VSL

National Metrology Institute

Results of interlaboratory comparison with gaseous reference materials

Webinar Metrology for indoor air quality

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11 April 2024 – Online

Introduction

- VOC gaseous reference materials
  - Production PRM & CRM
  - Analysis
  - Uncertainty
  - Storage and stability
  - Conclusion
- Interlaboratory comparison
  - Comparison
  - Results
  - Conclusion

Relevant VOCs

- VOCs from according to EN 16516 (8.2.2.3)
  - *n*-Hexane
  - MIBK (methyl isobutyl keton)
  - Toluene
  - Butyl acetate
  - Cyclohexanone
  - *o*-Xylene
  - Phenol
  - ***1,3,5***-trimethylbenzene
  - ~~n-Hexadecane~~ (not suitable for preparation of static gas mixtures)

- 1,2,3-trimethylbenzene: pure component has low purity (80%)
  - Impurities: 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene
  - GC-analysis: possible overlap with phenol & bias due to impurities

Preparation Primary Reference Materials (PRM)

Static gas mixtures (ISO 6142)

Dynamic gas mixtures (ISO 6145)

Preparation Primary Reference Materials (PRM)

- Static gas mixture preparation (ISO 6142)

- Dynamic gas mixture preparation
  - Continuous injection (ISO 6145-4)

Preparation Calibrated Reference Materials (CRM)

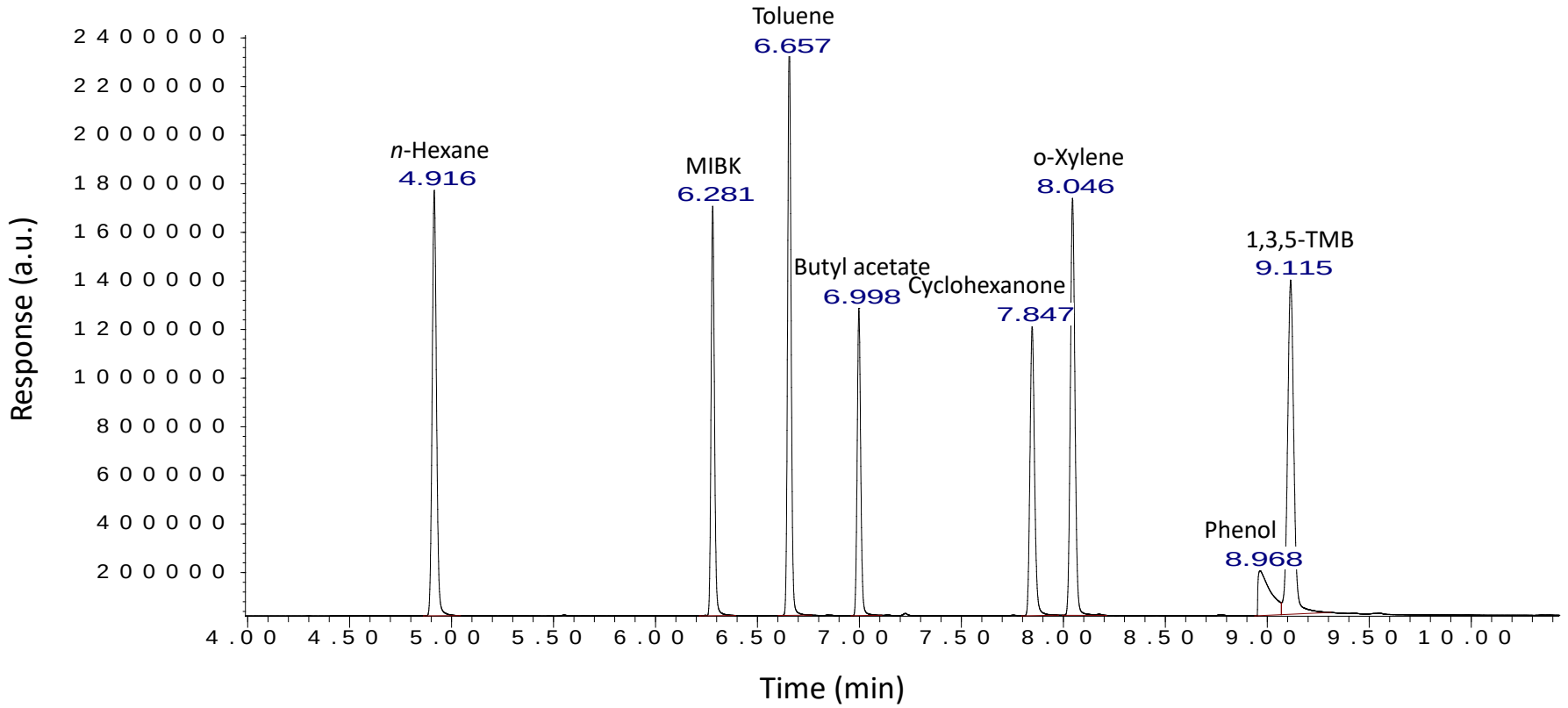
- Dynamic gas mixture preparation
- Sorbent tube sampling → pumped sampling (ISO 16017-1)
  - Tenax TA (TTA)
  - Materials Emissions/Soil Gas Monitoring (ME)

