-0.97	67.4	15	62.5	67.2	66.7	4.2	6.2	6
Ethylbenzene$_{TE}$	ng/sample	IA1		0.22	66.1	35	68.7	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		0.53	81.3	20	85.6	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		0.25	107	30	111	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		2.09	180	20	218	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		-0.37	161	30	152	203	197	31	16.0	8
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		1.16	64.5	15	70.1	67.5	65.8	4.1	6.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		-3.19	40.3	30	21.0	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		-1.76	109	20	90	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		-1.92	228	35	152	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		1.00	74.0	20	81.4	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		-0.69	81.7	30	73.3	97.1	96.7	32.3	33.4	8

Participant 2												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		2.58	69.2	35	100.5	84.1	78.5	13.6	17.3	6
1-Butanol$_{TE}$	ng/sample	IA1		-0.22	60.5	25	58.8	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-0.45	58.3	30	54.4	65.0	64.3	14.7	22.8	7
2EH$_{TE}$	ng/sample	IA1		0.76	74.1	30	82.5	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{TE}$	ng/sample	IA1					248	184	189	36	19.1	7
Decane$_{TE}$	ng/sample	IA1		2.22	96.9	35	134.5	117.0	112.3	25.3	22.5	7
Ethylbenzene$_{TE}$	ng/sample	IA1		2.29	66.1	35	92.6	79.7	81.1	13.9	17.1	8
Naphthalene$_{TE}$	ng/sample	IA1		1.36	107	30	129	129	125	26	21.1	8
Styrene$_{TE}$	ng/sample	IA1		2.04	161	30	210	203	197	31	16.0	8
Tetrachloroethylene$_{TE}$	ng/sample	IA1		6.93	40.3	30	82.2	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		0.71	109	20	117	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		0.95	228	35	266	271	258	74	28.8	8
TXIB$_{TE}$	ng/sample	IA1		2.55	81.7	30	112.9	97.1	96.7	32.3	33.4	8

Participant 3												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		3.13	69.2	35	107.1	84.1	78.5	13.6	17.3	6
1-Butanol$_{TE}$	ng/sample	IA1		3.11	60.5	25	84.0	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{TE}$	ng/sample	IA1		2.62	58.3	30	81.2	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		4.60	107	20	156	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		2.24	74.1	30	99.0	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{TE}$	ng/sample	IA1					219	184	189	36	19.1	7
Decane$_{TE}$	ng/sample	IA1		2.81	96.9	35	144.5	117.0	112.3	25.3	22.5	7
Ethylbenzene$_{TE}$	ng/sample	IA1		3.43	66.1	35	105.8	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		2.88	81.3	20	104.7	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		3.02	107	30	156	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		3.87	180	20	250	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		3.60	161	30	248	203	197	31	16.0	8
Tetrachloroethylene$_{TE}$	ng/sample	IA1		3.71	40.3	30	62.7	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		2.51	109	20	136	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		3.35	228	35	362	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		2.91	74.0	20	95.5	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		1.84	81.7	30	104.2	97.1	96.7	32.3	33.4	8

Participant 4												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{RCRF}$	ng/sample	IA1		1.51	63.5	15	70.7	66.3	65.9	5.9	9.0	5
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		0.94	69.2	35	80.6	84.1	78.5	13.6	17.3	6
1-Butanol$_{RCRF}$	ng/sample	IA1		-0.07	186	20	185	171	172	11	6.2	5
1-Butanol$_{TE}$	ng/sample	IA1		14.16	60.5	25	167.6	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		3.76	154	20	212	132	133	11	8.1	4
2-Butoxyethanol$_{TE}$	ng/sample	IA1		7.42	58.3	30	123.2	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		1.30	107	20	121	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		4.49	74.1	30	124.0	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		1.08	150	20	166	166	161	18	10.9	5
Alpha-Pinene$_{TE}$	ng/sample	IA1					180	184	189	36	19.1	7
Decane$_{RCRF}$	ng/sample	IA1		7.16	105	20	180	114	111	10	9.0	3
Decane$_{TE}$	ng/sample	IA1		4.46	96.9	35	172.5	117.0	112.3	25.3	22.5	7
Ethylbentzene$_{RCRF}$	ng/sample	IA1		0.56	67.4	15	70.2	67.2	66.7	4.2	6.2	6
Ethylbenzene$_{TE}$	ng/sample	IA1		0.57	66.1	35	72.7	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		0.32	81.3	20	83.9	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		-0.88	107	30	93	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		0.31	180	20	186	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		1.34	161	30	193	203	197	31	16.0	8
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.58	64.5	15	67.3	67.5	65.8	4.1	6.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		-1.65	40.3	30	30.4	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		0.13	109	20	110	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		1.74	228	35	298	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		20.68	74.0	20	227.0	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		2.15	81.7	30	108.1	97.1	96.7	32.3	33.4	8

Participant 5												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{RCRF}$	ng/sample	IA1		1.87	63.5	15	72.4	66.3	65.9	5.9	9.0	5
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		1.52	69.2	35	87.6	84.1	78.5	13.6	17.3	6
1-Butanol$_{TE}$	ng/sample	IA1		-0.89	60.5	25	53.8	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-0.51	154	20	146	132	133	11	8.1	4
2-Butoxyethanol$_{TE}$	ng/sample	IA1		1.84	58.3	30	74.4	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		1.46	107	20	123	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		1.92	74.1	30	95.4	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		0.47	150	20	157	166	161	18	10.9	5
Alpha-Pinene$_{TE}$	ng/sample	IA1					172	184	189	36	19.1	7
Decane$_{TE}$	ng/sample	IA1		1.19	96.9	35	117.0	117.0	112.3	25.3	22.5	7
Ethylbentzene$_{RCRF}$	ng/sample	IA1		0.26	67.4	15	68.7	67.2	66.7	4.2	6.2	6
Ethylbenzene$_{TE}$	ng/sample	IA1		0.72	66.1	35	74.4	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		-0.17	81.3	20	79.9	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		2.99	107	30	155	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		2.56	180	20	226	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		1.95	161	30	208	203	197	31	16.0	8
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.64	64.5	15	67.6	67.5	65.8	4.1	6.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		1.42	40.3	30	48.9	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		-0.37	109	20	105	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		2.42	228	35	325	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		0.16	74.0	20	75.2	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		6.06	81.7	30	156.0	97.1	96.7	32.3	33.4	8

Participant 6												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{RCRF}$	ng/sample	IA1		0.60	63.5	15	66.3	66.3	65.9	5.9	9.0	5
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		1.57	69.2	35	88.2	84.1	78.5	13.6	17.3	6
1-Butanol$_{RCRF}$	ng/sample	IA1		-1.05	186	20	166	171	172	11	6.2	5
1-Butanol$_{TE}$	ng/sample	IA1		1.69	60.5	25	73.3	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-1.14	154	20	137	132	133	11	8.1	4
2-Butoxyethanol$_{TE}$	ng/sample	IA1		2.01	58.3	30	75.9	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		-0.68	107	20	100	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		-1.12	74.1	30	61.7	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		1.55	150	20	173	166	161	18	10.9	5
Alpha-Pinene$_{TE}$	ng/sample	IA1					184	184	189	36	19.1	7
Decane$_{RCRF}$	ng/sample	IA1		0.84	105	20	114	114	111	10	9.0	3
Decane$_{TE}$	ng/sample	IA1		-1.12	96.9	35	77.9	117.0	112.3	25.3	22.5	7
Ethylbentzene$_{RCRF}$	ng/sample	IA1		0.83	67.4	15	71.6	67.2	66.7	4.2	6.2	6
Ethylbenzene$_{TE}$	ng/sample	IA1		1.63	66.1	35	85.0	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		0.37	81.3	20	84.3	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		1.39	107	30	129	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		0.36	180	20	187	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		1.56	161	30	199	203	197	31	16.0	8
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		0.78	64.5	15	68.3	67.5	65.8	4.1	6.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		2.10	40.3	30	53.0	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		-1.20	109	20	96	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		-0.08	228	35	225	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		-0.10	74.0	20	73.2	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		0.05	81.7	30	82.3	97.1	96.7	32.3	33.4	8

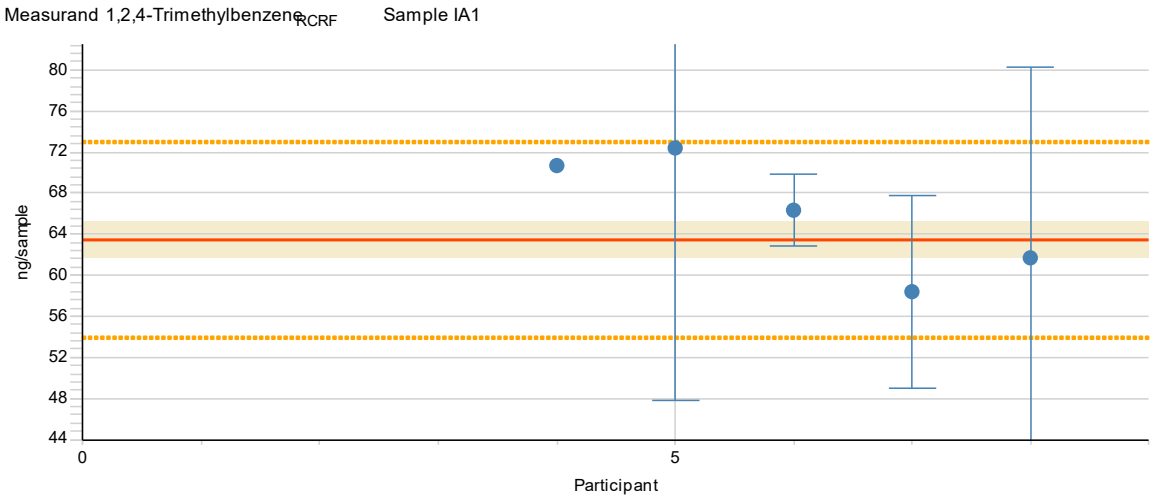
Participant 7												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{RCRF}$	ng/sample	IA1		-1.07	63.5	15	58.4	66.3	65.9	5.9	9.0	5
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		-0.64	69.2	35	61.4	84.1	78.5	13.6	17.3	6
1-Butanol$_{RCRF}$	ng/sample	IA1		-0.32	186	20	180	171	172	11	6.2	5
1-Butanol$_{TE}$	ng/sample	IA1		-1.56	60.5	25	48.7	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-1.66	154	20	128	132	133	11	8.1	4
2-Butoxyethanol$_{TE}$	ng/sample	IA1		-2.24	58.3	30	38.7	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		-1.08	107	20	95	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		-2.43	74.1	30	47.1	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		-1.21	150	20	132	166	161	18	10.9	5
Alpha-Pinene$_{TE}$	ng/sample	IA1					134	184	189	36	19.1	7
Decane$_{RCRF}$	ng/sample	IA1		-0.49	105	20	100	114	111	10	9.0	3
Decane$_{TE}$	ng/sample	IA1		-0.83	96.9	35	82.8	117.0	112.3	25.3	22.5	7
Ethylbentzene$_{RCRF}$	ng/sample	IA1		-1.17	67.4	15	61.5	67.2	66.7	4.2	6.2	6
Ethylbenzene$_{TE}$	ng/sample	IA1		-0.21	66.1	35	63.7	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		-1.21	81.3	20	71.5	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		-1.28	107	30	86	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		-1.09	180	20	160	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		-0.29	161	30	154	203	197	31	16.0	8
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		-0.66	64.5	15	61.3	67.5	65.8	4.1	6.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		0.55	40.3	30	43.6	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		-1.38	109	20	94	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		-1.65	228	35	162	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		-2.19	74.0	20	57.8	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		-2.87	81.7	30	46.5	97.1	96.7	32.3	33.4	8

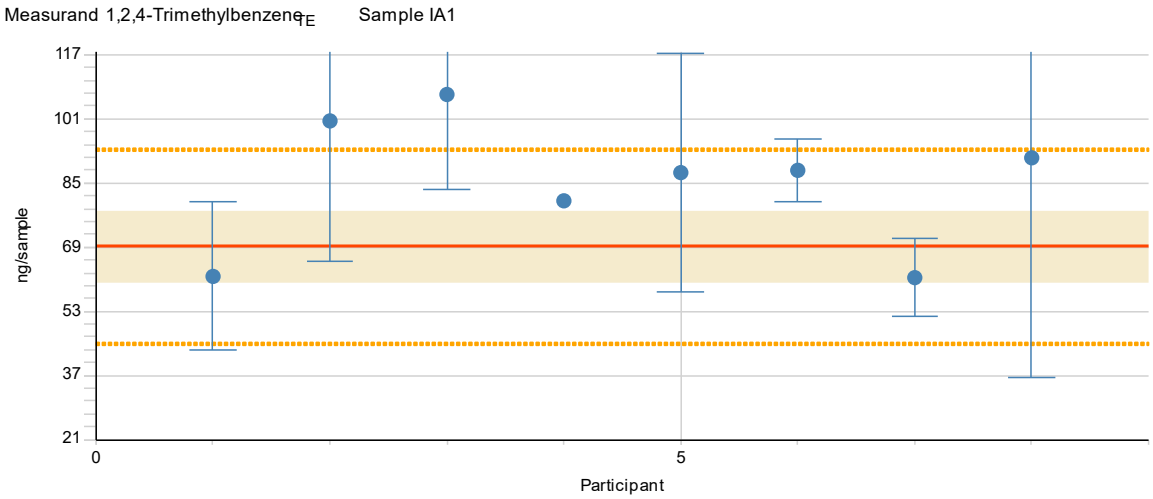
Participant 8												
Measurand	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2×s_{pt} %**	**Participant's result**	**Md**	**Mean**	**s**	**s %**	**n_{stat}**
1,2,4-Trimethylbenzene$_{RCRF}$	ng/sample	IA1		-0.38	63.5	15	61.7	66.3	65.9	5.9	9.0	5
1,2,4-Trimethylbenzene$_{TE}$	ng/sample	IA1		1.82	69.2	35	91.3	84.1	78.5	13.6	17.3	6
1-Butanol$_{RCRF}$	ng/sample	IA1		-0.79	186	20	171	171	172	11	6.2	5
1-Butanol$_{TE}$	ng/sample	IA1		0.20	60.5	25	62.0	62.0	63.4	11.9	18.8	7
2-Butoxyethanol$_{RCRF}$	ng/sample	IA1		-2.13	154	20	121	132	133	11	8.1	4
2-Butoxyethanol$_{TE}$	ng/sample	IA1		0.77	58.3	30	65.0	65.0	64.3	14.7	22.8	7
2EH$_{RCRF}$	ng/sample	IA1		-0.10	107	20	106	103	107	12	11.5	6
2EH$_{TE}$	ng/sample	IA1		1.10	74.1	30	86.3	90.9	90.0	17.9	19.9	6
Alpha-Pinene$_{RCRF}$	ng/sample	IA1		1.63	150	20	175	166	161	18	10.9	5
Alpha-Pinene$_{TE}$	ng/sample	IA1					185	184	189	36	19.1	7
Decane$_{RCRF}$	ng/sample	IA1		1.36	105	20	119	114	111	10	9.0	3
Decane$_{TE}$	ng/sample	IA1		1.69	96.9	35	125.5	117.0	112.3	25.3	22.5	7
Ethylbentzene$_{RCRF}$	ng/sample	IA1		-0.34	67.4	15	65.7	67.2	66.7	4.2	6.2	6
Ethylbenzene$_{TE}$	ng/sample	IA1		1.70	66.1	35	85.8	79.7	81.1	13.9	17.1	8
Naphthalene$_{RCRF}$	ng/sample	IA1		-0.16	81.3	20	80.0	83.9	84.3	10.2	12.1	7
Naphthalene$_{TE}$	ng/sample	IA1		2.24	107	30	143	129	125	26	21.1	8
Styrene$_{RCRF}$	ng/sample	IA1		0.11	180	20	182	187	201	31	15.4	7
Styrene$_{TE}$	ng/sample	IA1		2.01	161	30	210	203	197	31	16.0	8
Tetrachloroethylene$_{RCRF}$	ng/sample	IA1		-0.91	64.5	15	60.1	67.5	65.8	4.1	6.2	6
Tetrachloroethylene$_{TE}$	ng/sample	IA1		1.69	40.3	30	50.5	49.7	49.0	18.8	38.3	8
Toluene$_{RCRF}$	ng/sample	IA1		-1.15	109	20	97	101	106	15	14.6	8
TVOC$_{Lab}$-Chamber blank	µg/m3	IA3		1.23	228	35	277	271	258	74	28.8	8
TXIB$_{RCRF}$	ng/sample	IA1		-2.49	74.0	20	55.6	74.2	73.1	14.9	20.4	6
TXIB$_{TE}$	ng/sample	IA1		0.68	81.7	30	90.0	97.1	96.7	32.3	33.4	8

APPENDIX 8: Results of participants and their uncertainties

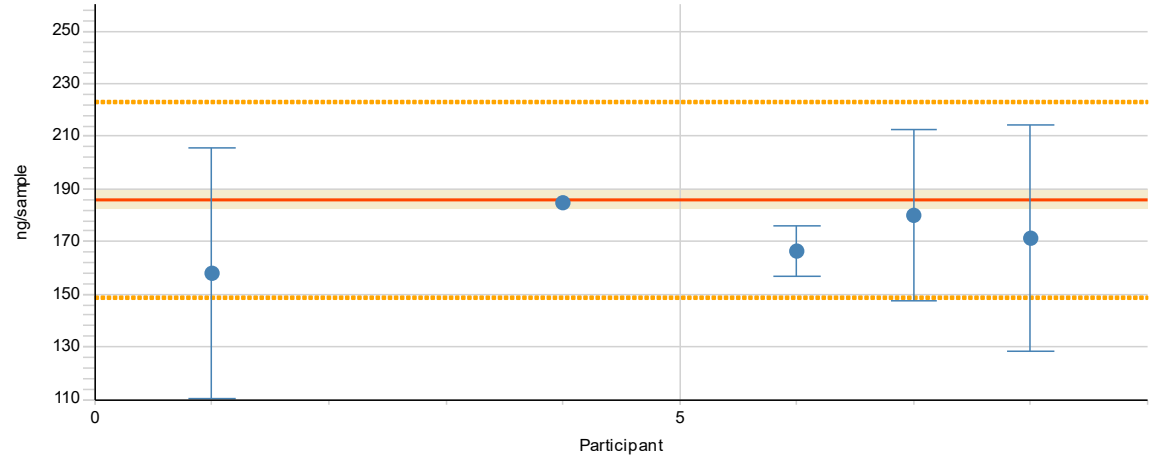
In figures:

- 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.

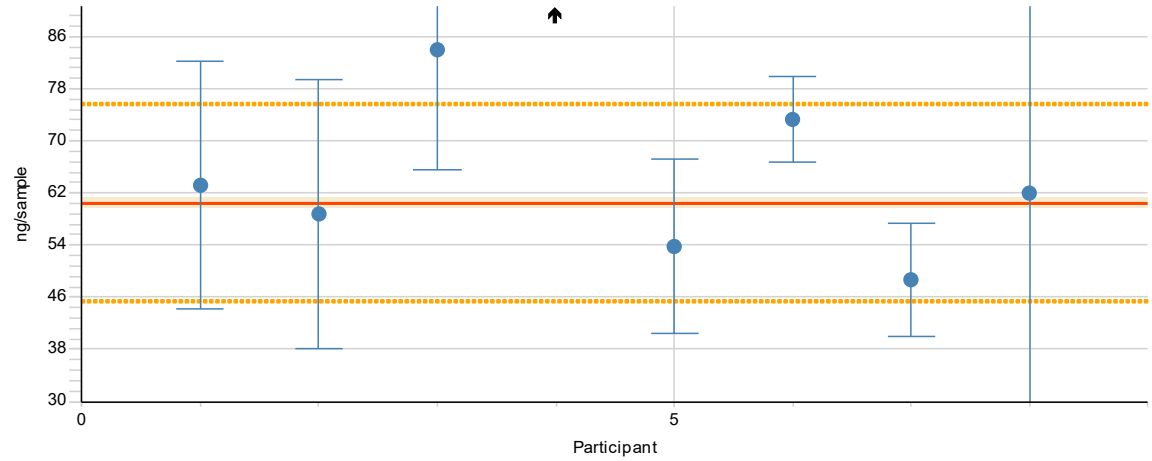




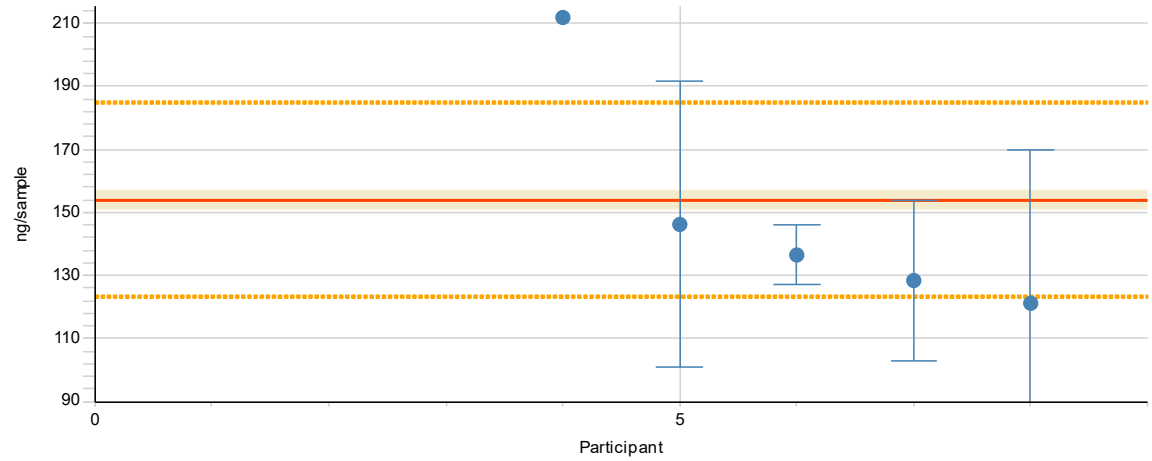
Measurand 1-Butanol$_{RCRF}$ Sample IA1

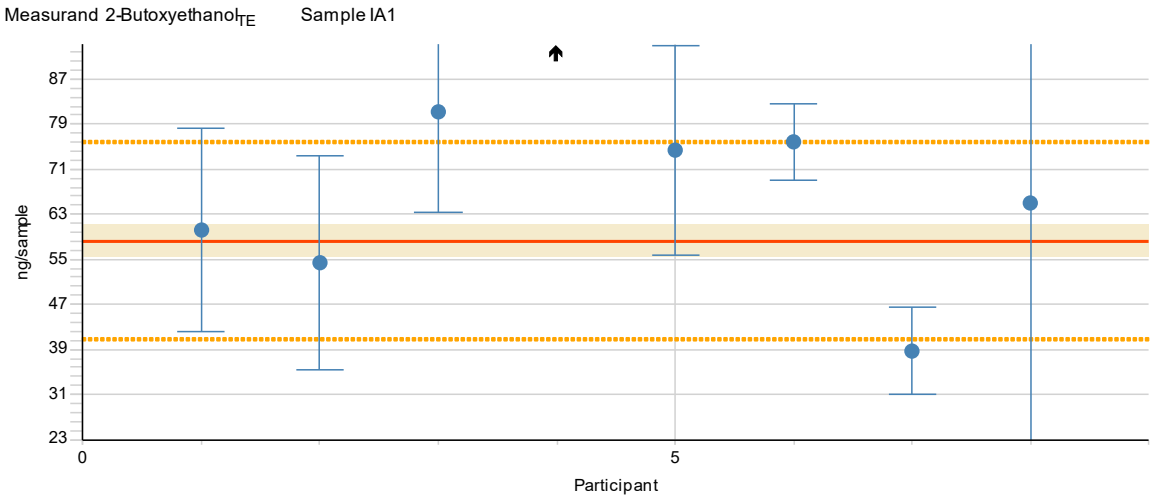


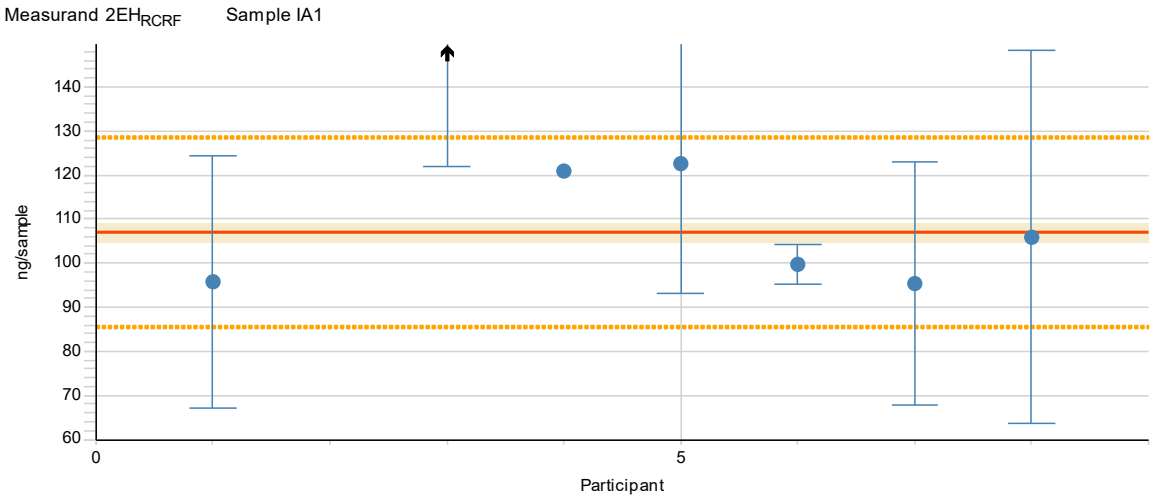
Measurand 1-Butanol$_{TE}$ Sample IA1

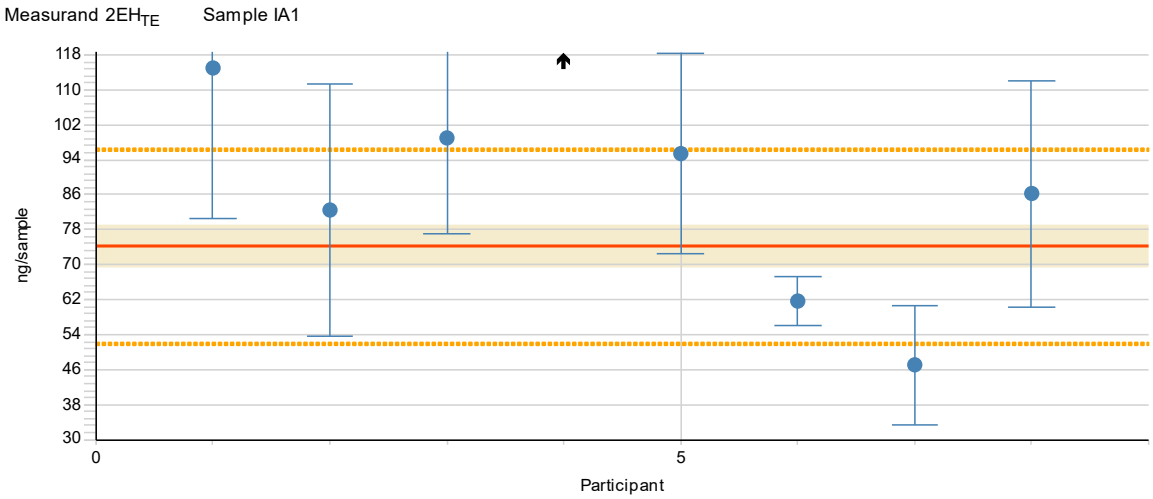


Measurand 2-Butoxyethanol$_{RCRF}$ Sample IA1

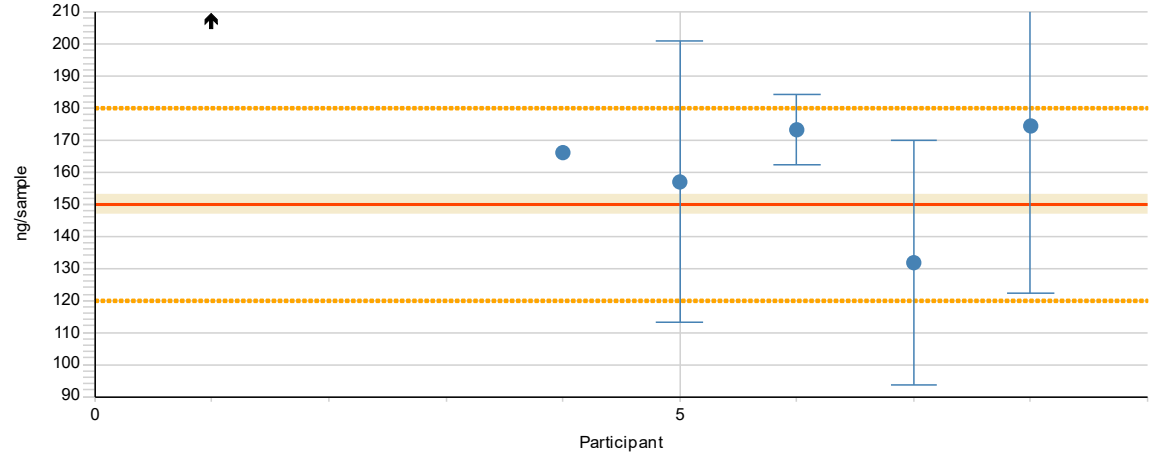



Measurand 2-Butoxyethanol$_{TE}$ Sample IA1
ng/sample
87
79
71
63
55
47
39
31
23
0
5
Participant

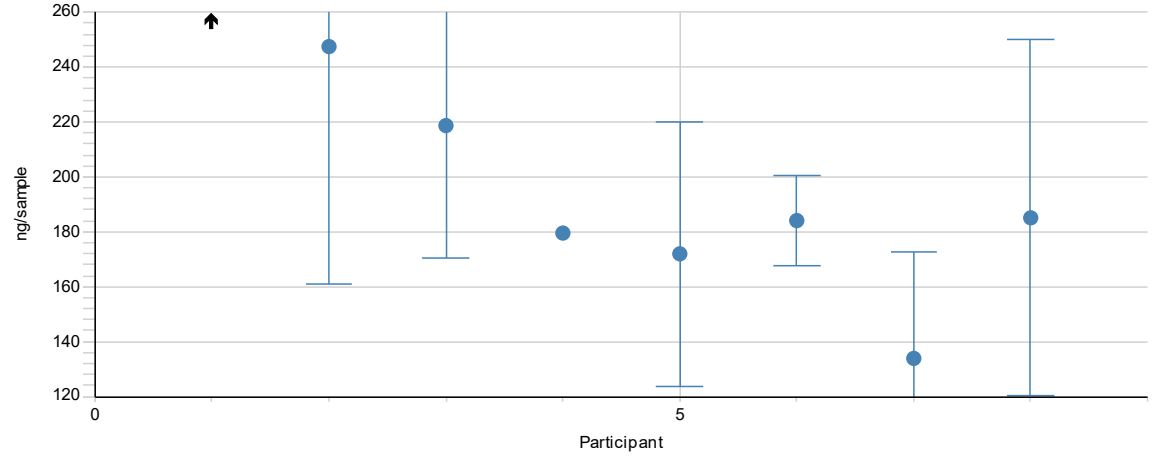

Measurand 2EH$_{RCRF}$ Sample IA1
ng/sample
140
130
120
110
100
90
80
70
60
0
5
Participant


Measurand 2EH$_{TE}$ Sample IA1
ng/sample
118
110
102
94
86
78
70
62
54
46
38
30
0
5
Participant

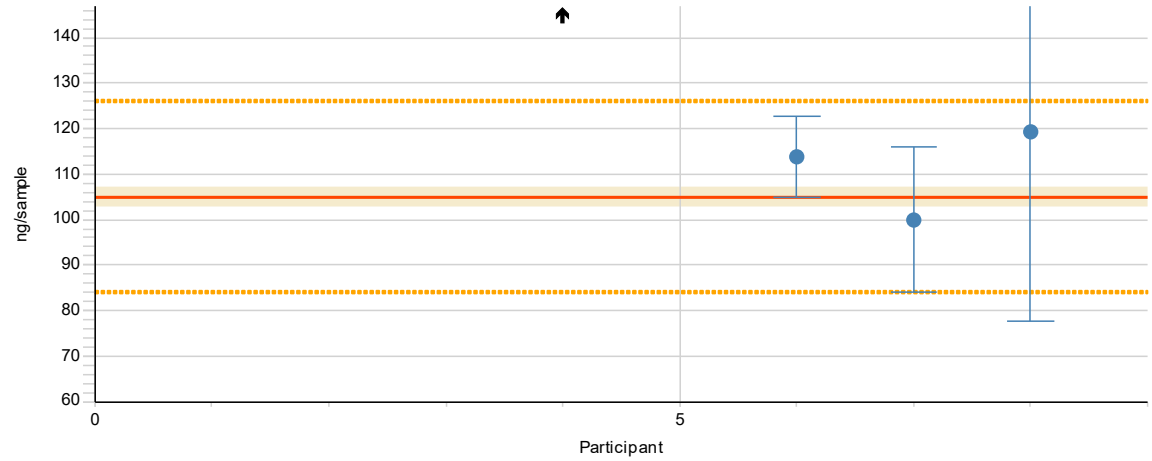
Measurand Alpha-Pinene$_{RCRF}$ Sample IA1

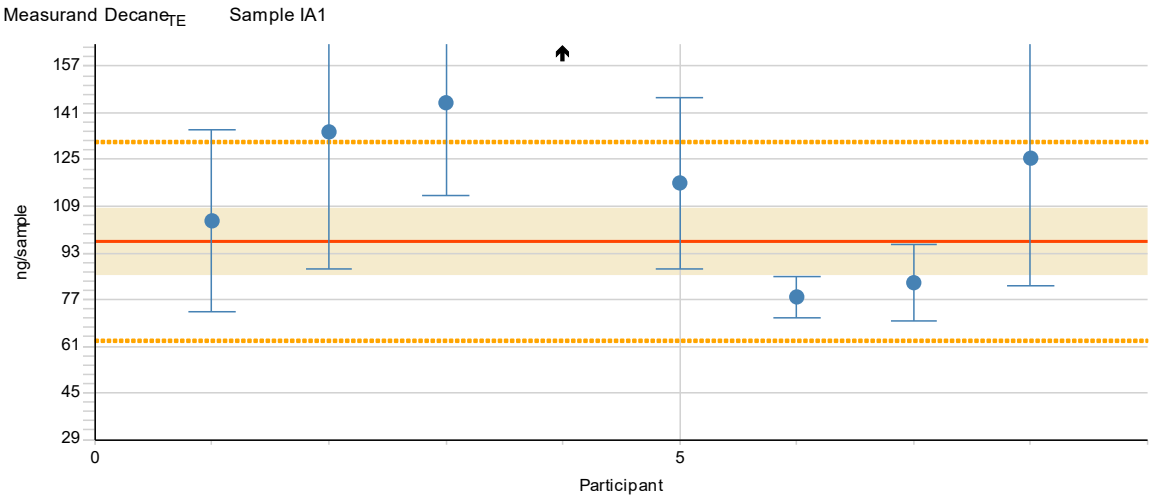


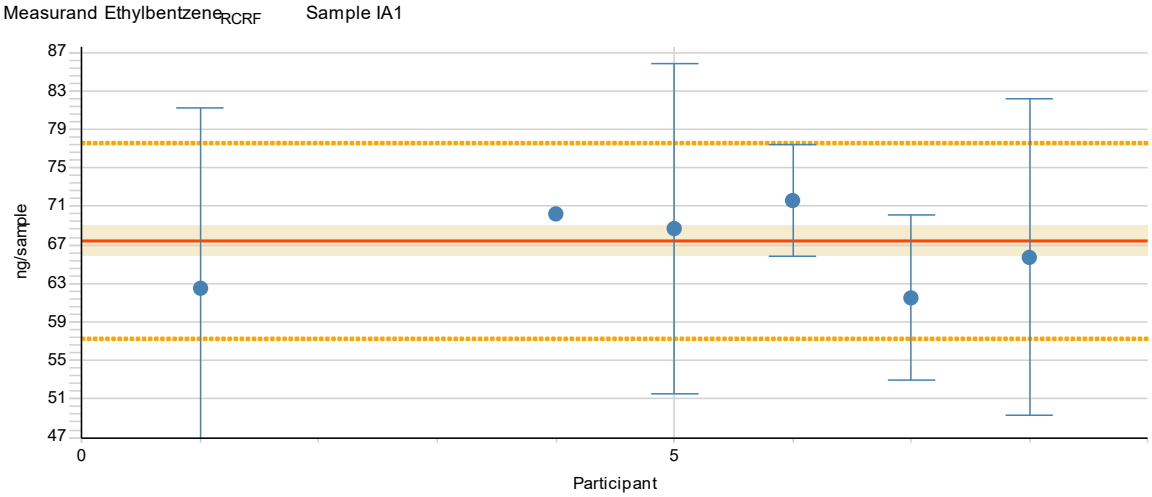
Measurand Alpha-Pinene$_{TE}$ Sample IA1

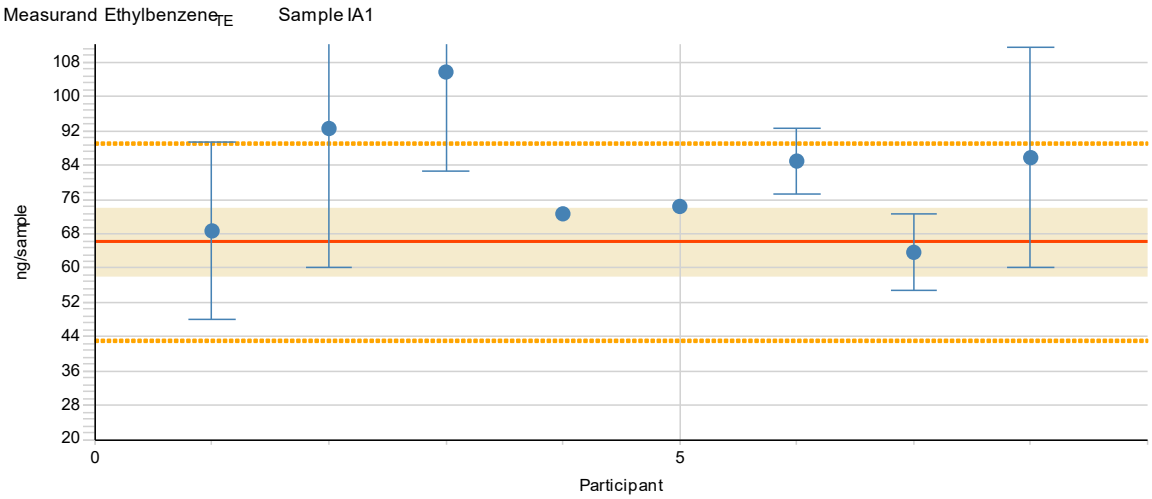


Measurand Decane$_{RCRF}$ Sample IA1

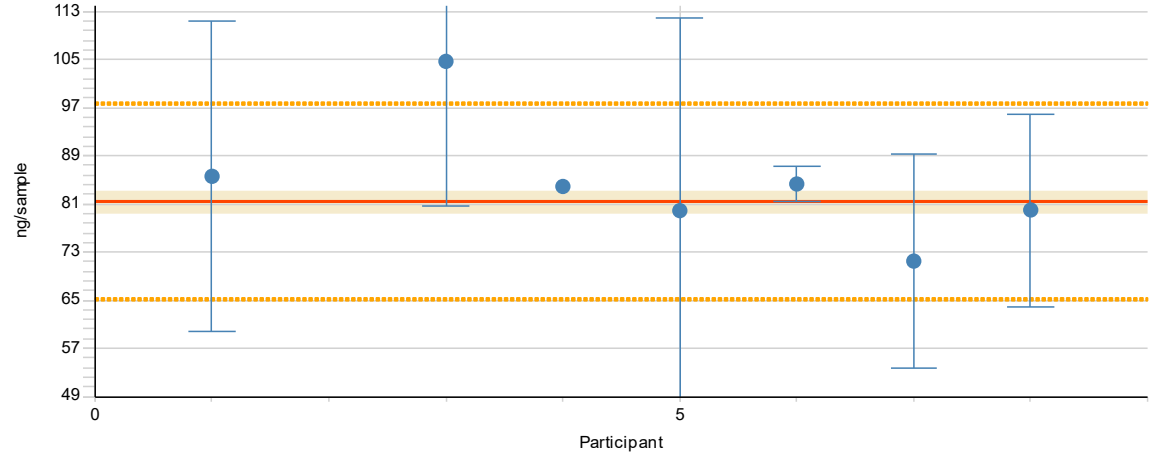



Measurand Decane$_{TE}$ Sample IA1
157
141
125
109
93
77
61
45
29
ng/sample
0
5
Participant

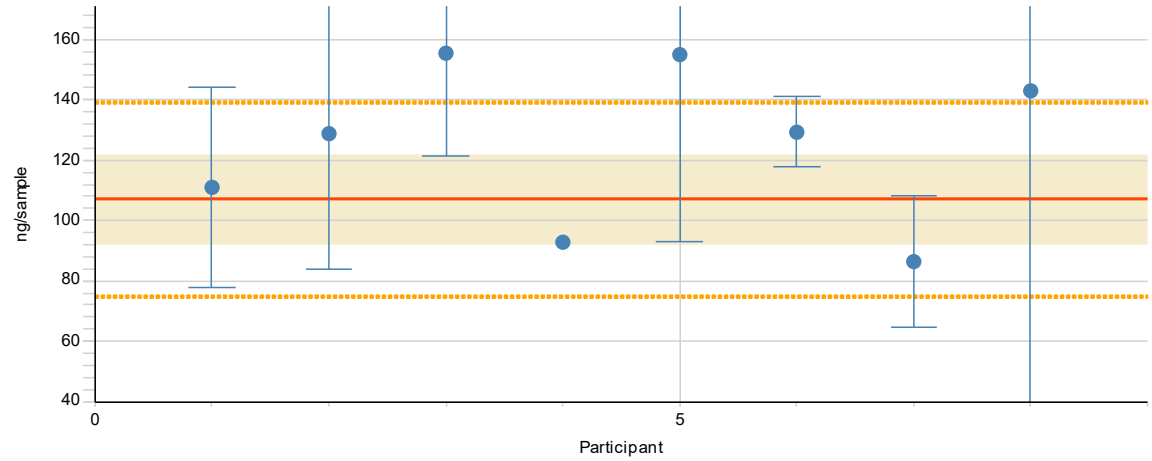

Measurand Ethylbentzene$_{RCRF}$ Sample IA1
87
83
79
75
71
67
63
59
55
51
47
ng/sample
0
5
Participant


Measurand Ethylbenzene$_{TE}$ Sample IA1
108
100
92
84
76
68
60
52
44
36
28
20
ng/sample
0
5
Participant

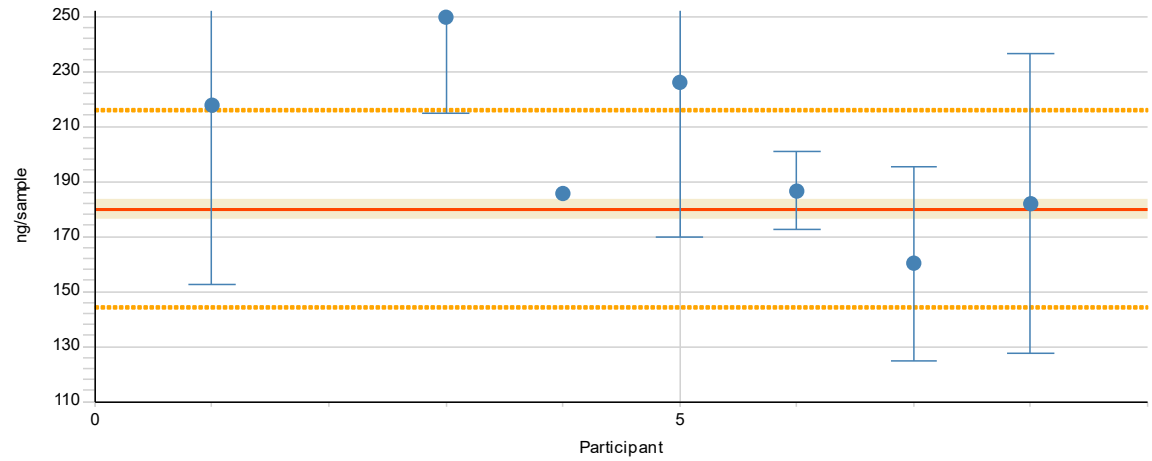
Measurand Naphthalene$_{RCRF}$ Sample IA1

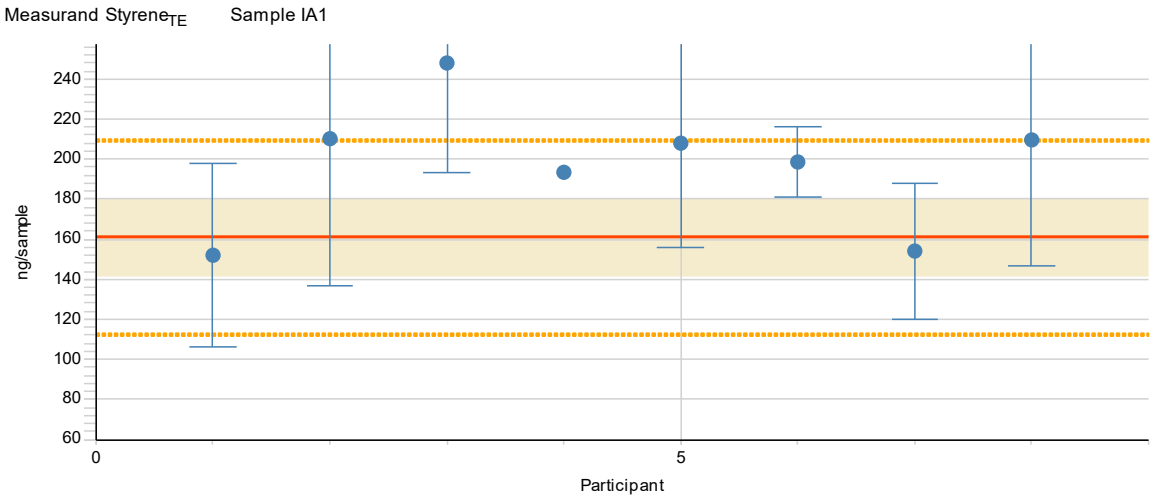


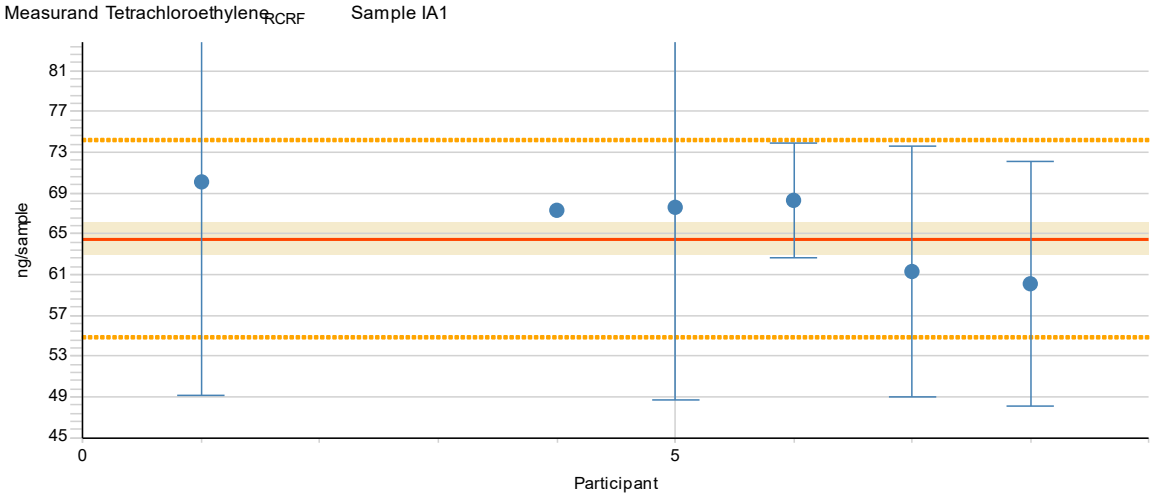
Measurand Naphthalene$_{TE}$ Sample IA1

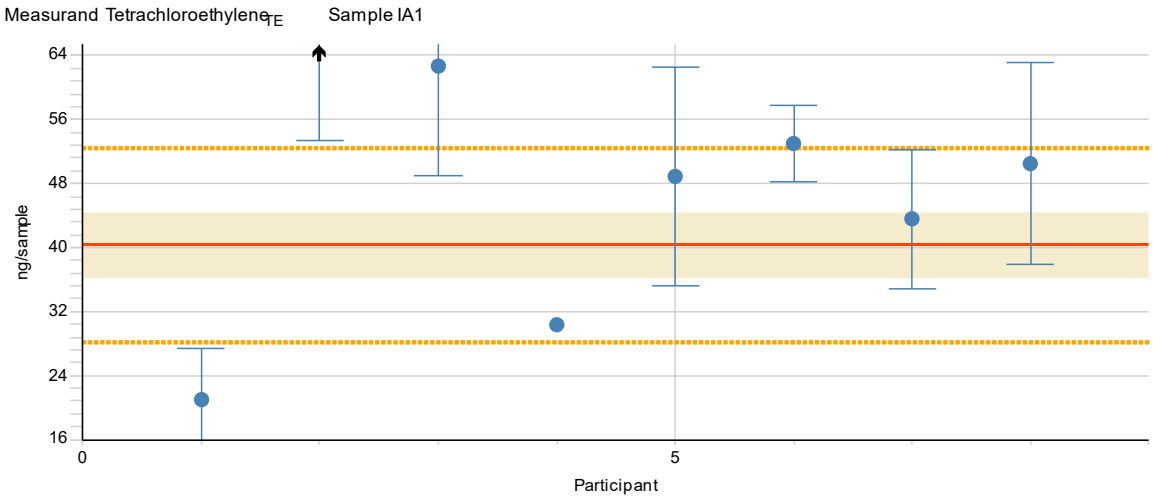


Measurand Styrene$_{RCRF}$ Sample IA1

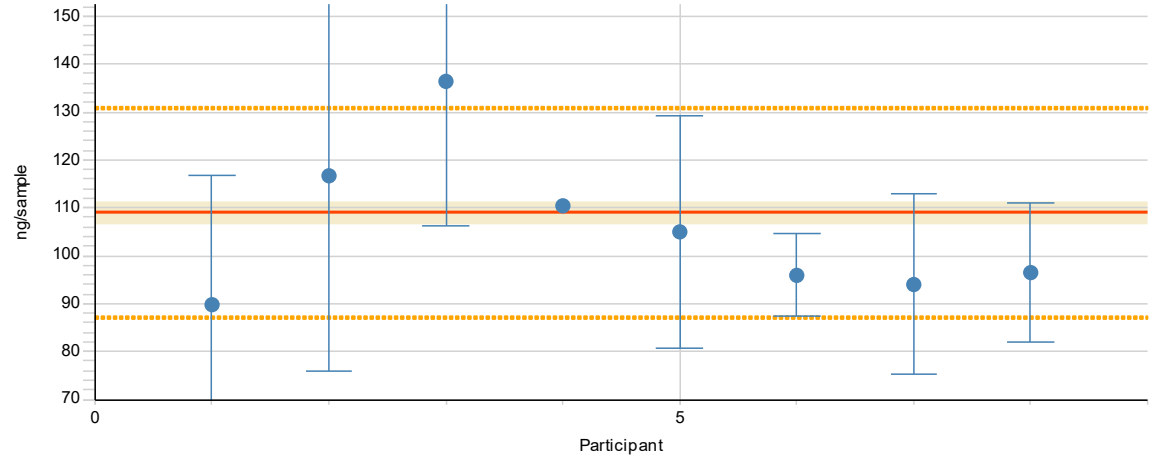



Measurand Styrene TE
Sample IA1
ng/sample
240
220
200
180
160
140
120
100
80
60
0
5
Participant