  - Nominal mass sampled into tubes was 125 ng per VOC

  - Develop and validate analytical method
  - Compare static and dynamic gas mixture preparation
  - Stability study of CRM

Analysis sorbent tubes

- TD-GC-FID
- DB-1, 30 m long, 0.32 mm internal diameter, 1.00 µm film thickness



Validation tube sampling & analysis method

- Breakthrough test sorbent tubes
  - TTA → *n*-hexane → 1.9%
  - ME → no breakthrough was observed
- Desorption efficiency test sorbent tubes
  - Full desorption for all components and sorbents
- Precision: repeatability (s_r) and reproducibility (s_R) → ANOVA calculation
  - TTA sorbent tubes

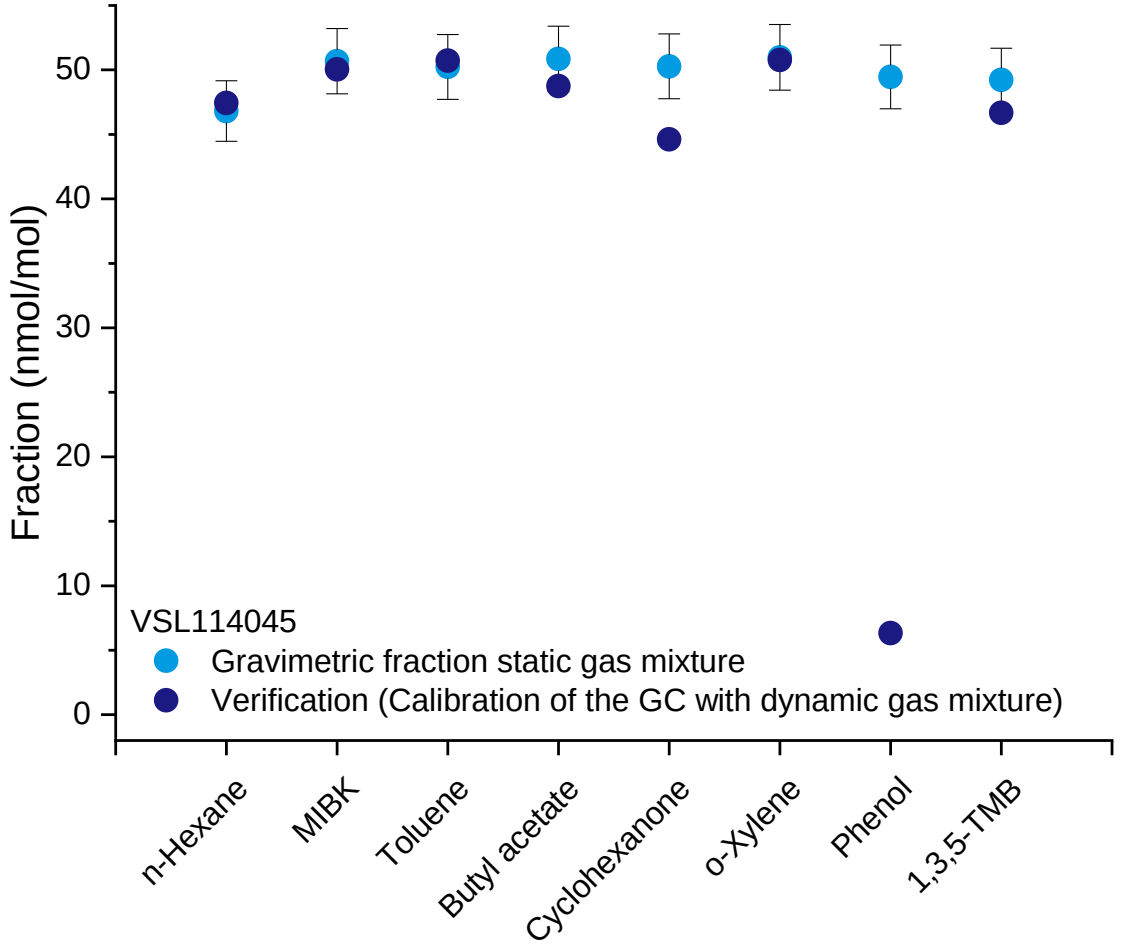
	n-Hexane	MIBK	Toluene	Butyl acetate	Cyclohexanone	*o*-Xylene	Phenol	1,3,5-TMB
s_r	1.66%	0.97%	0.62%	2.03%	3.43%	0.64%	11.03%	1.17%
s_R	2.57%	1.34%	1.16%	2.22%	3.50%	1.26%	14.69%	1.92%