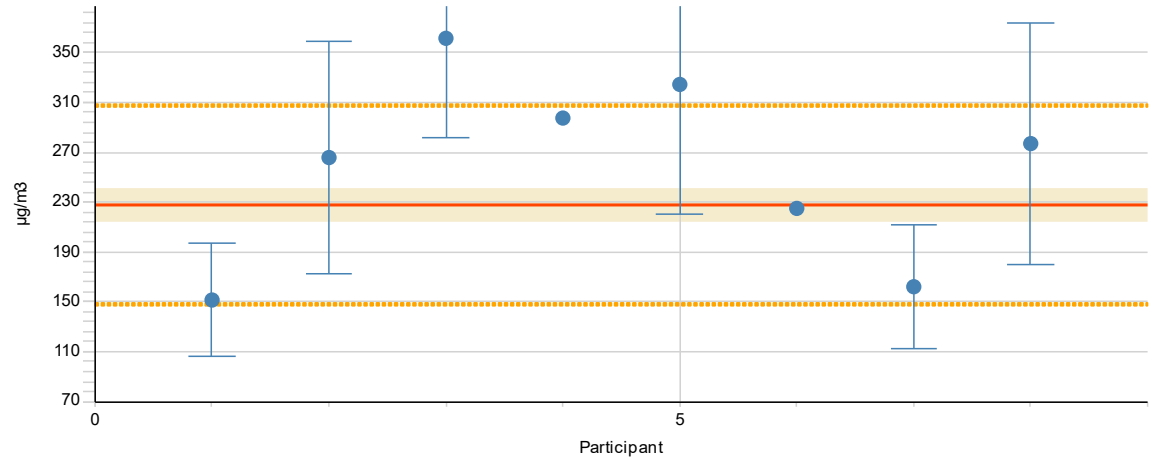

Measurand Tetrachloroethylene RCRF
Sample IA1
ng/sample
81
77
73
69
65
61
57
53
49
45
0
5
Participant


Measurand Tetrachloroethylene TE
Sample IA1
ng/sample
64
56
48
40
32
24
16
0
5
Participant

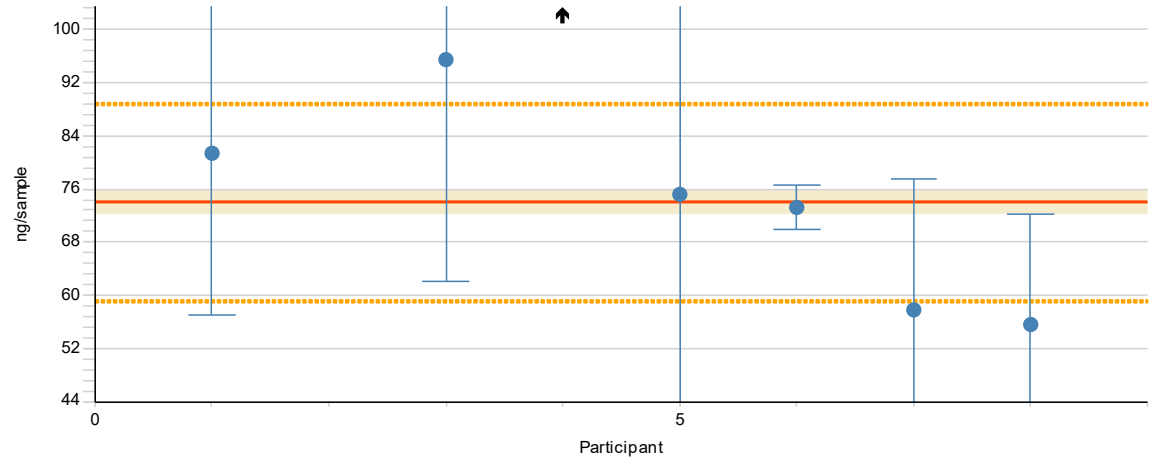
Measurand $Toluene_{RCRF}$ Sample IA1

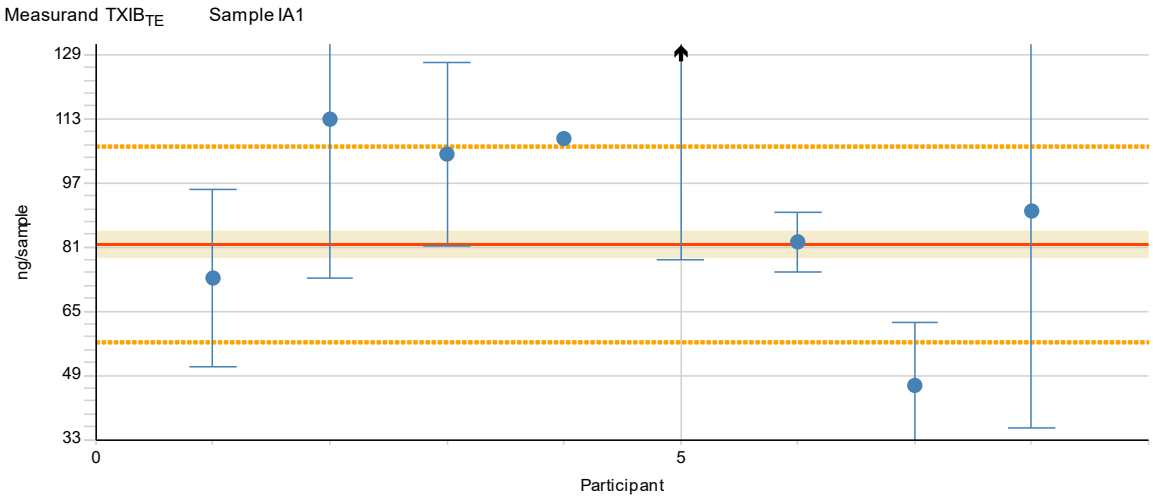


Measurand $TVOC_{Lab}$- Chamber blank Sample IA3



Measurand $TXIB_{RCRF}$ Sample IA1




Measurand TXIB$_{TE}$
Sample IA1
129
113
97
81
65
49
33
ng/sample
0
5
Participant

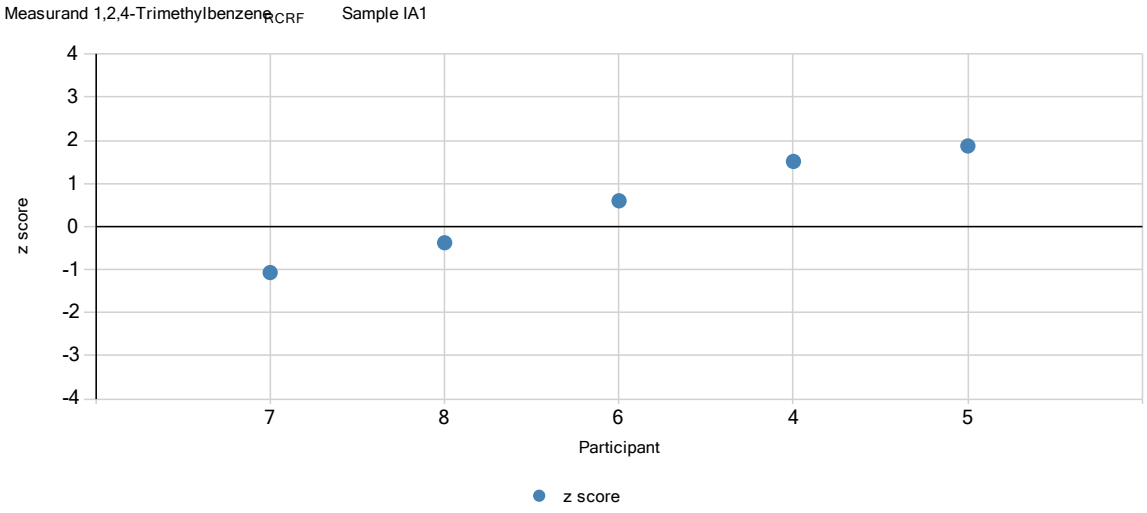
APPENDIX 9: Summary of the z scores

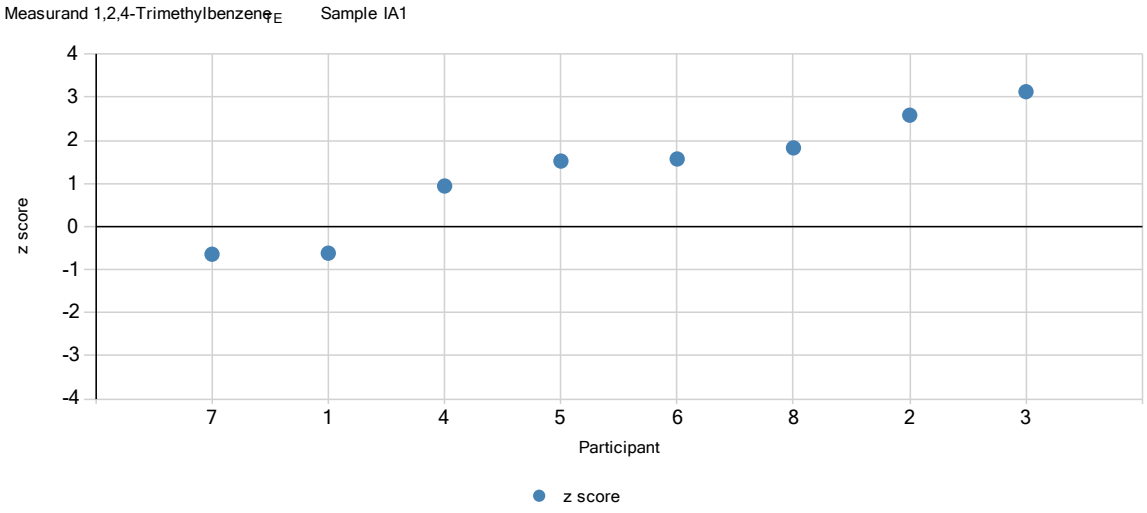
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
1,2,4-Trimethylbenzene$_{RCRF}$	IA1	.	.	.	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
1,2,4-Trimethylbenzene$_{TE}$	IA1	**S**	**Q**	**U**	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
1-Butanol$_{RCRF}$	IA1	**S**	.	.	*S*	.	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
1-Butanol$_{TE}$	IA1	**S**	**S**	**U**	*U*	*S*	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
2-Butoxyethanol$_{RCRF}$	IA1	.	.	.	*U*	**S**	*S*	**S**	**q**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	60.0
2-Butoxyethanol$_{TE}$	IA1	**S**	**S**	**Q**	*U*	**S**	*Q*	**q**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	50.0
2EH$_{RCRF}$	IA1	**S**	.	**U**	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	85.7
2EH$_{TE}$	IA1	**U**	**S**	**Q**	*U*	**S**	*S*	**q**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	50.0
Alpha-Pinene$_{RCRF}$	IA1	*U*	.	.	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	83.3
Alpha-Pinene$_{TE}$	IA1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
Decane$_{RCRF}$	IA1	.	.	.	*U*	.	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
Decane$_{TE}$	IA1	**S**	**Q**	**Q**	*U*	*S*	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	62.5
Ethylbentzene$_{RCRF}$	IA1	**S**	.	.	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
Ethylbenzene$_{TE}$	IA1	**S**	**Q**	**U**	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
Naphthalene$_{RCRF}$	IA1	**S**	.	**Q**	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	85.7
Naphthalene$_{TE}$	IA1	**S**	**S**	**U**	*S*	**Q**	*S*	**S**	**Q**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	62.5
Styrene$_{RCRF}$	IA1	**Q**	.	**U**	*S*	**Q**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	57.1
Styrene$_{TE}$	IA1	**S**	**Q**	**U**	*S*	**S**	*S*	**S**	**Q**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	62.5
Tetrachloroethylene$_{RCRF}$	IA1	**S**	.	.	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
Tetrachloroethylene$_{TE}$	IA1	**u**	**U**	**U**	*S*	**S**	*Q*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	50.0
Toluene$_{RCRF}$	IA1	**S**	**S**	**Q**	*S*	**S**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87.5
TVOC$_{Lab}$-Chamber blank	IA3	**S**	**S**	**U**	*S*	**Q**	*S*	**S**	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
TXIB$_{RCRF}$	IA1	**S**	.	**Q**	*U*	**S**	*S*	**q**	**q**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	42.9
TXIB$_{TE}$	IA1	**S**	**Q**	**S**	*Q*	**U**	S	q	**S**	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	50.0
%		80	50	6	65	81	91	83	83																
accredited		19	12	16		19		22	23																

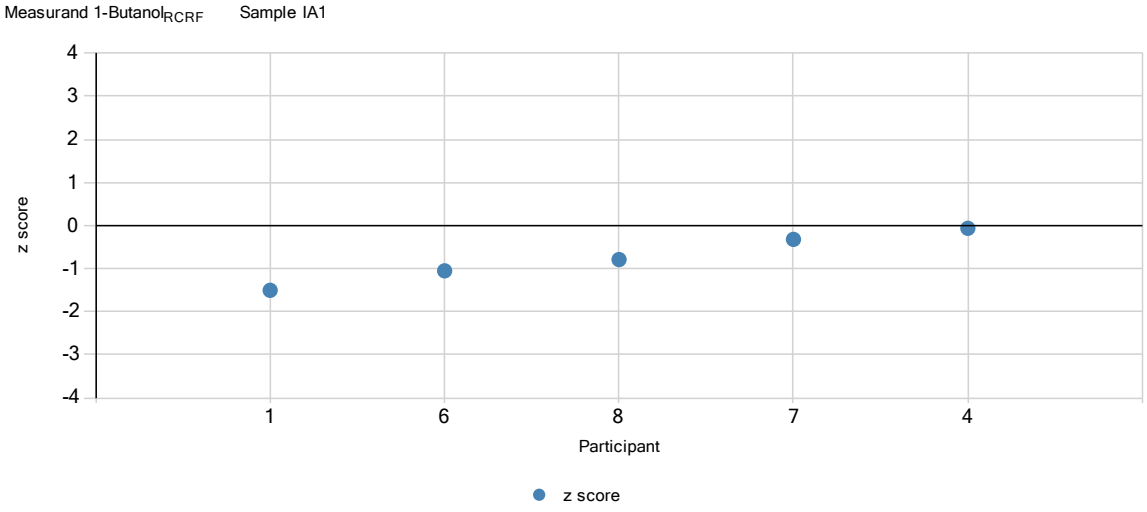
S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - unknown
% - percentage of satisfactory results

Totally satisfactory, % in all: 71 % in accredited: 68 % in non-accredited: 77

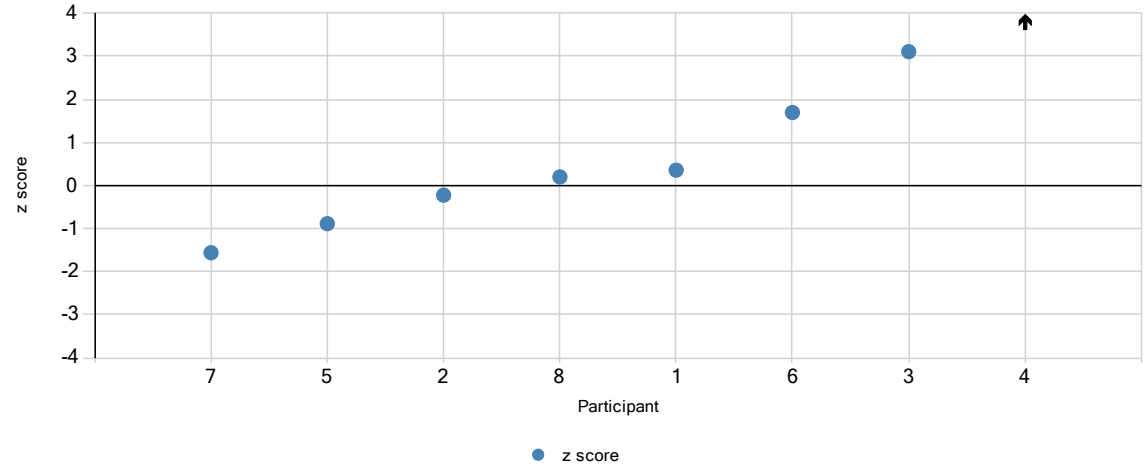
APPENDIX 10: z scores in ascending order



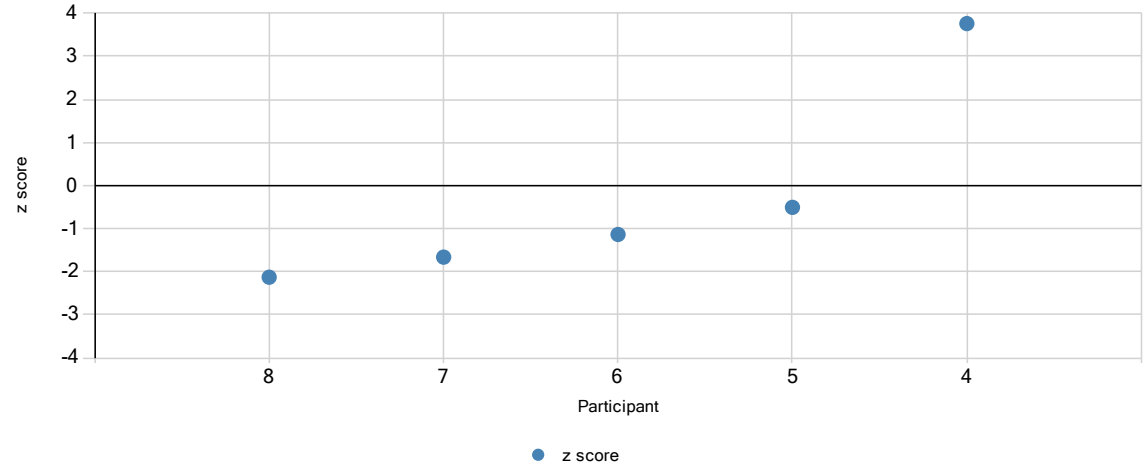




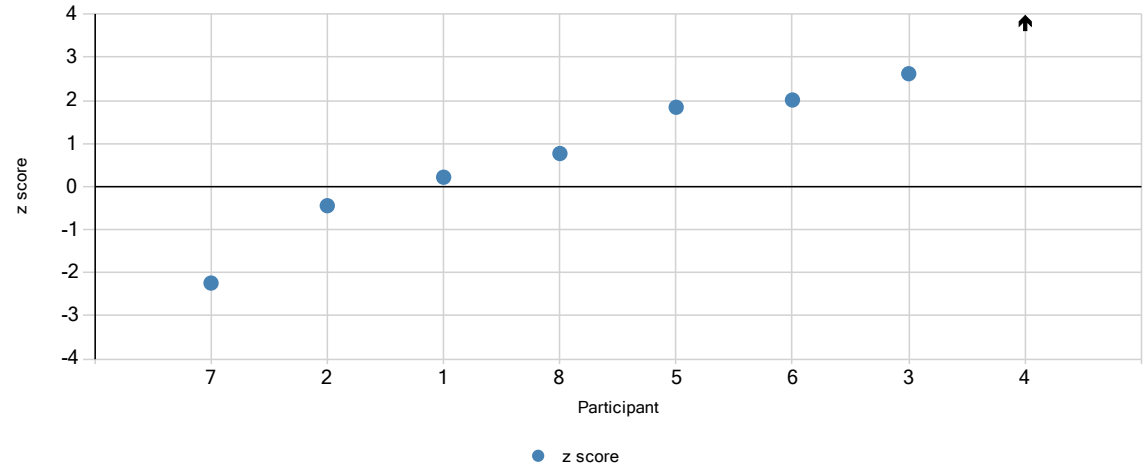
Measurand 1-Butanol$_{TE}$ Sample IA1



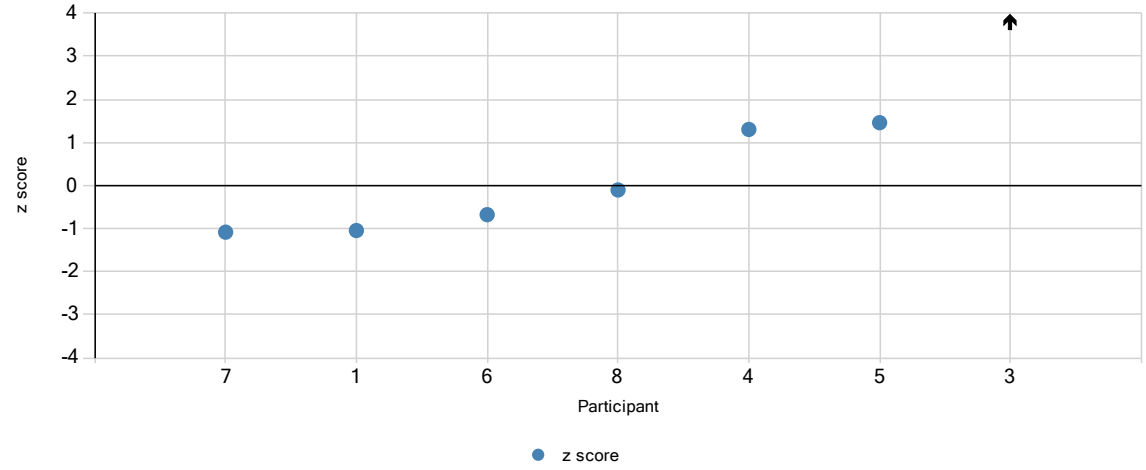
Measurand 2-Butoxyethanol$_{RCRF}$ Sample IA1



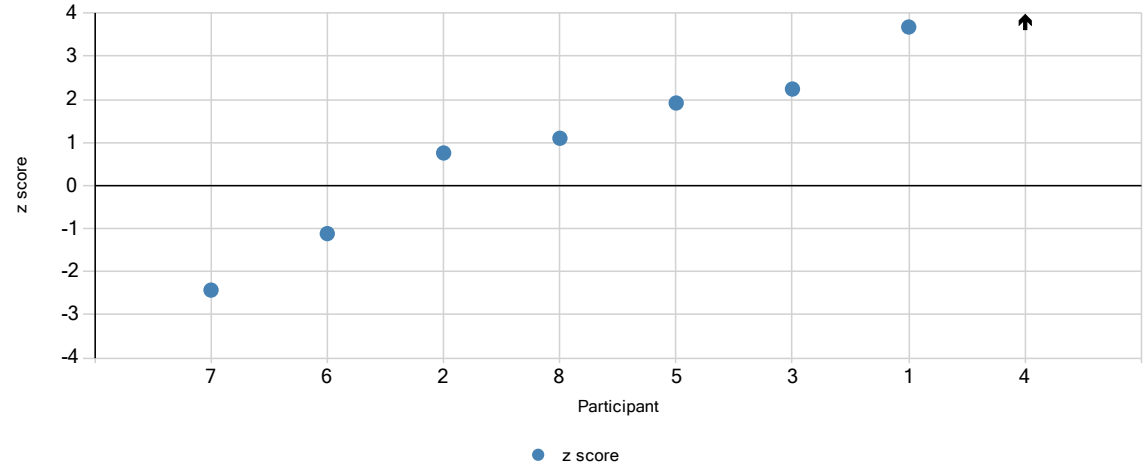
Measurand 2-Butoxyethanol$_{TE}$ Sample IA1



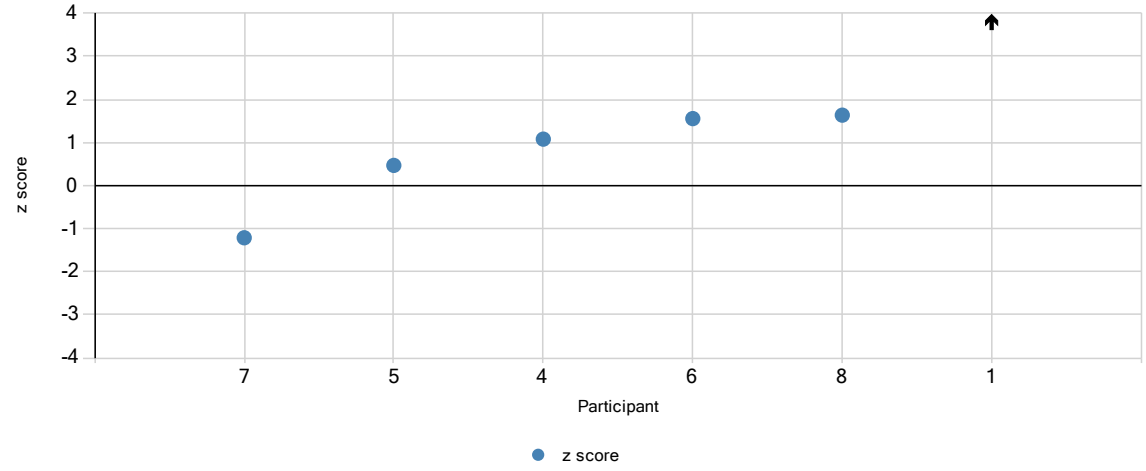
Measurand $2EH_{RCRF}$ Sample IA1



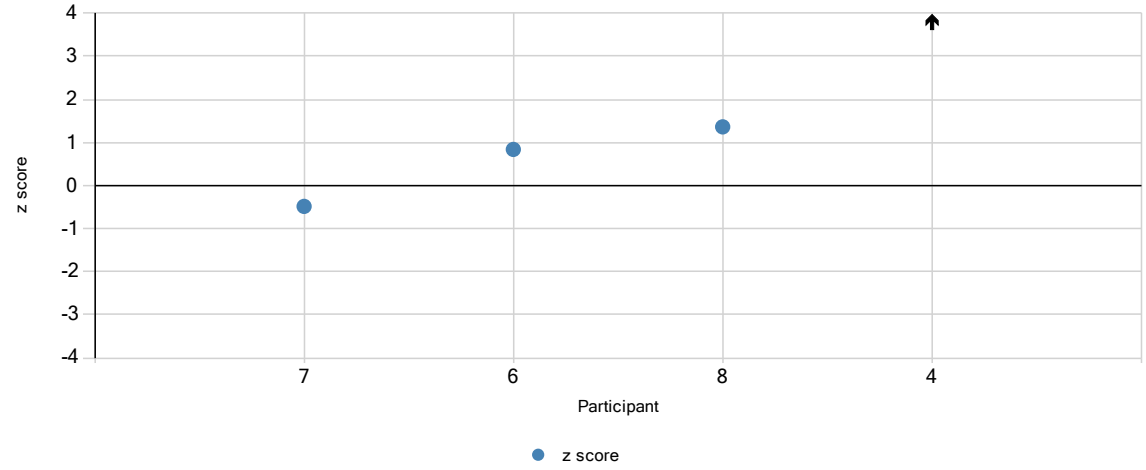
Measurand $2EH_{TE}$ Sample IA1



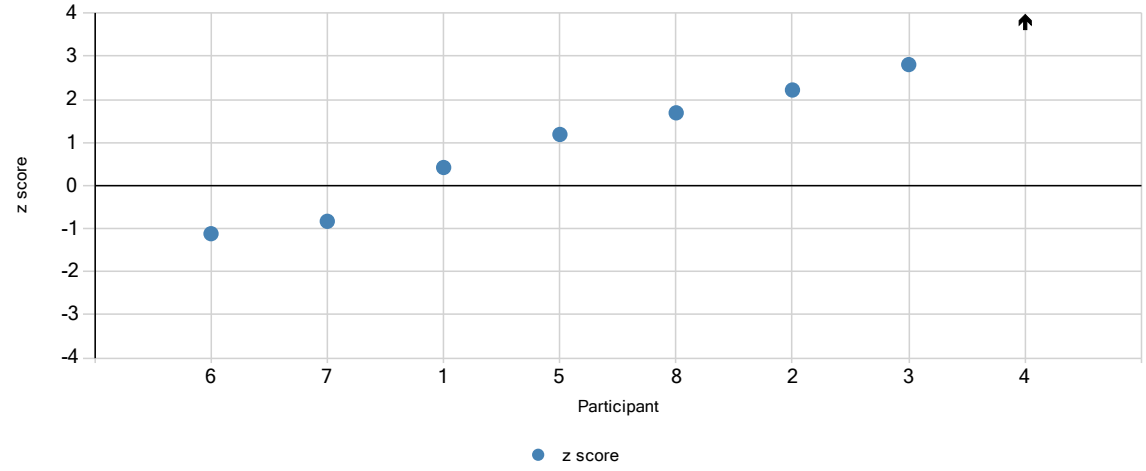
Measurand Alpha-Pinene$_{RCRF}$ Sample IA1



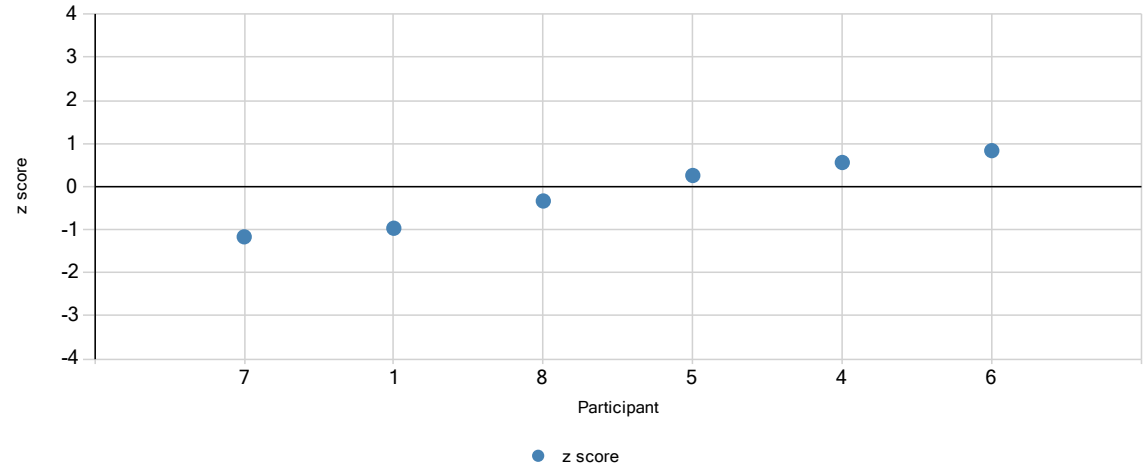
Measurand Decane$_{RCRF}$ Sample IA1



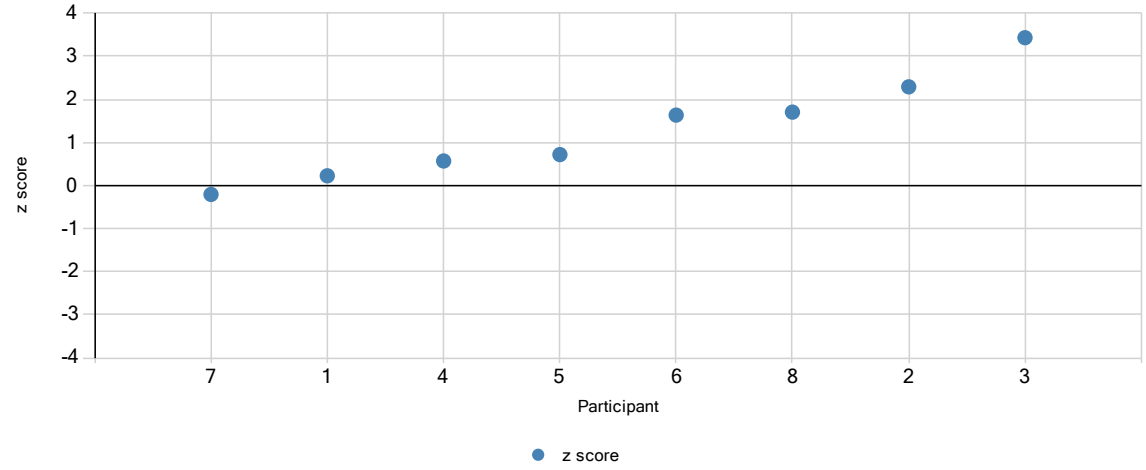
Measurand Decane$_{TE}$ Sample IA1



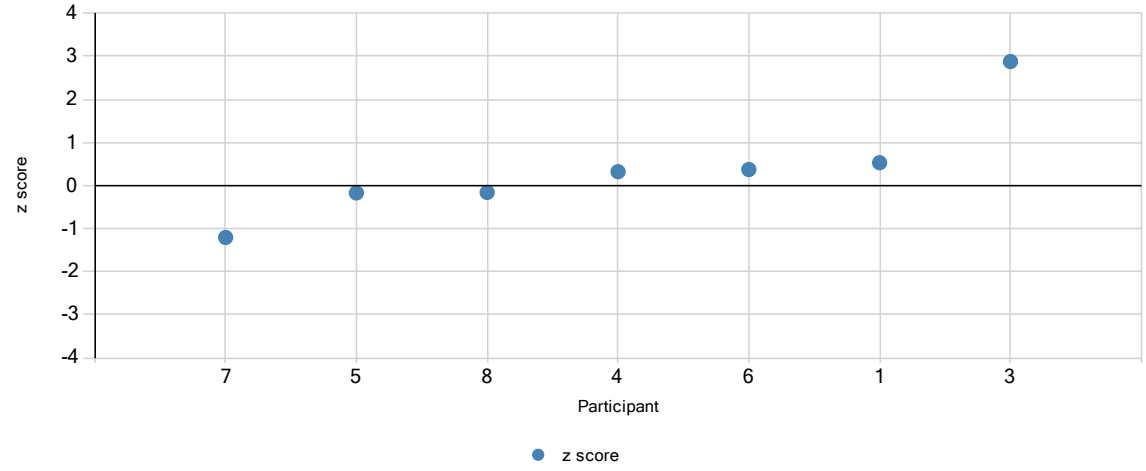
Measurand Ethylbentzene$_{RCRF}$ Sample IA1



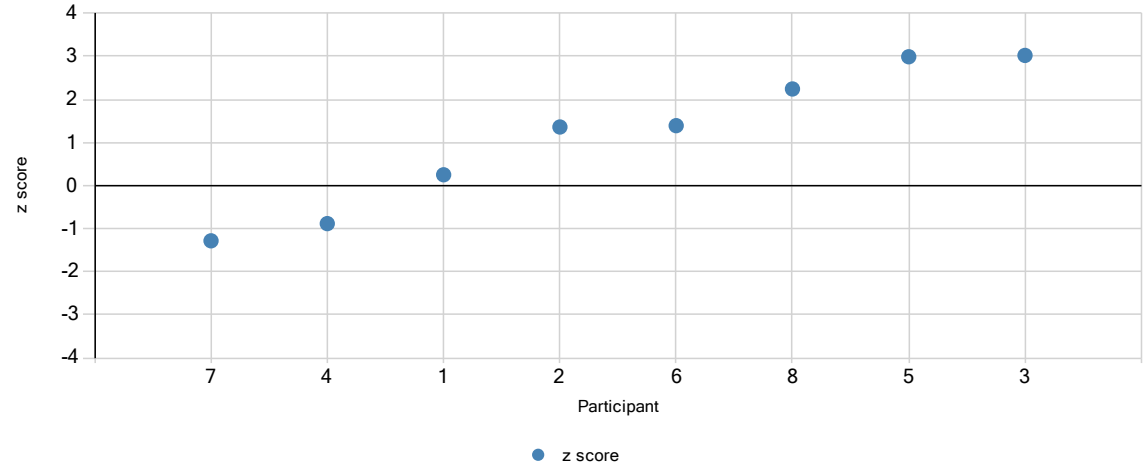
Measurand Ethylbenzene$_{TE}$ Sample IA1



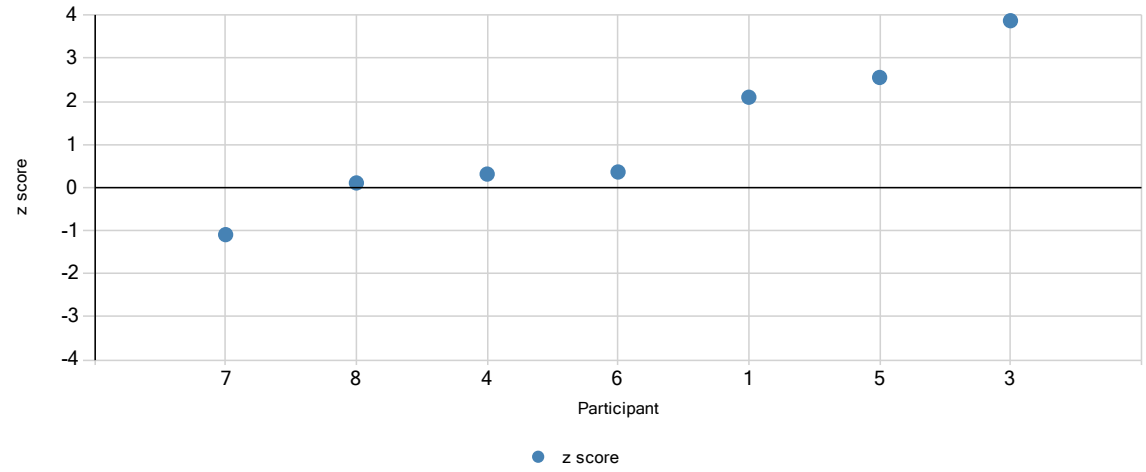
Measurand Naphthalene$_{RCRF}$ Sample IA1



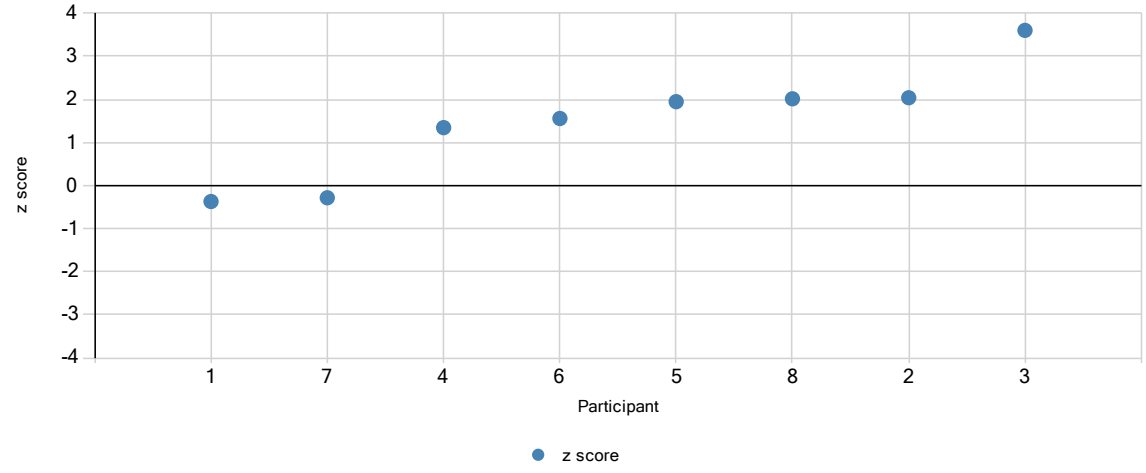
Measurand Naphthalene$_{TE}$ Sample IA1



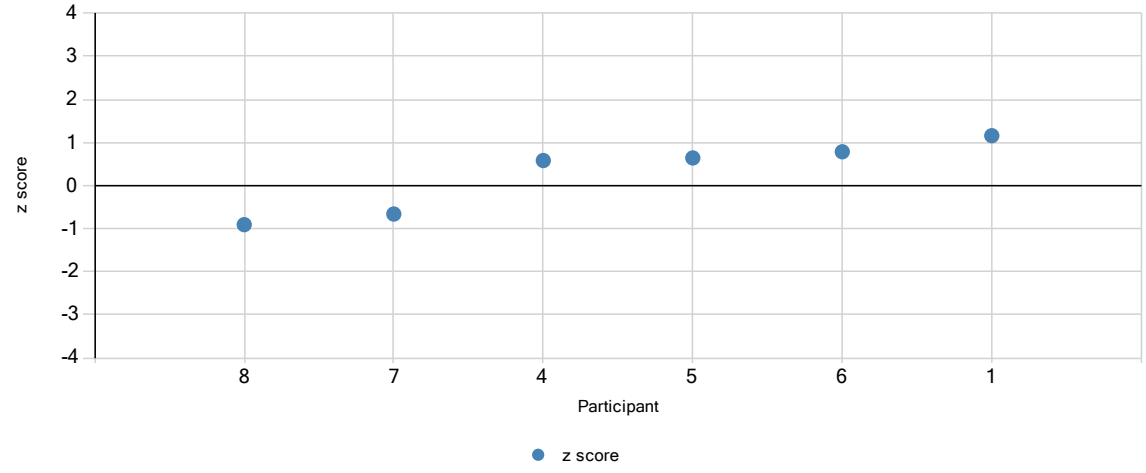
Measurand Styrene$_{RCRF}$ Sample IA1



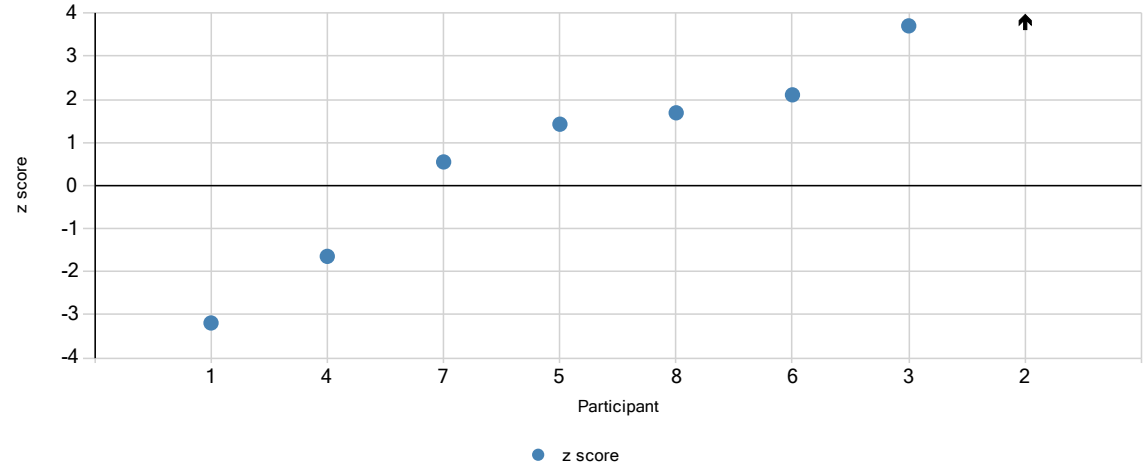
Measurand Styrene$_{TE}$ Sample IA1



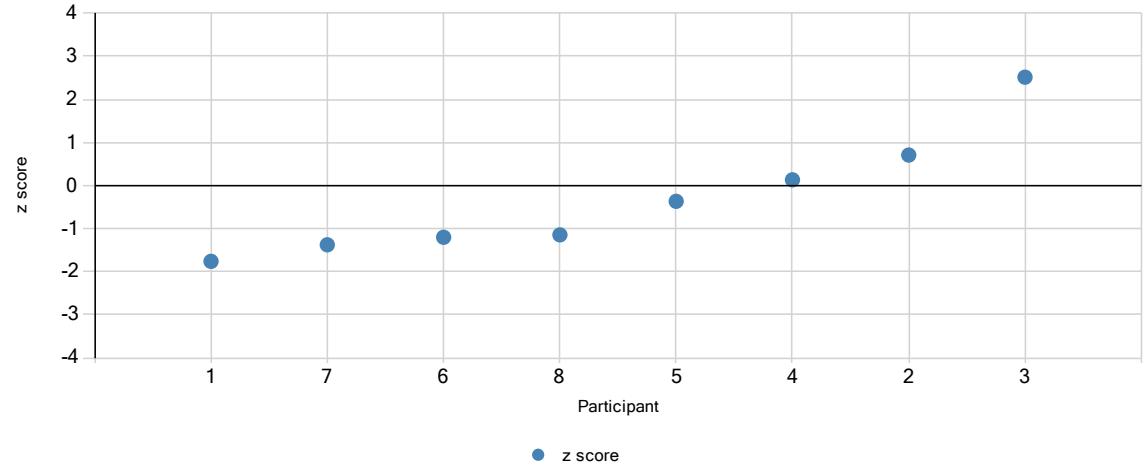
Measurand Tetrachloroethylene$_{RCRF}$ Sample IA1



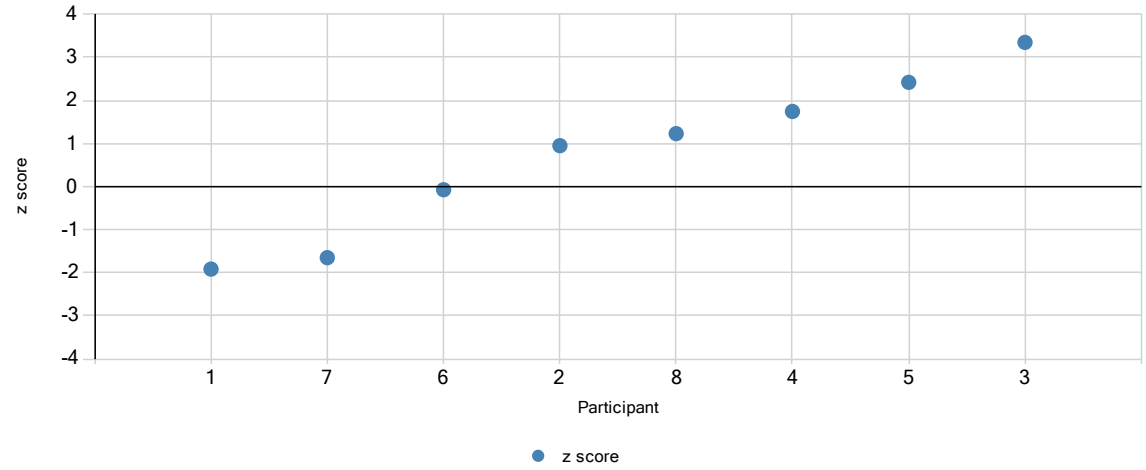
Measurand Tetrachloroethylene$_{TE}$ Sample IA1



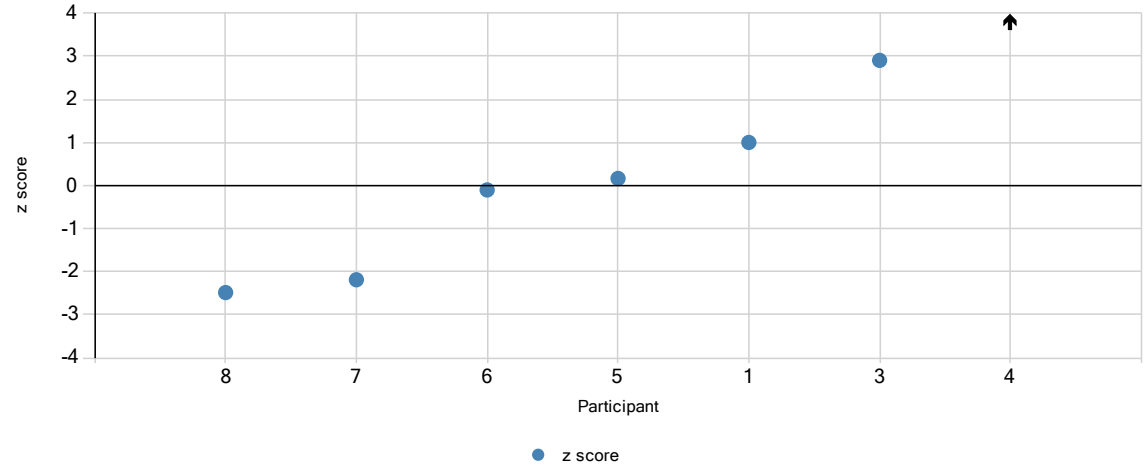
Measurand Toluene$_{RCRF}$ Sample IA1



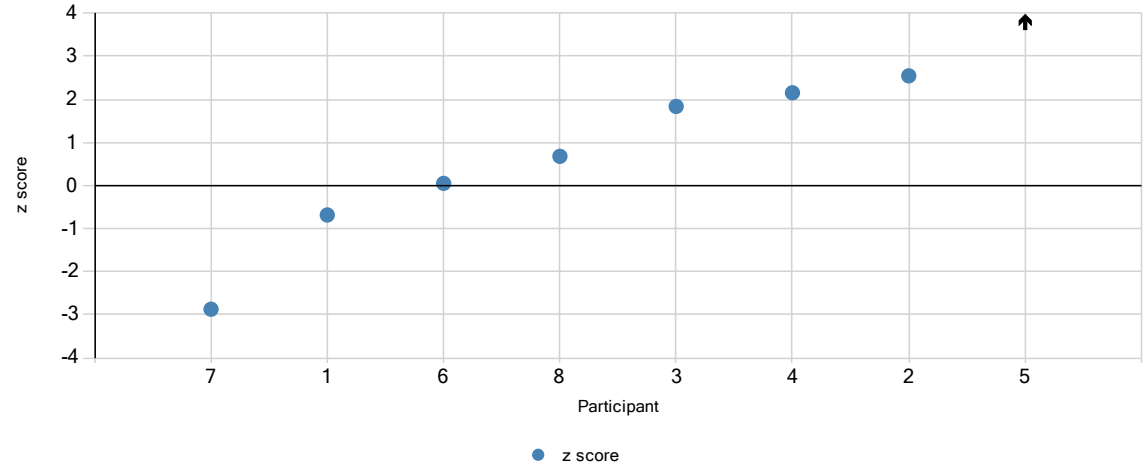
Measurand TVOC$_{Lab}$- Chamber blank Sample IA3



Measurand $TXIB_{RCRF}$ Sample IA1



Measurand $TXIB_{TE}$ Sample IA1

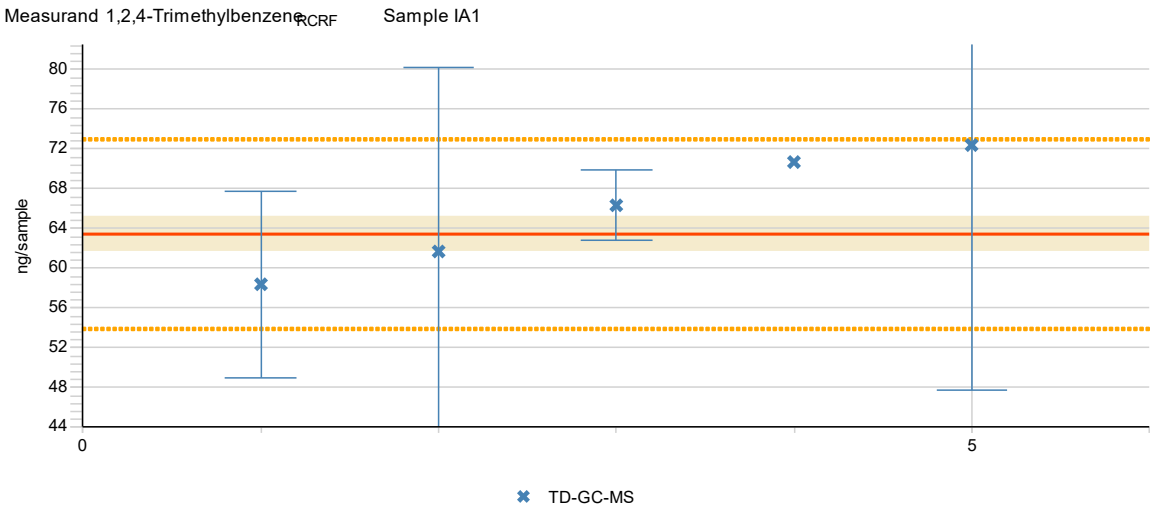


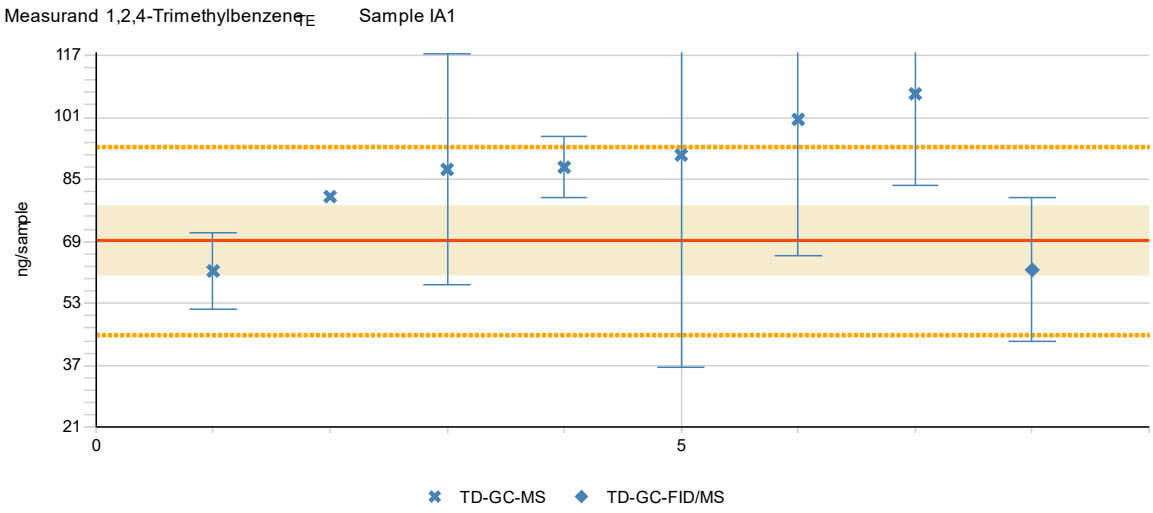
APPENDIX 11: Analytical methods

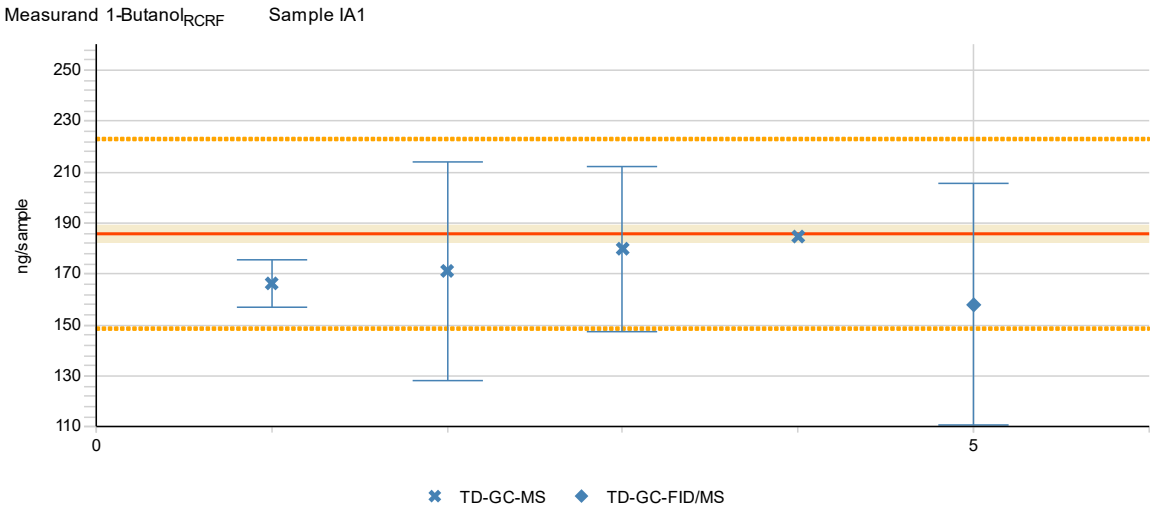
Participant	1	5	6	7	8
What kind of thermodesorption system/instrument was used?	Markes TD 100 (Autosampler ja Trap Module), 7890B GC, 5977A MSD	Markes TD	Perkin Elmer, ATD 350	TD-100 (Markes)	Markes TD100
What desorption temperature was used, in (°C)?	300	270	260 ºC	320	280
What desorption flow was the used, in ml/min?	20	30	30 ml/min	Tube desorption 50 ml/min Cold trap desortpion split flow 1 ml/min and split flow 30 ml/min (31 ml/min)	50
How long was desorption time, in minutes?	8	10	10 min	Tube desorption 8 min Cold trap desorption 5 min	10
What was the temperature of the cryo cold trap and the heating temperature, in °C?	- 10 -> 310 C	-10, 300	cryo temperature = -35ºC; heating temperature = 300ºC	15 C to 320 C	-20 300
What was flow rate of carrier gas, in ml/min?	1	2	1,0 ml/min	1 ml/min	1
Which type of analytical column was used?	HP5-MSUI, 30x0.25x0.25	HP-5ms	HP-5MS (50 m, 0.2mm, 0.33 um)	Agilent HP-5ms (50m x 0,2 mm x 0,33 µm)	HP-5MS
What kind of detector(s) was used?	FID and MSD	MSD	MSD 5977B	Agilent 5977A Inert MSD Turbo Pump	MSD
Did your results include the recovery rate?	no	no	no	no	yes
Do you have suggestions for substances for the next intercomparison?			1,4-dichlorobenzene trichloroethylene benzene	Texanol, propanoic acid and more compounds that have hetero (oxygen, nitrogen, silicon) atoms in their structure	

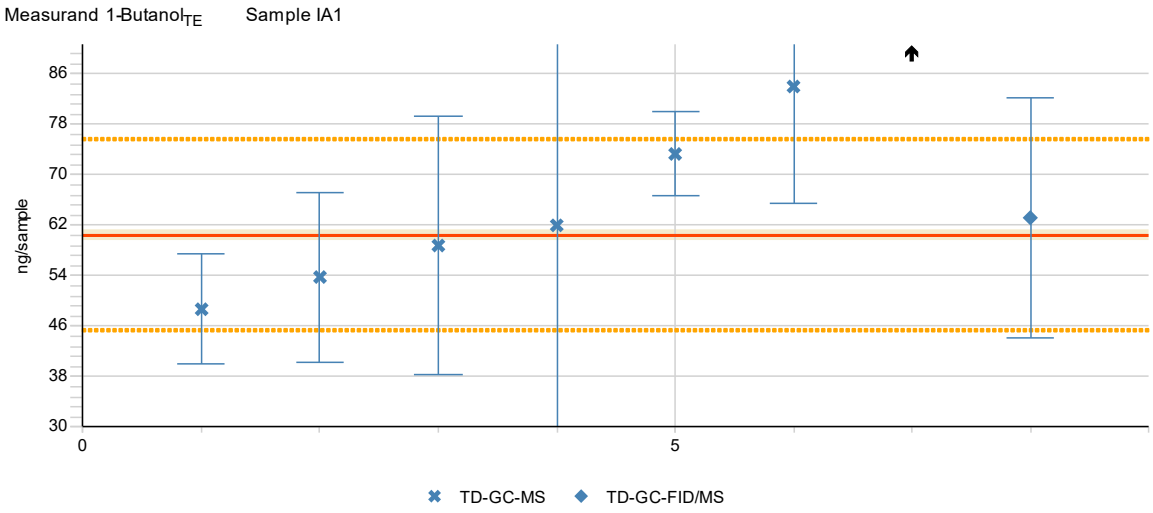
APPENDIX 12: Results grouped according to the methods

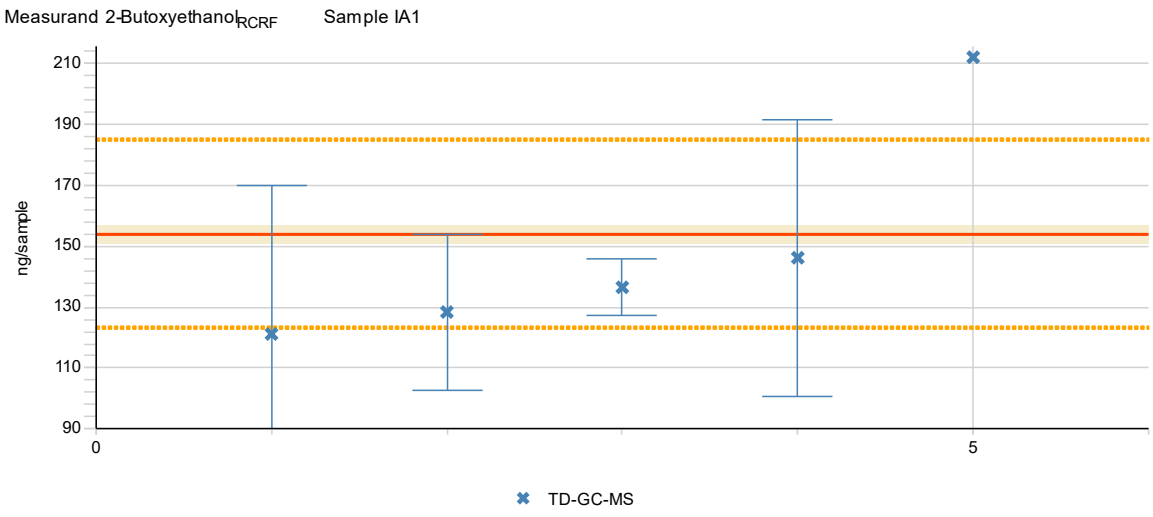
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.



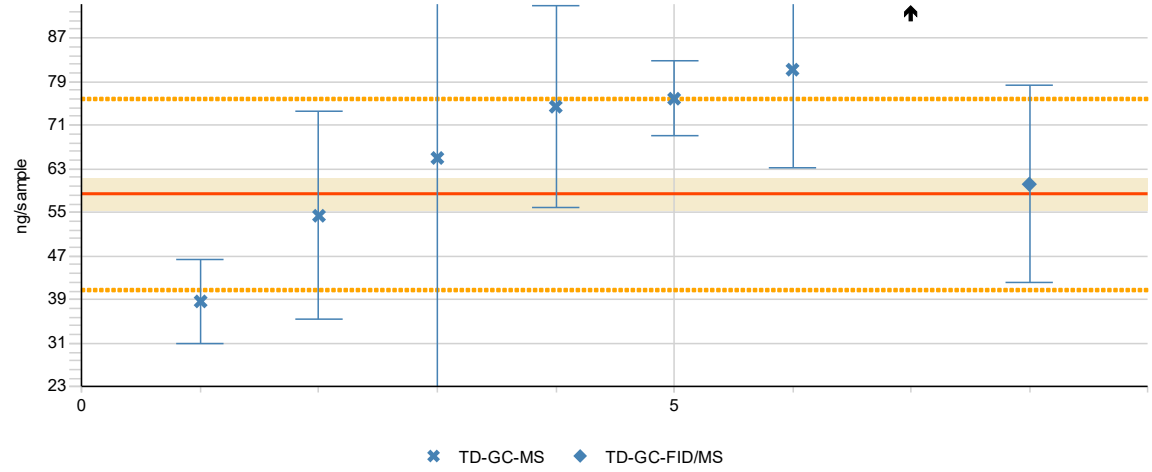



Measurand 1-Butanol$_{RCRF}$ Sample IA1
ng/sample
250
230
210
190
170
150
130
110
0
5
TD-GC-MS
TD-GC-FID/MS

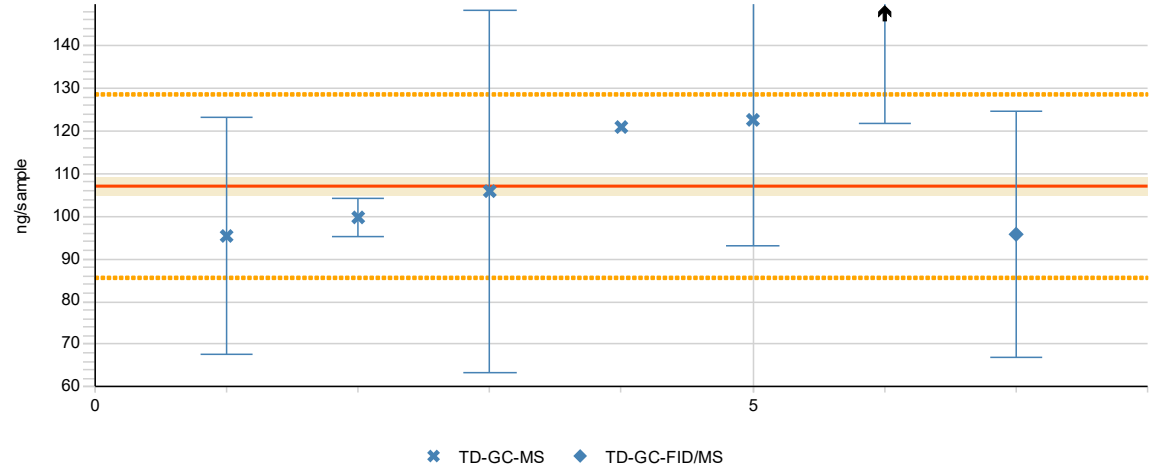

Measurand 1-Butanol$_{TE}$ Sample IA1
ng/sample
86
78
70
62
54
46
38
30
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand 2-Butoxyethanol$_{RCRF}$ Sample IA1
ng/sample
210
190
170
150
130
110
90
0
5
TD-GC-MS

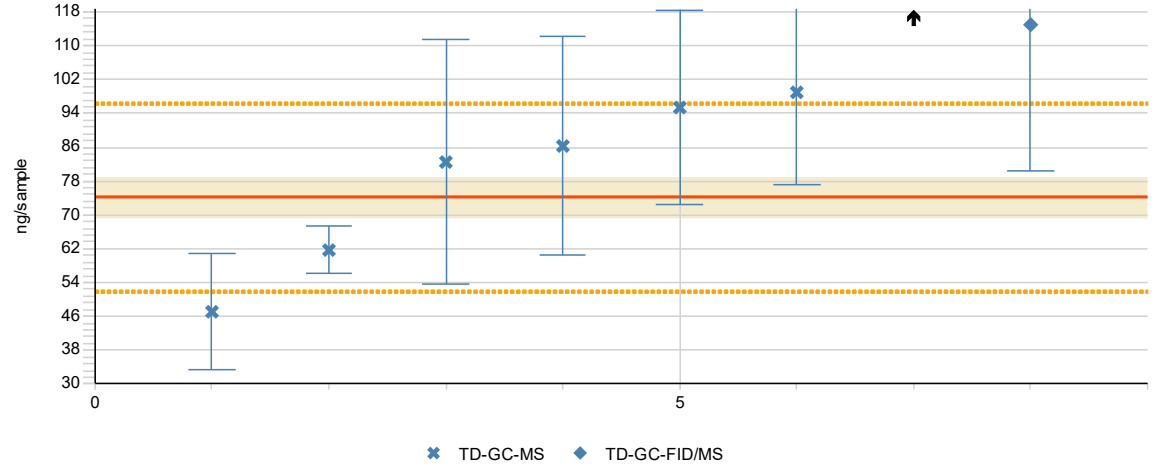
Measurand 2-Butoxyethanol$_{TE}$ Sample IA1

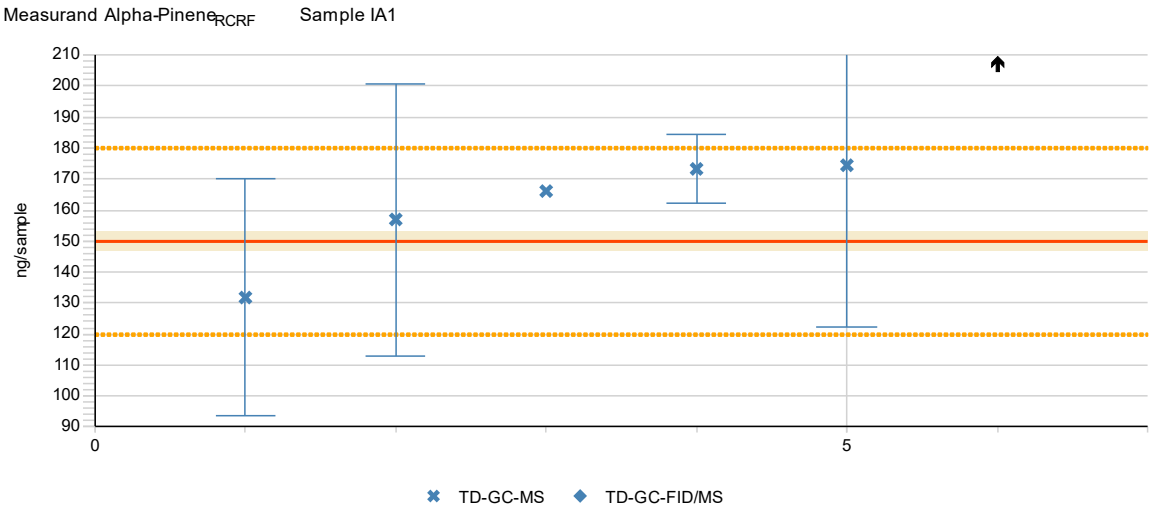


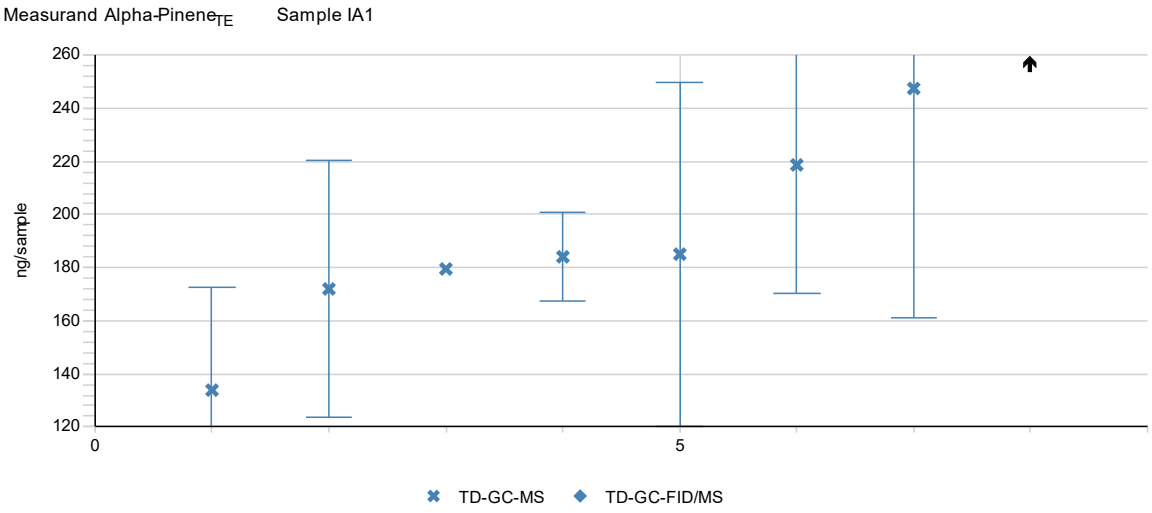
Measurand 2EH$_{RCRF}$ Sample IA1

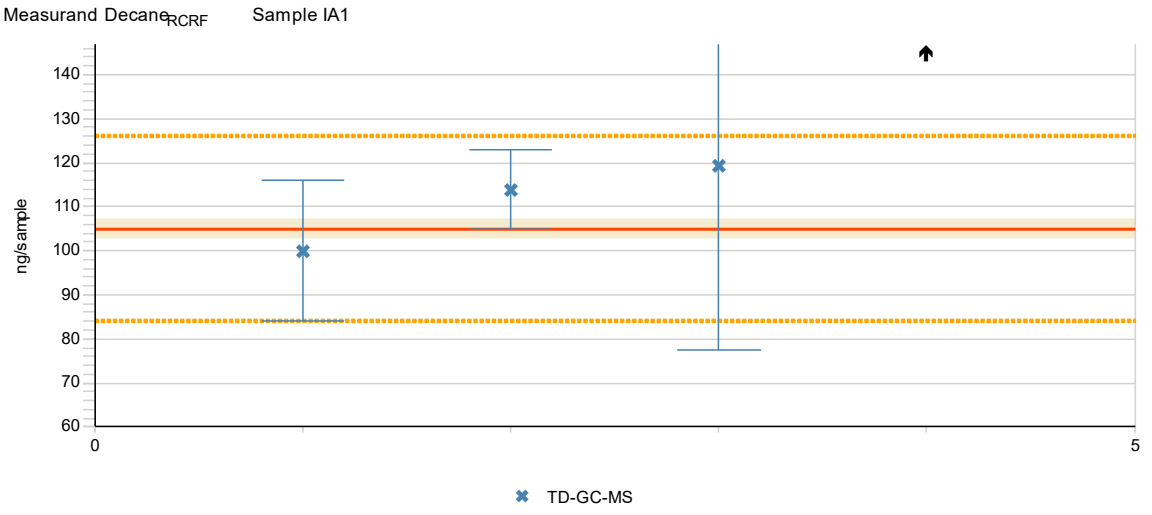


Measurand 2EH$_{TE}$ Sample IA1

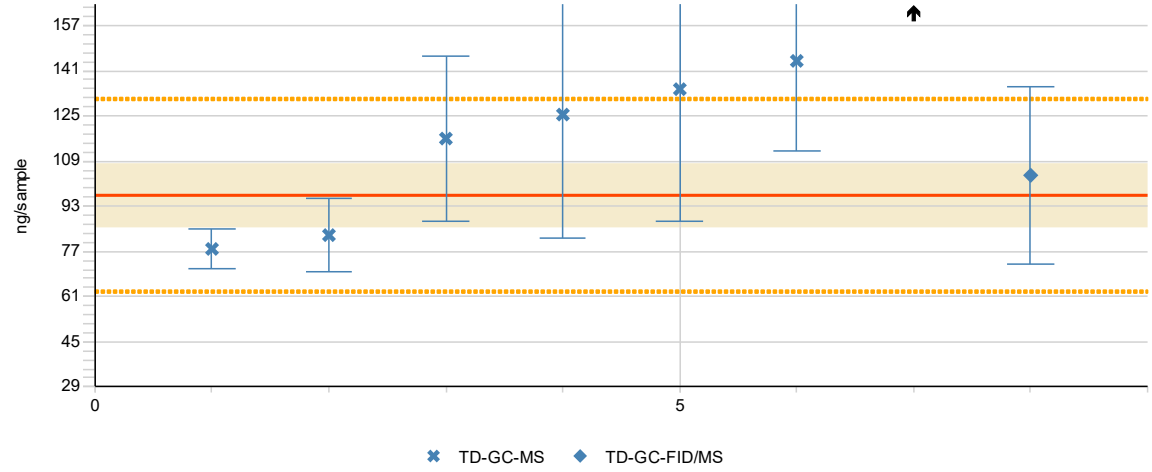



Measurand Alpha-Pinene$_{RCRF}$ Sample IA1
ng/sample
210
200
190
180
170
160
150
140
130
120
110
100
90
0
5
TD-GC-MS
TD-GC-FID/MS

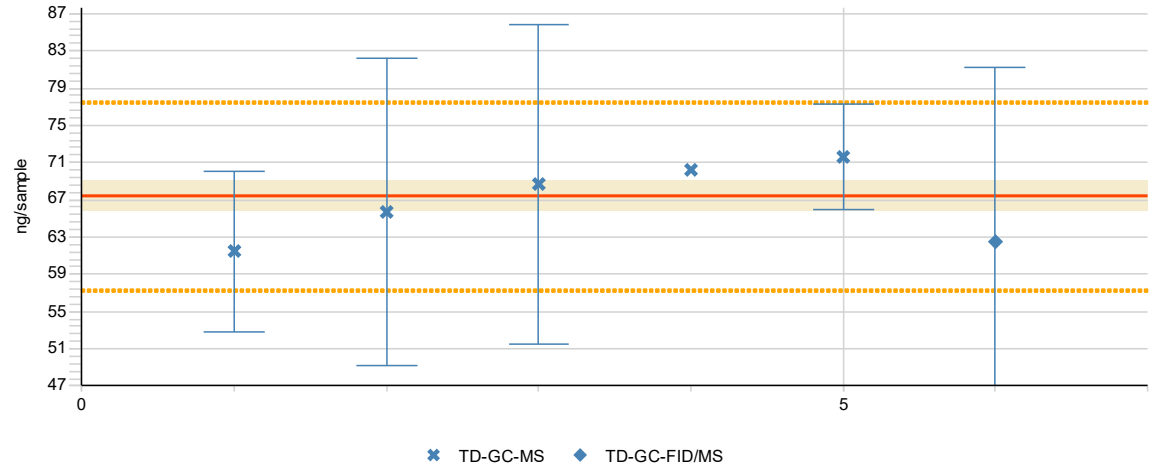

Measurand Alpha-Pinene$_{TE}$ Sample IA1
ng/sample
260
240
220
200
180
160
140
120
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Decane$_{RCRF}$ Sample IA1
ng/sample
140
130
120
110
100
90
80
70
60
0
5
TD-GC-MS

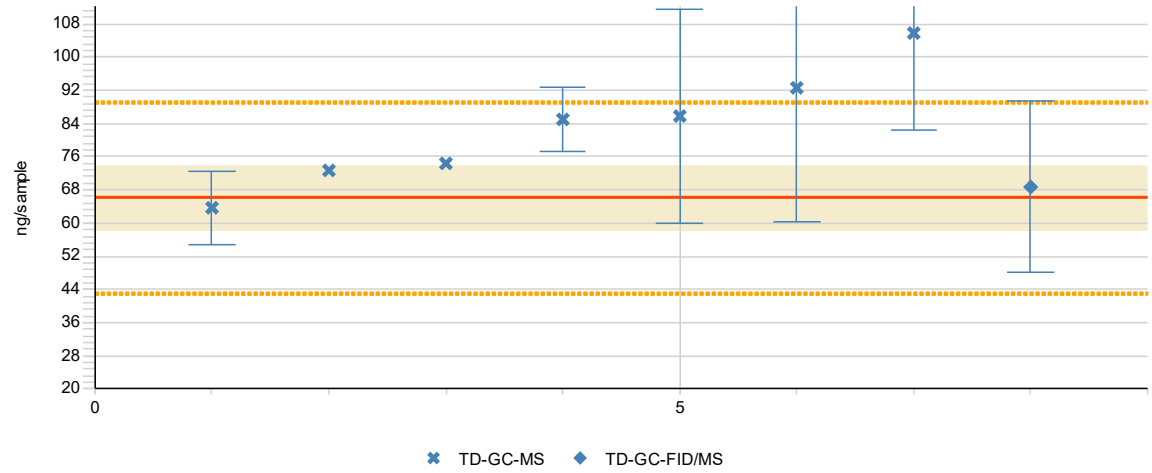
Measurand Decane$_{TE}$ Sample IA1

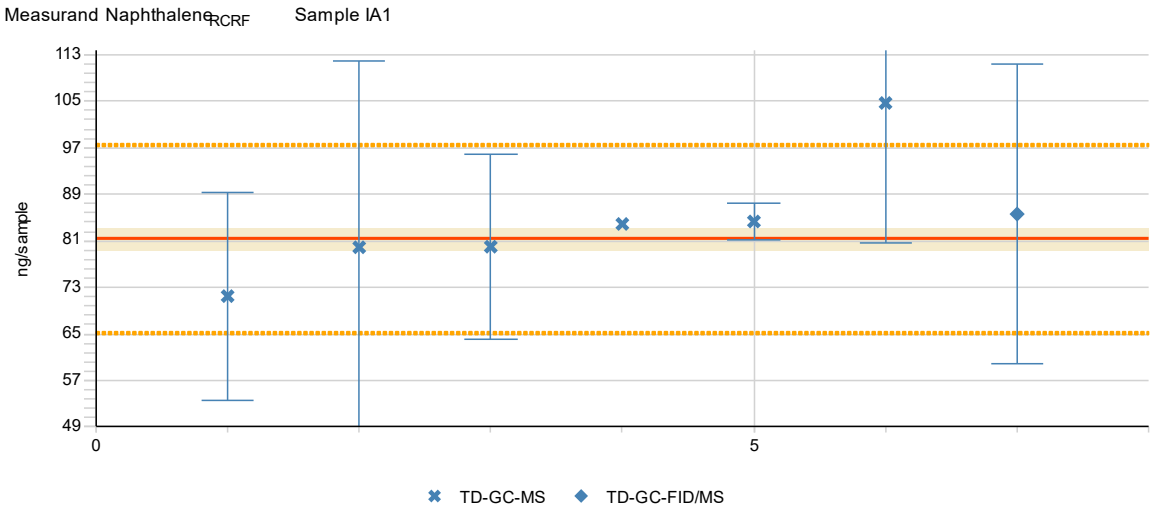


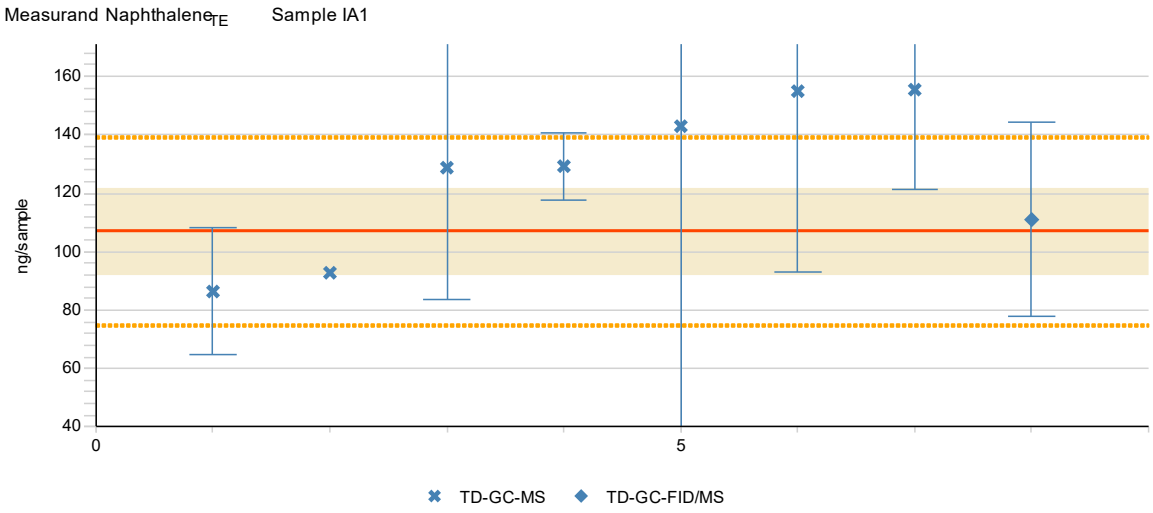
Measurand Ethylbentzene$_{RCRF}$ Sample IA1

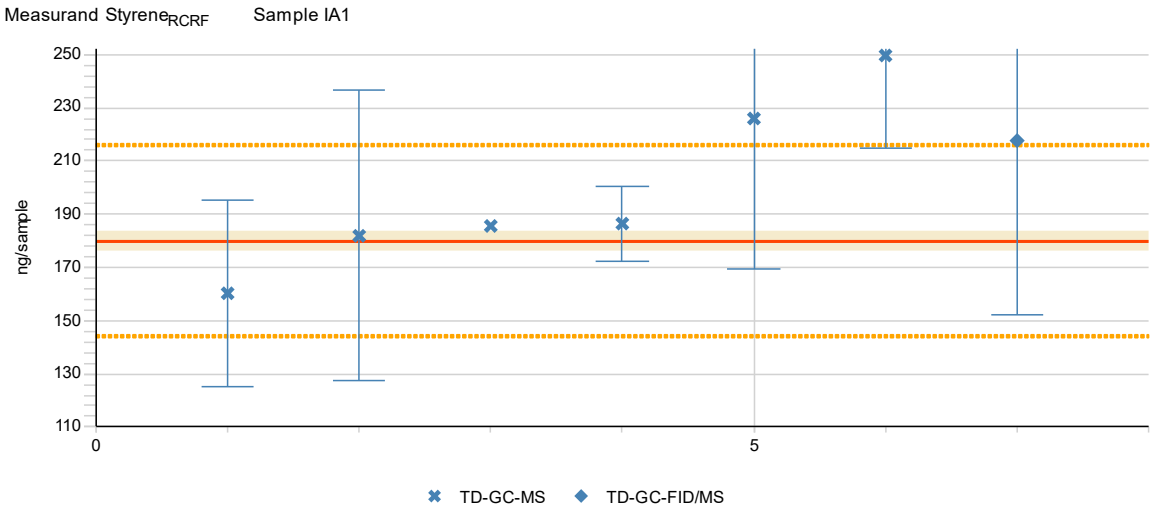


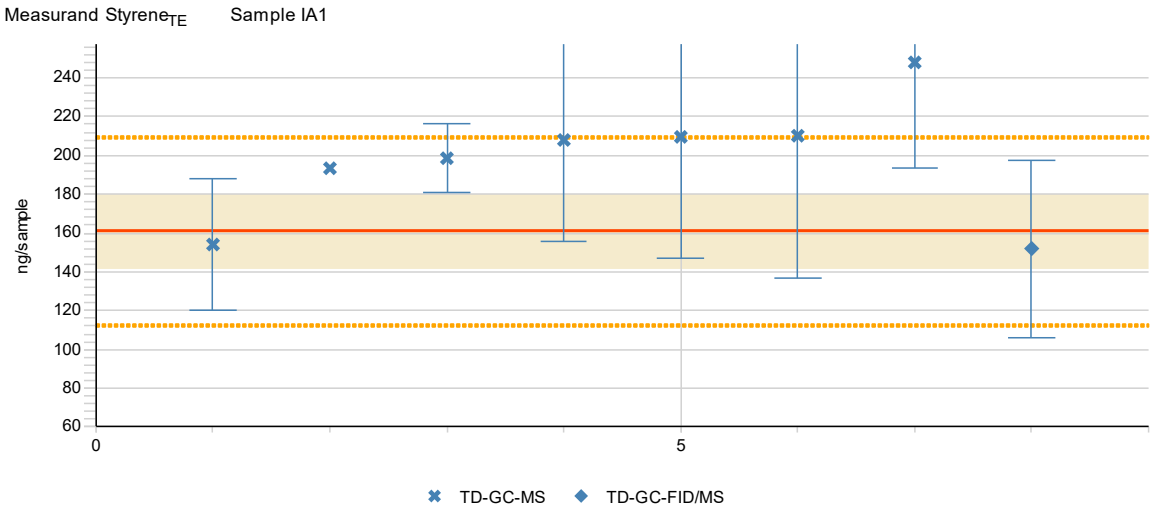
Measurand Ethylbenzene$_{TE}$ Sample IA1

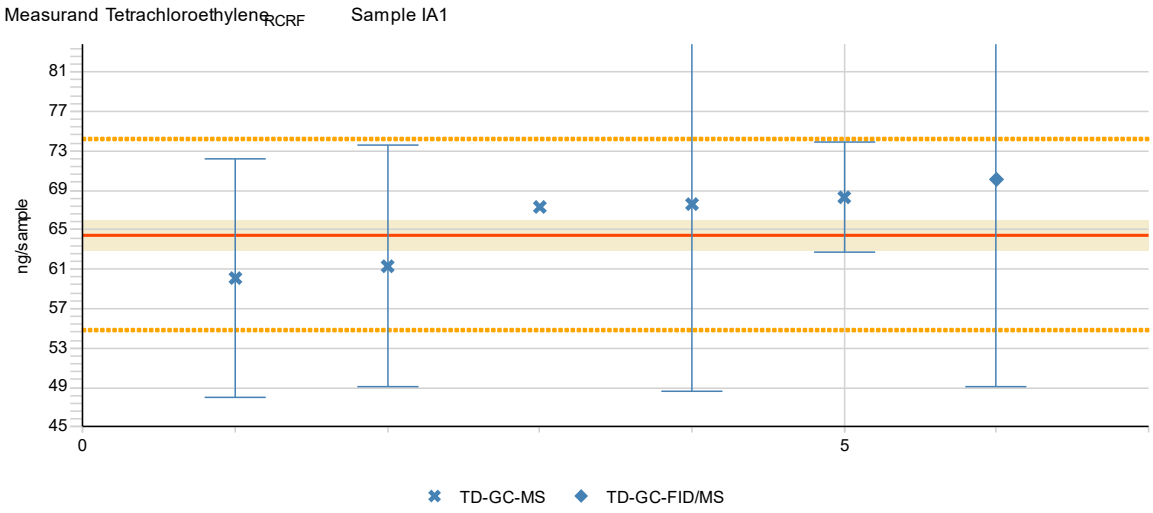


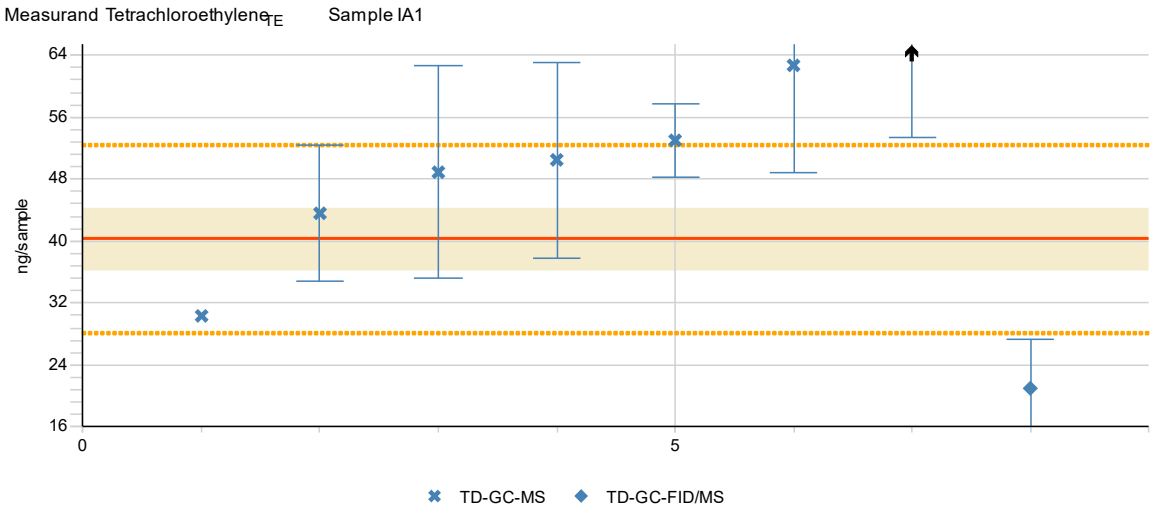

Measurand Naphthalene RCRF
Sample IA1
ng/sample
113
105
97
89
81
73
65
57
49
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Naphthalene TE
Sample IA1
ng/sample
160
140
120
100
80
60
40
0
5
TD-GC-MS
TD-GC-FID/MS

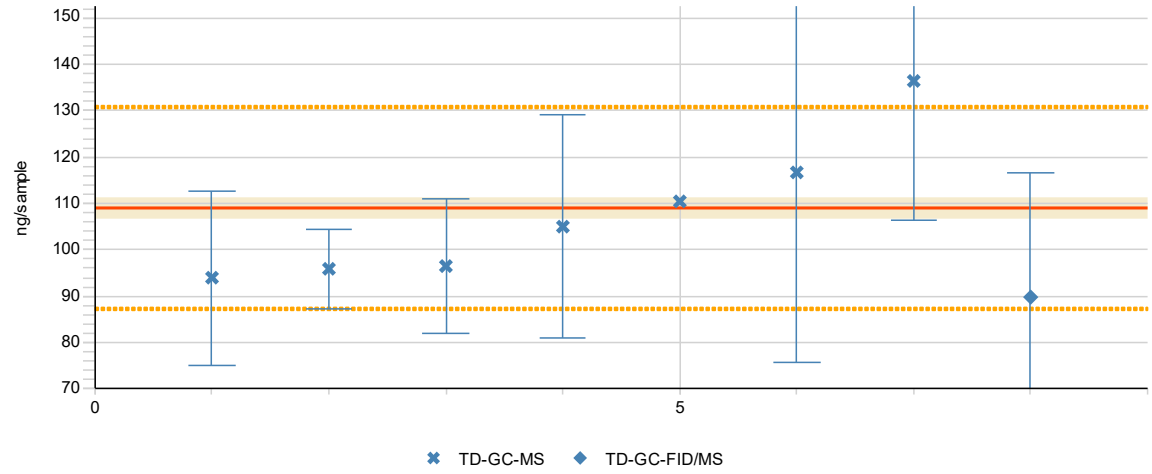

Measurand Styrene RCRF
Sample IA1
ng/sample
250
230
210
190
170
150
130
110
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Styrene$_{TE}$ Sample IA1
ng/sample
240
220
200
180
160
140
120
100
80
60
0
5
TD-GC-MS
TD-GC-FID/MS

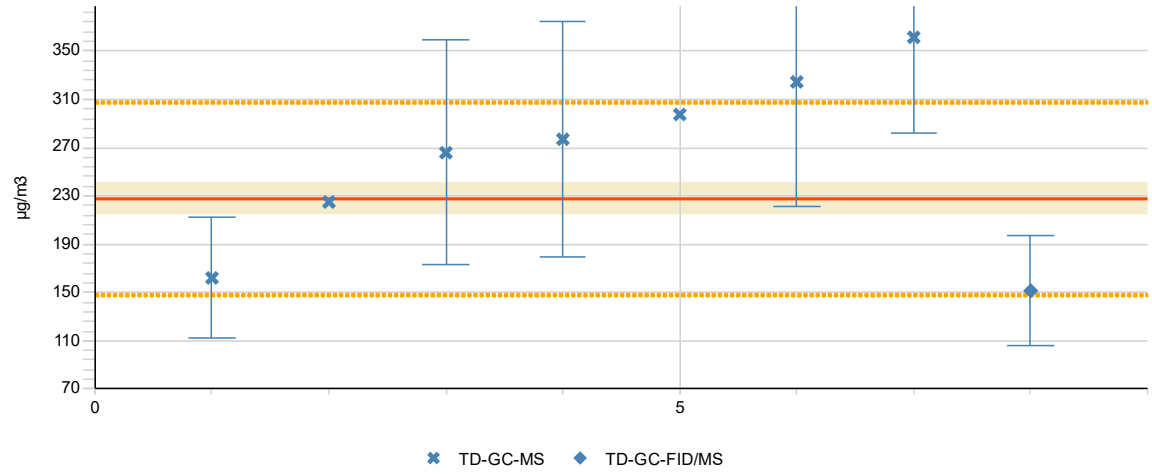

Measurand Tetrachloroethylene$_{RCRF}$ Sample IA1
ng/sample
81
77
73
69
65
61
57
53
49
45
0
5
TD-GC-MS
TD-GC-FID/MS


Measurand Tetrachloroethylene$_{TE}$ Sample IA1
ng/sample
64
56
48
40
32
24
16
0
5
TD-GC-MS
TD-GC-FID/MS

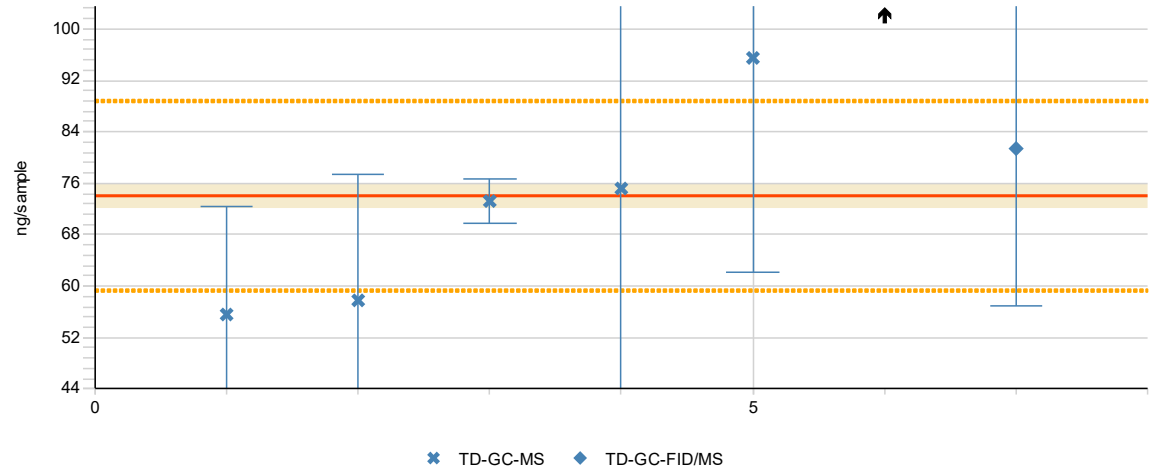
Measurand $Toluene_{RCRF}$ Sample IA1

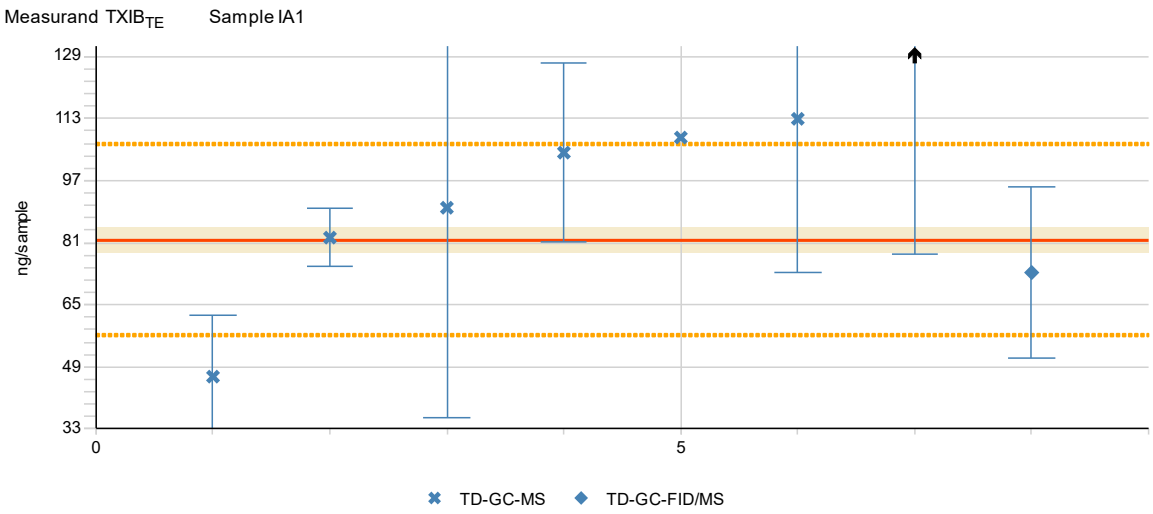


Measurand $TVOC_{Lab}$- Chamber blank Sample IA3



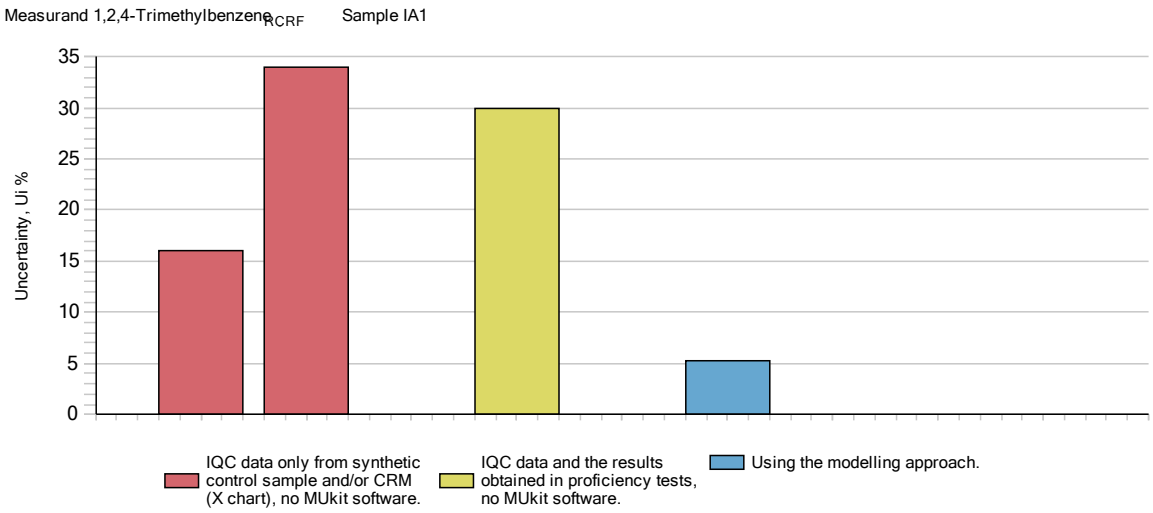
Measurand $TXIB_{RCRF}$ Sample IA1

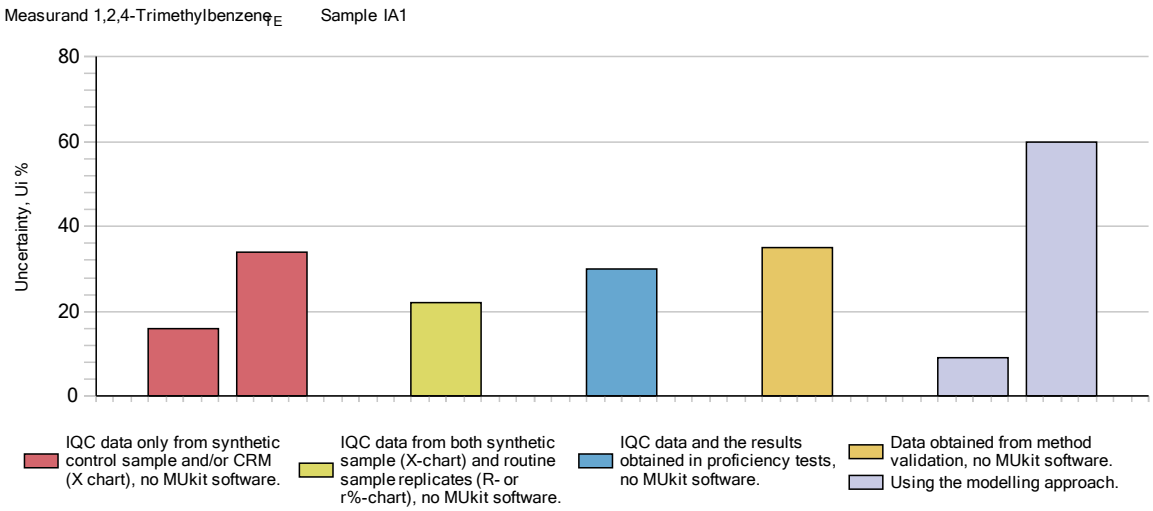



Measurand TXIB$_{TE}$
Sample IA1
129
113
97
81
65
49
33
ng/sample
0
5
TD-GC-MS
TD-GC-FID/MS

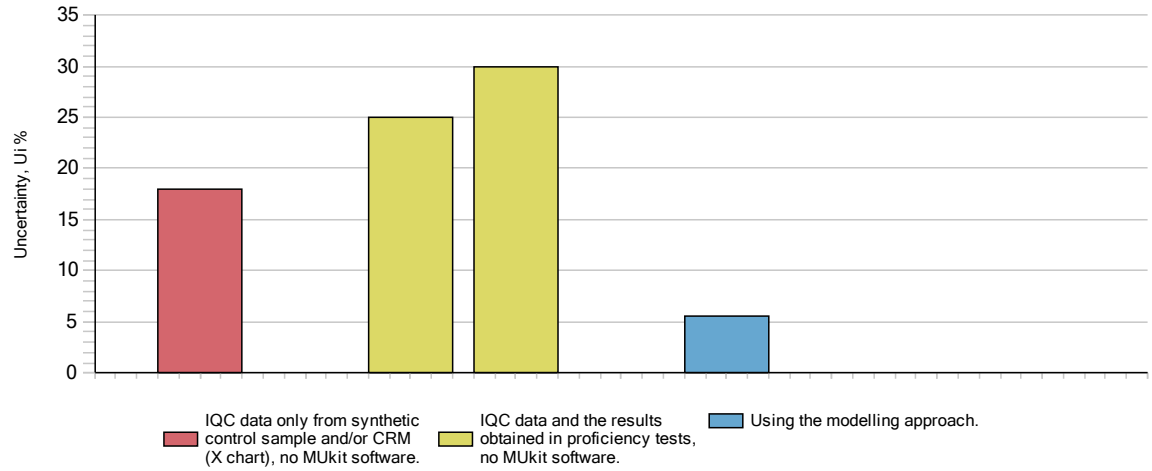
APPENDIX 13: Examples of measurement uncertainties reported by the participants

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].

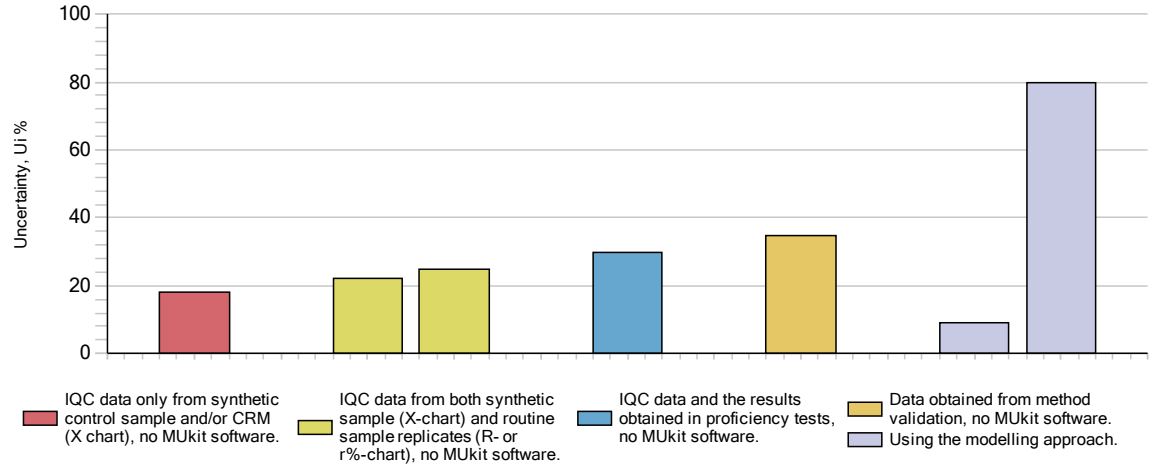




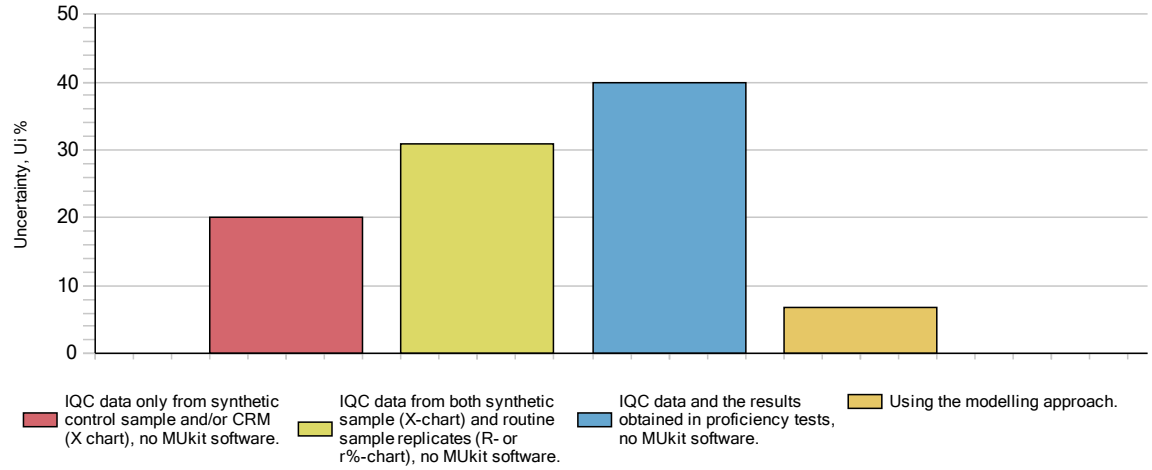
Measurand 1-Butanol$_{RCRF}$ Sample IA1



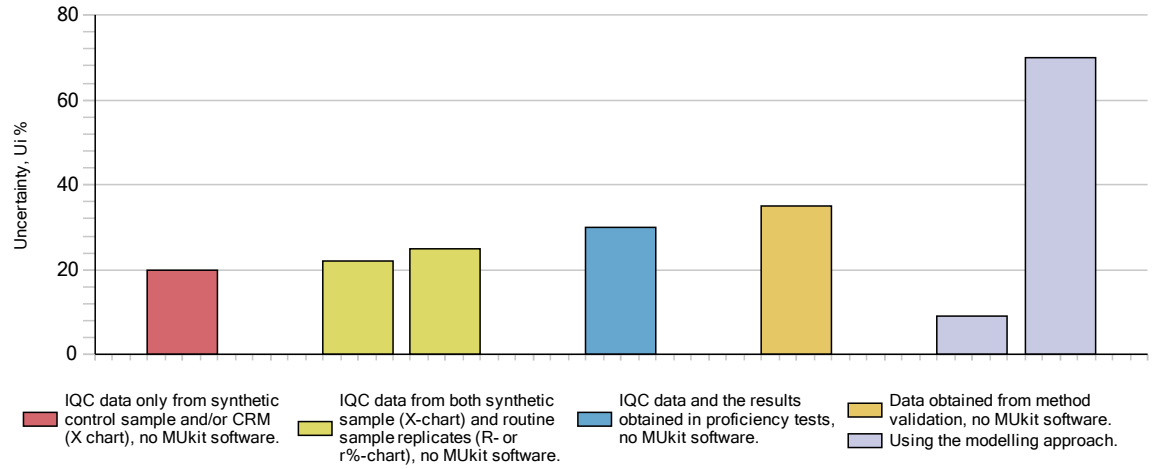
Measurand 1-Butanol$_{TE}$ Sample IA1



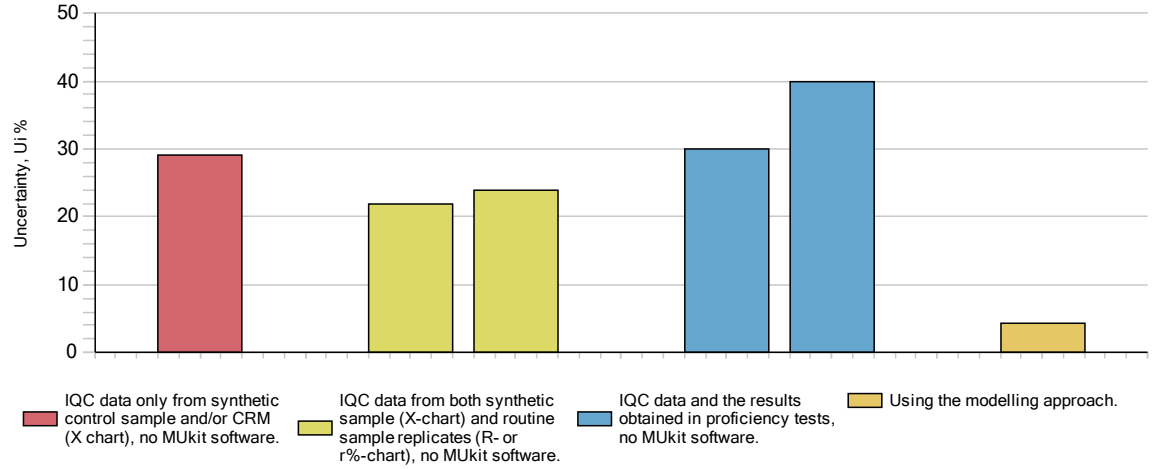
Measurand 2-Butoxyethanol$_{RCRF}$ Sample IA1



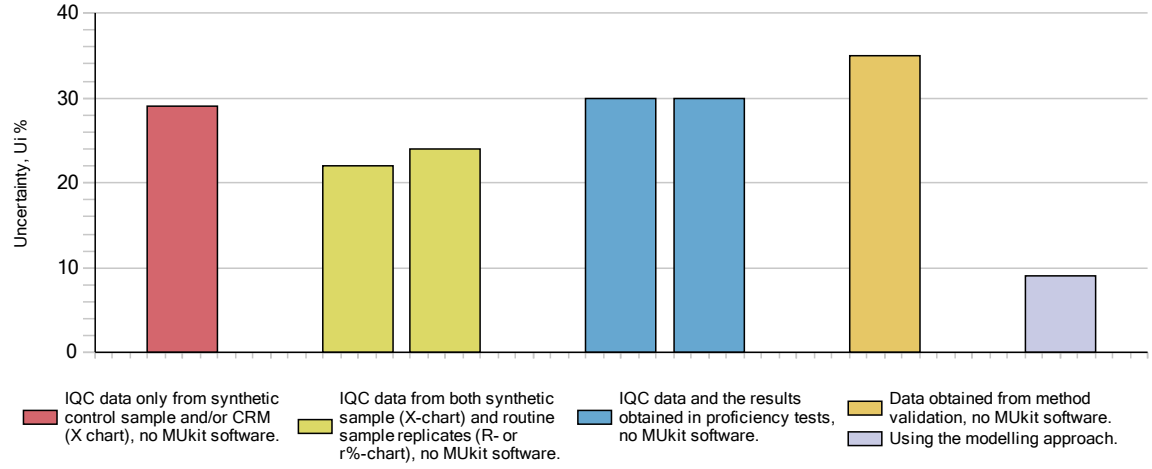
Measurand 2-Butoxyethanol$_{TE}$ Sample IA1



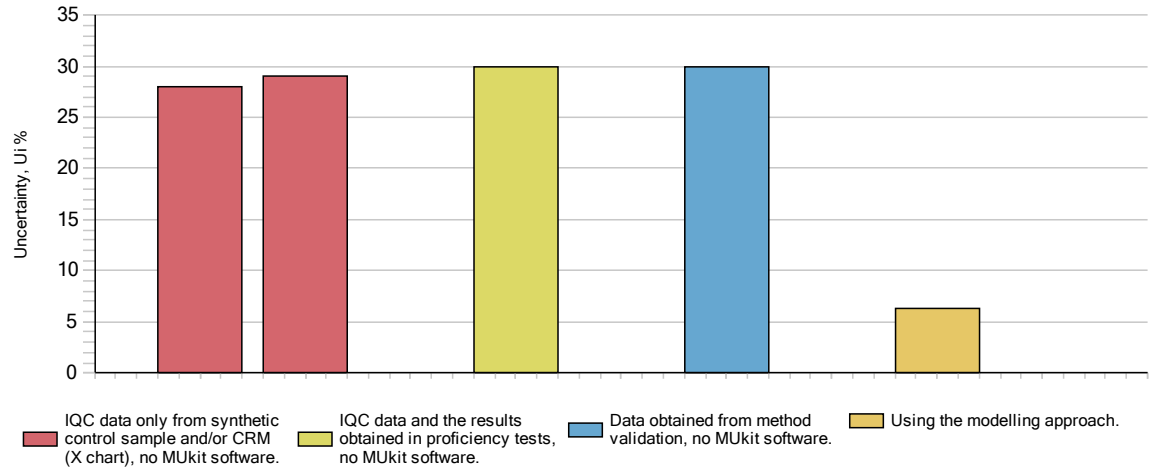
Measurand 2EH$_{RCRF}$ Sample IA1



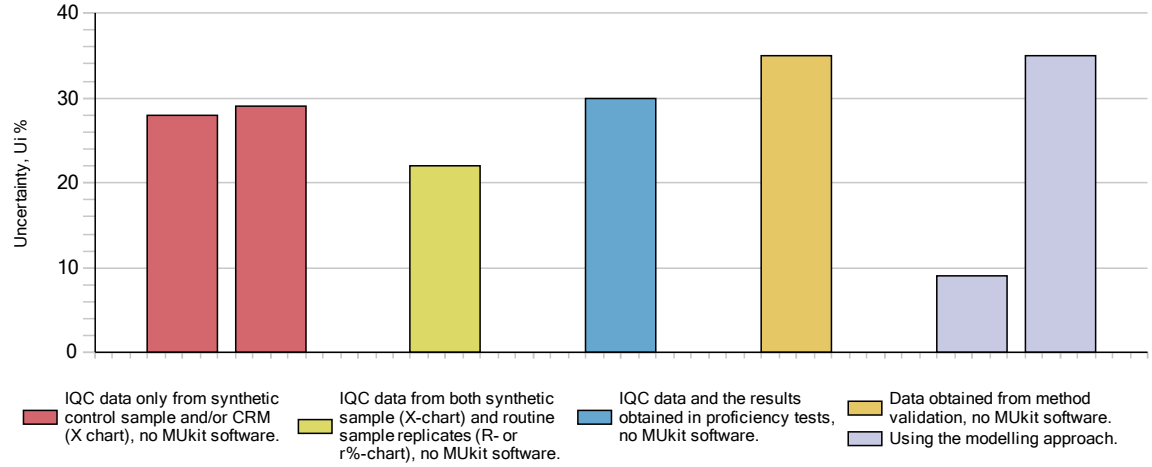
Measurand 2EH$_{TE}$ Sample IA1



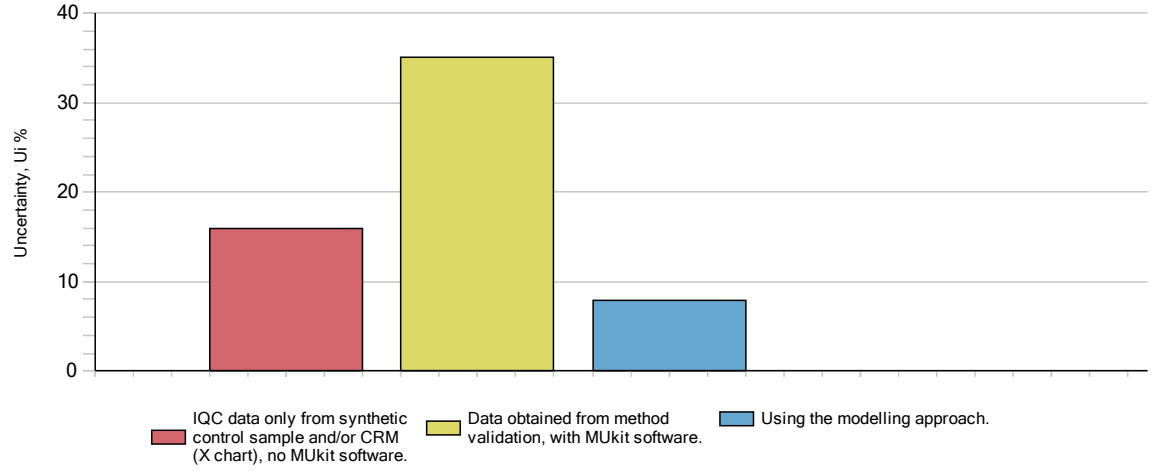
Measurand Alpha-Pinene$_{RCRF}$ Sample IA1



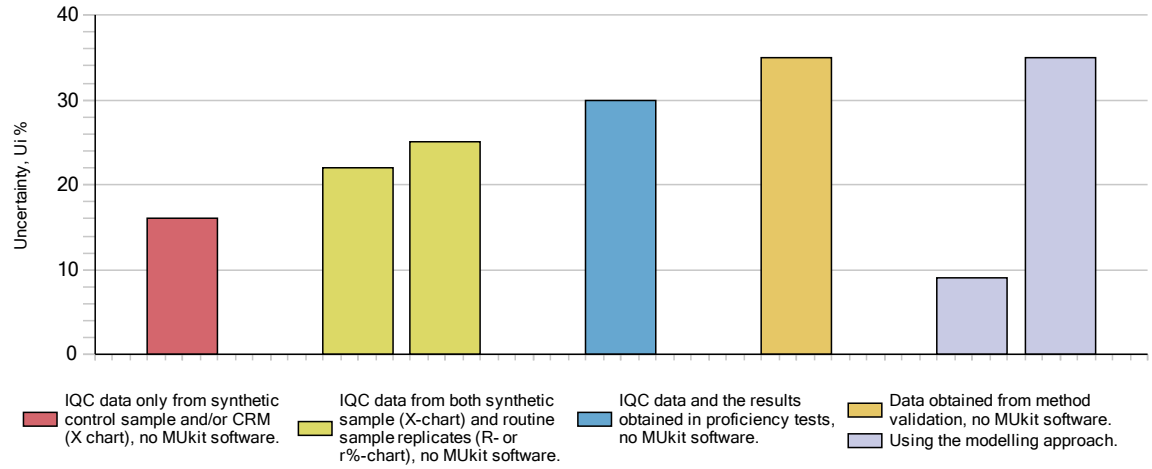
Measurand Alpha-Pinene$_{TE}$ Sample IA1



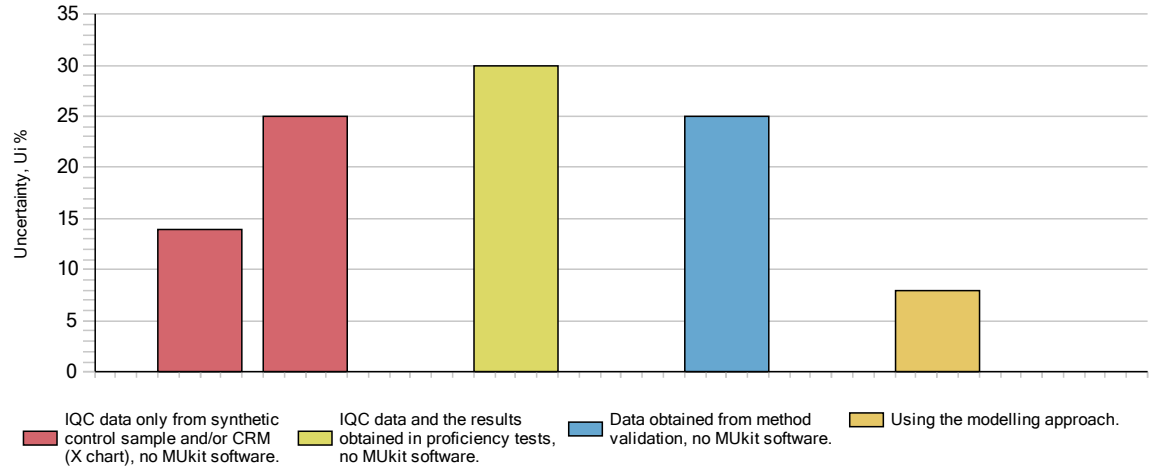
Measurand Decane$_{RCRF}$ Sample IA1



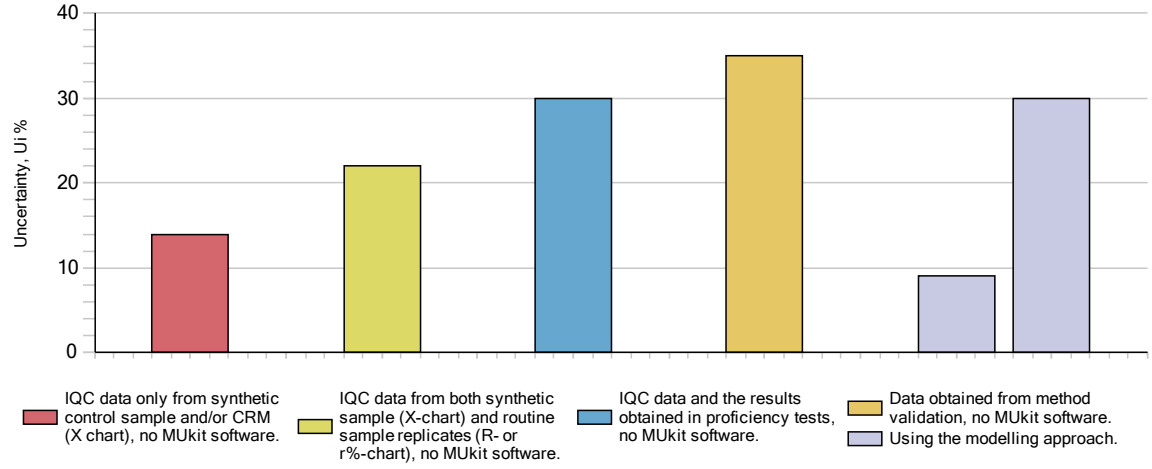
Measurand Decane$_{TE}$ Sample IA1



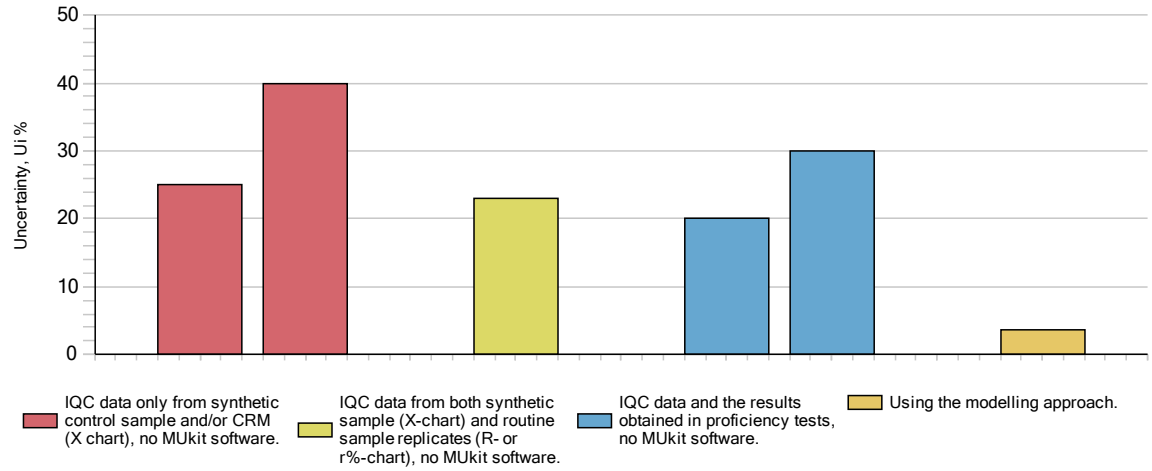
Measurand Ethylbentzene$_{RCRF}$ Sample IA1



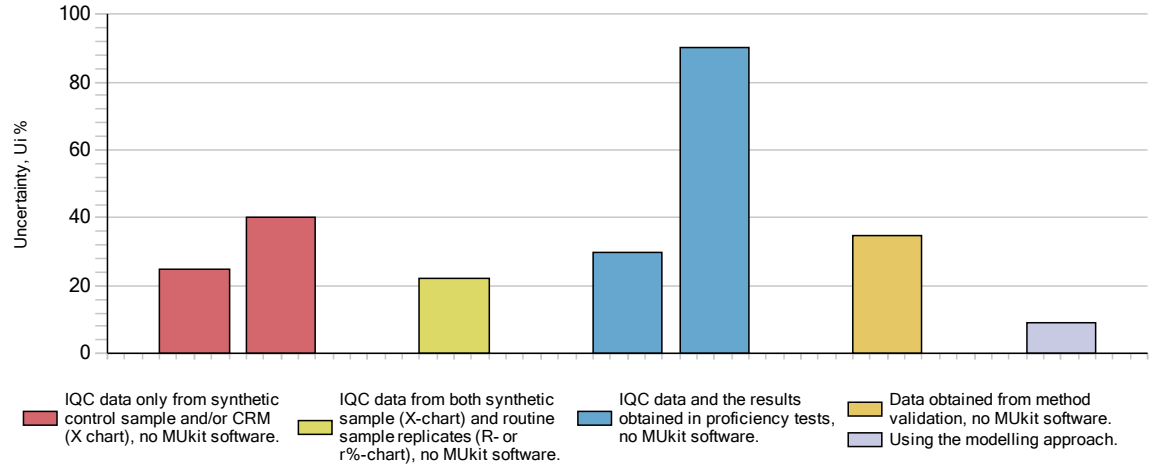
Measurand Ethylbenzene$_{TE}$ Sample IA1



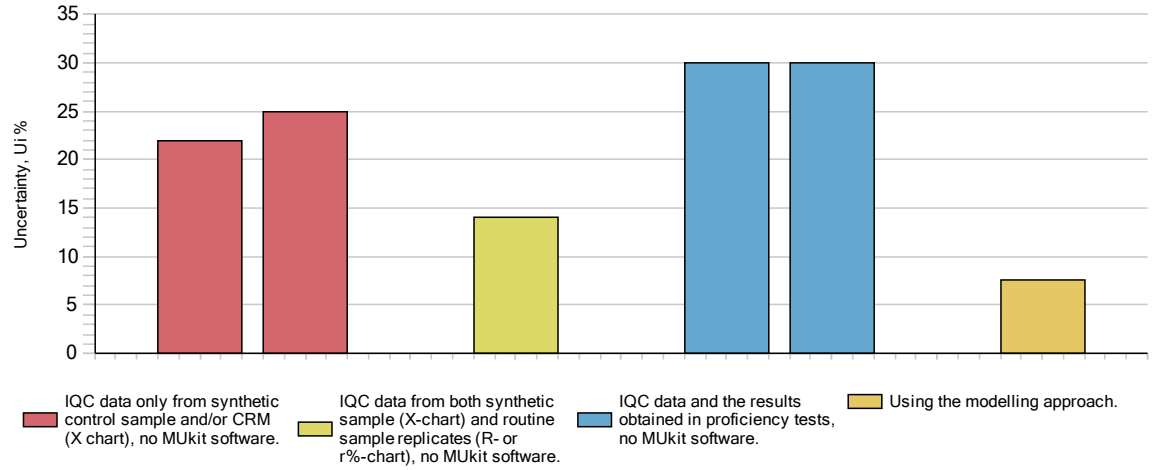
Measurand Naphthalene$_{RCRF}$ Sample IA1

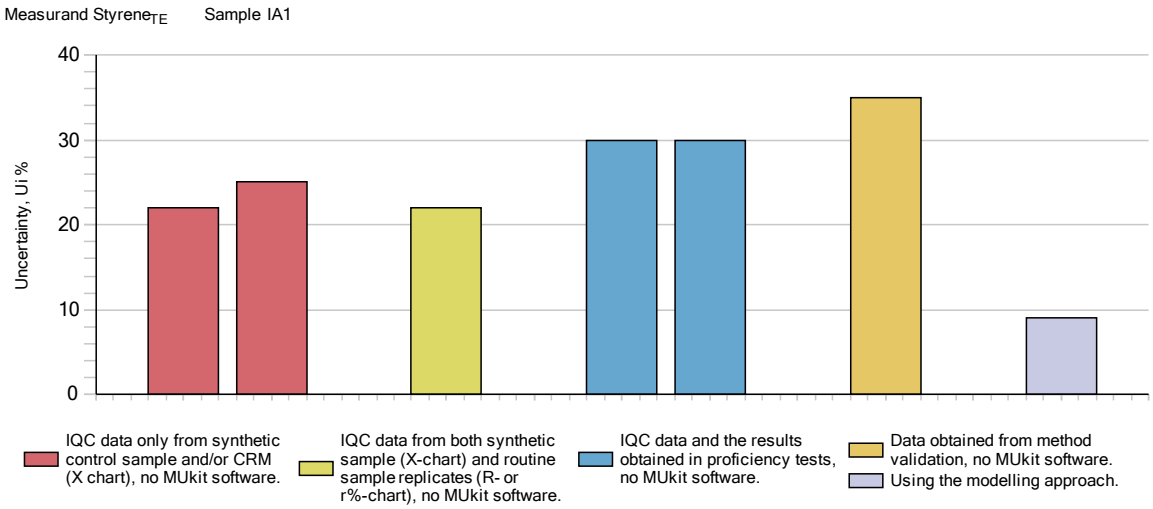


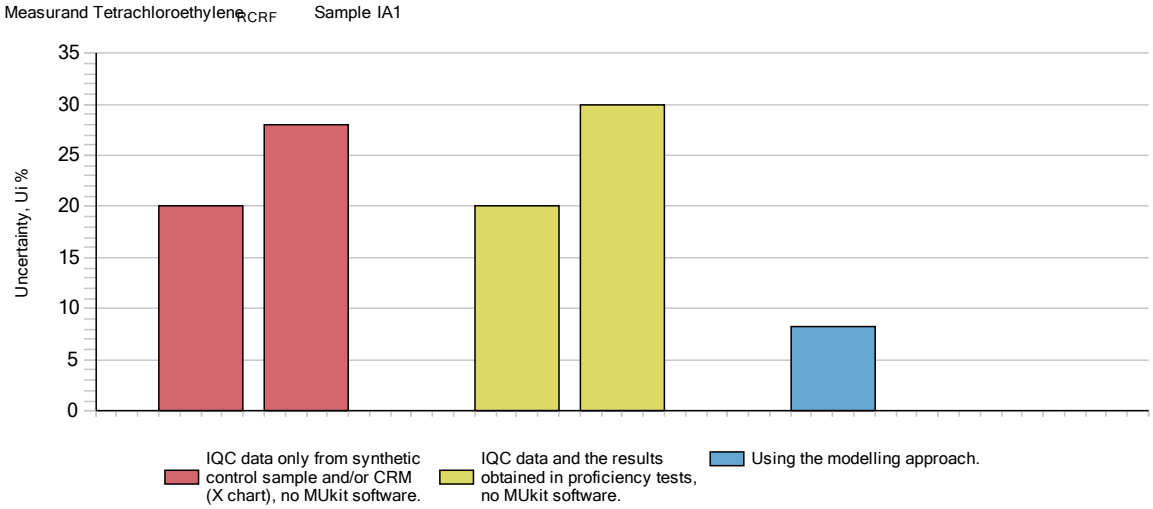
Measurand Naphthalene$_{TE}$ Sample IA1

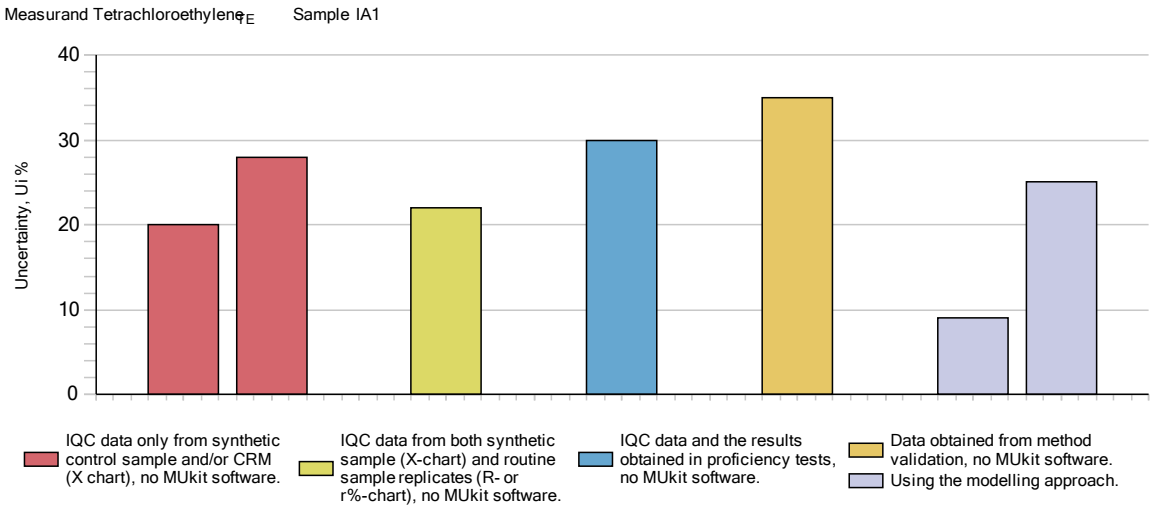


Measurand Styrene$_{RCRF}$ Sample IA1

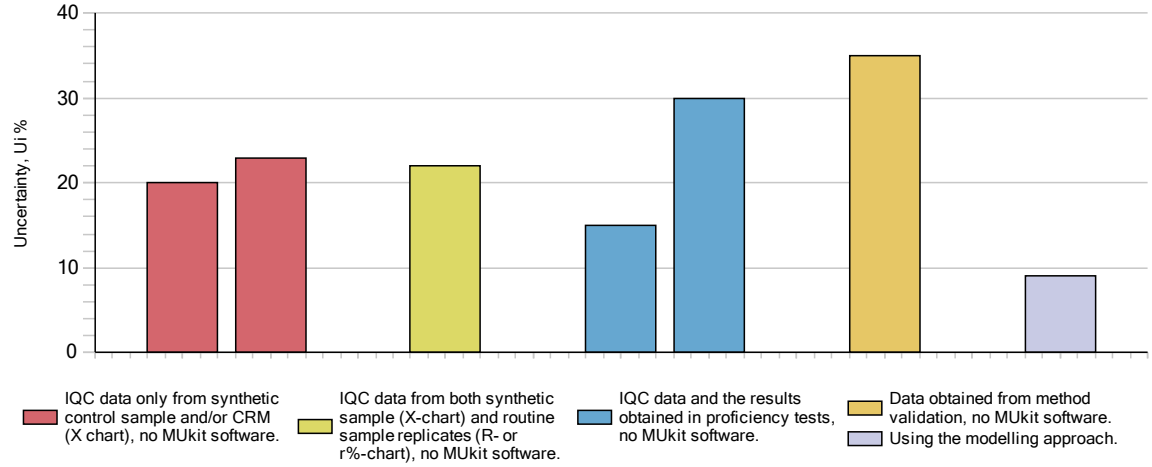



Measurand Styrene$_{TE}$ Sample IA1
Uncertainty, Ui %
40
30
20
10
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in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

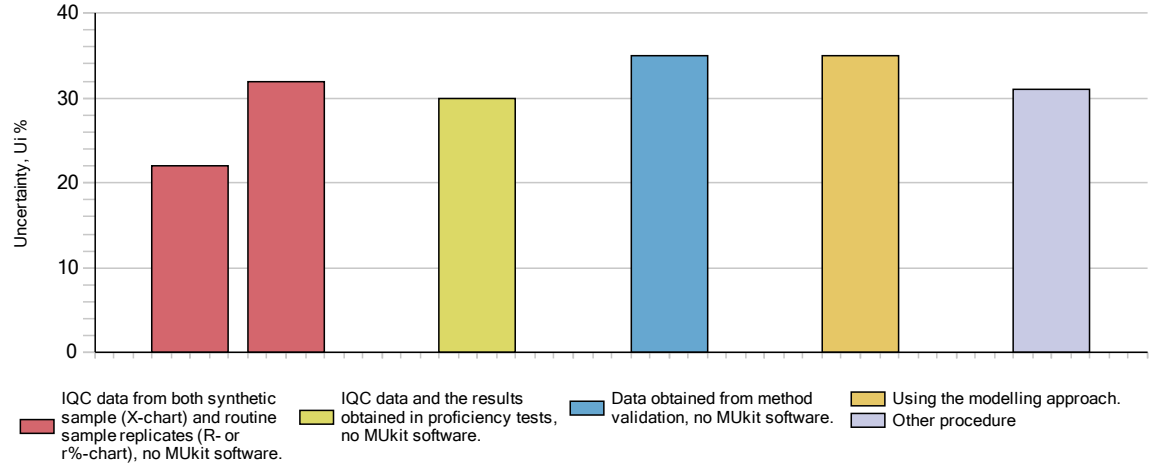

Measurand Tetrachloroethylene$_{RCRF}$ Sample IA1
Uncertainty, Ui %
35
30
25
20
15
10
5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Using the modelling approach.


Measurand Tetrachloroethylene$_{TE}$ 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 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.

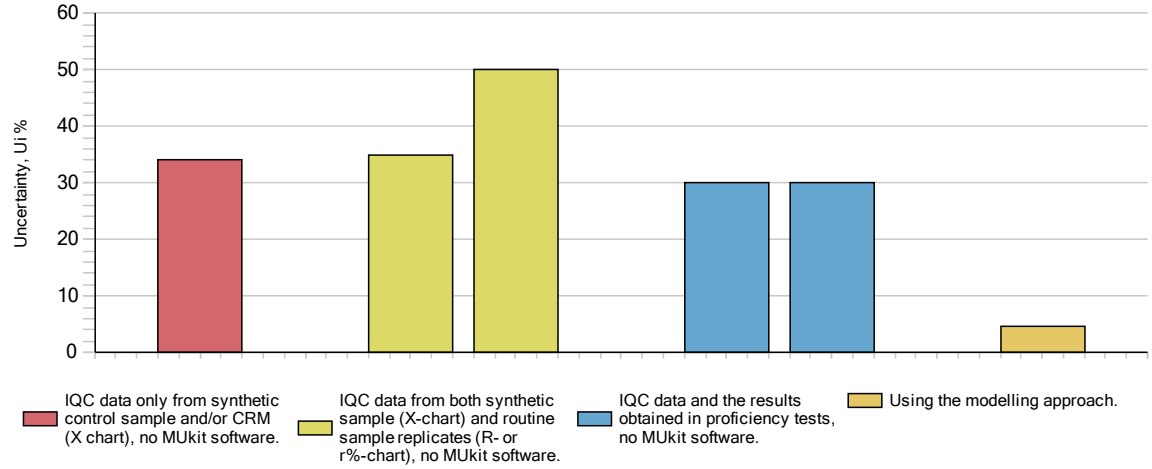
Measurand $Toluene_{RCRF}$ Sample IA1

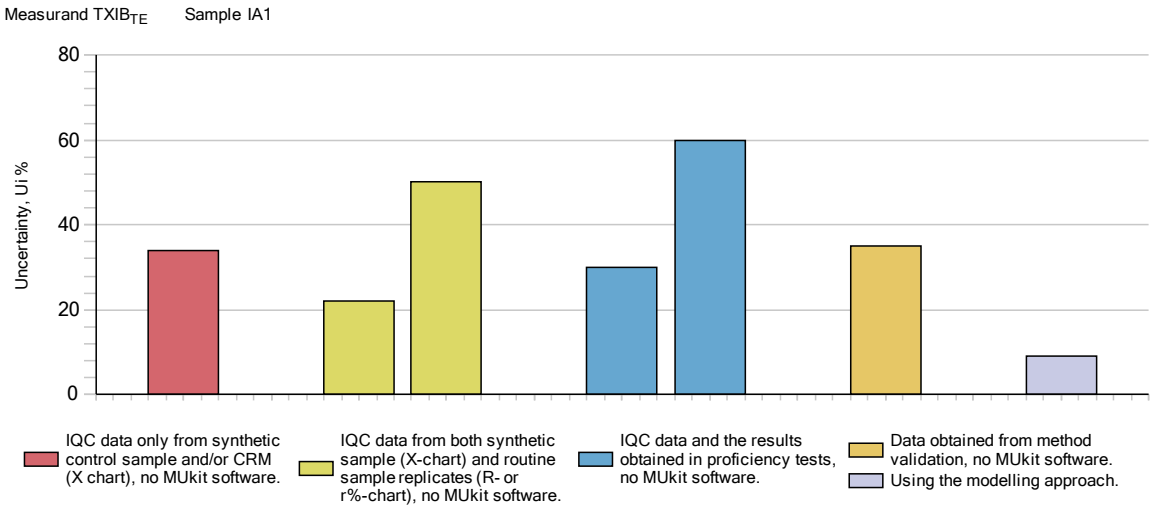


Measurand $TVOC_{Lab}$- Chamber blank Sample IA3



Measurand $TXIB_{RCRF}$ Sample IA1




Measurand TXIB$_{TE}$
Sample IA1
80
60
40
20
0
Uncertainty, Ui %
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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