  - ME sorbent tubes

	n-Hexane	MIBK	Toluene	Butyl acetate	Cyclohexanone	*o*-Xylene	Phenol	1,3,5-TMB
s_r	0.64%	0.74%	0.70%	1.51%	2.51%	0.61%	6.19%	0.51%
s_R	1.17%	1.11%	1.24%	1.60%	2.51%	1.12%	9.89%	1.47%

- Measurement uncertainty

Comparison static and dynamic gas mixtures



Uncertainty static PRM

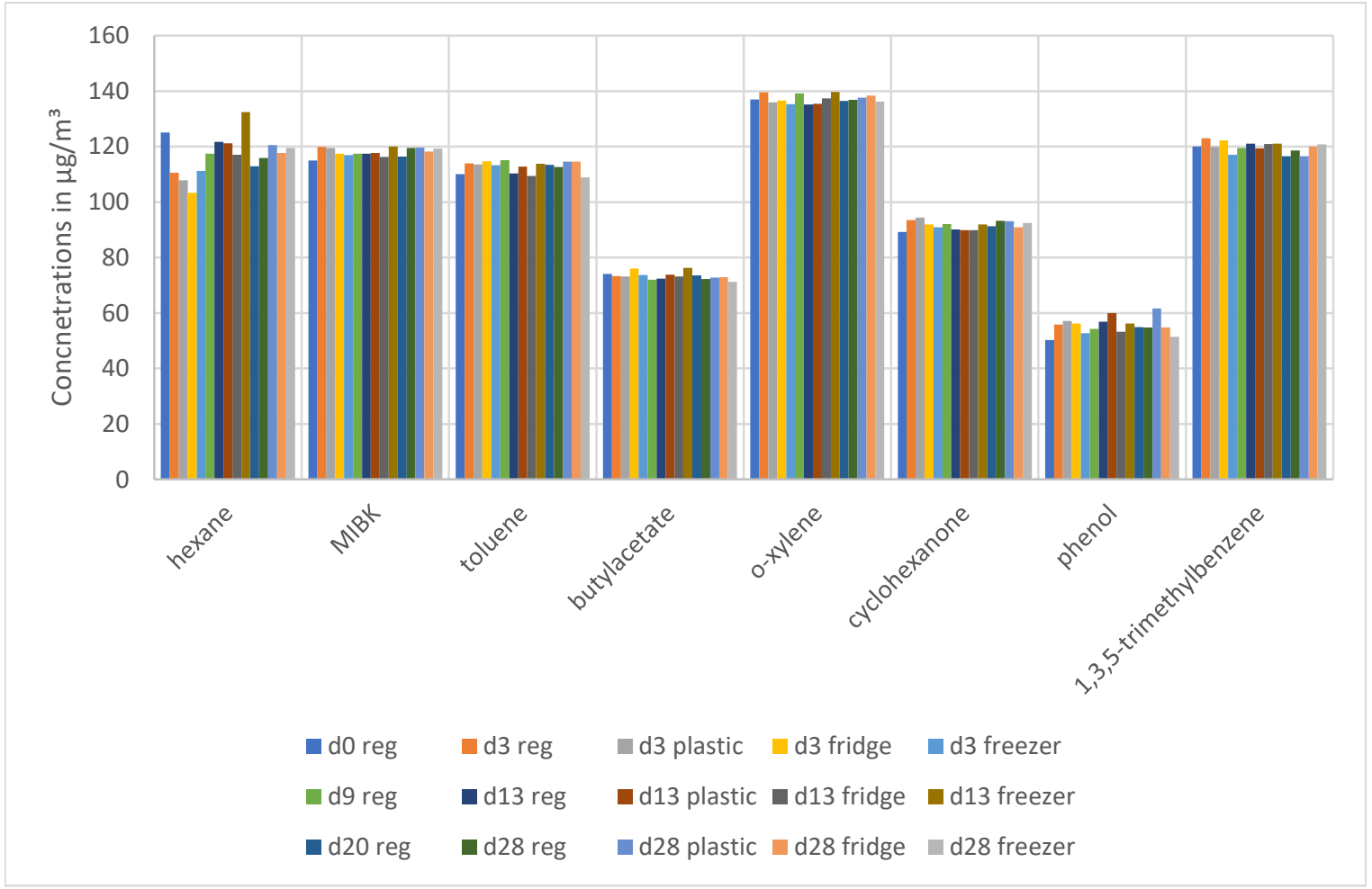
- Uncertainty sources
  - Preparation and sampling into sorbent tubes → 1% (k = 2)
  - Calibration GC with the dynamic PRM → 5% (k = 2)
  - Measurement uncertainty (k = 2)

VOC	U_{meas} (%)	U (%)
***n*-hexane**	2.4	6
MIBK	2.2	6
Toluene	2.4	6
Butyl acetate	3.2	6
Cyclohexanone	5	7
***o*-Xylene**	2.2	6
Phenol	20	20
1,3,5-TMB	3.0	6

Storage and stability

- CRM → TTA sorbent tubes
  - Storage
    - Room temperature
    - Fridge
    - Freezer
  - Packaging
    - Regular
    - Dark packing
  - t = 0, 3, 9, 13, 20 and 28 days

Stability study CRM



Conclusion preparation PRM and CRM

- PRM and CRM developed with selected VOCs from EN16516
  - Phenol decomposes or precipitates in a cylinder.
  - Dynamic gas mixture with phenol can be obtained
- Successful sampling into sorbent tubes
  - Keep in mind the save sampling volume of *n*-hexane when using TTA
  - Used for calibration of GC or other measurement systems
  - Used for interlaboratory comparison
- Uncertainty
  - Dynamic PRM 5 %
  - Static PRM 6 % - 20 %
- Stability CRM tested 1 year
  - 28 days at room temperature in ME and TTA sorbent tubes

Report

- Published
  - **D3** Guideline for the preparation and analysis of gPRMs and gCRMs of indoor air pollutants stated in the EU-LCI list with relative uncertainties below 5 % (k = 2) and a shelf life of at least 1 year (zenodo.org)

Interlaboratory comparison

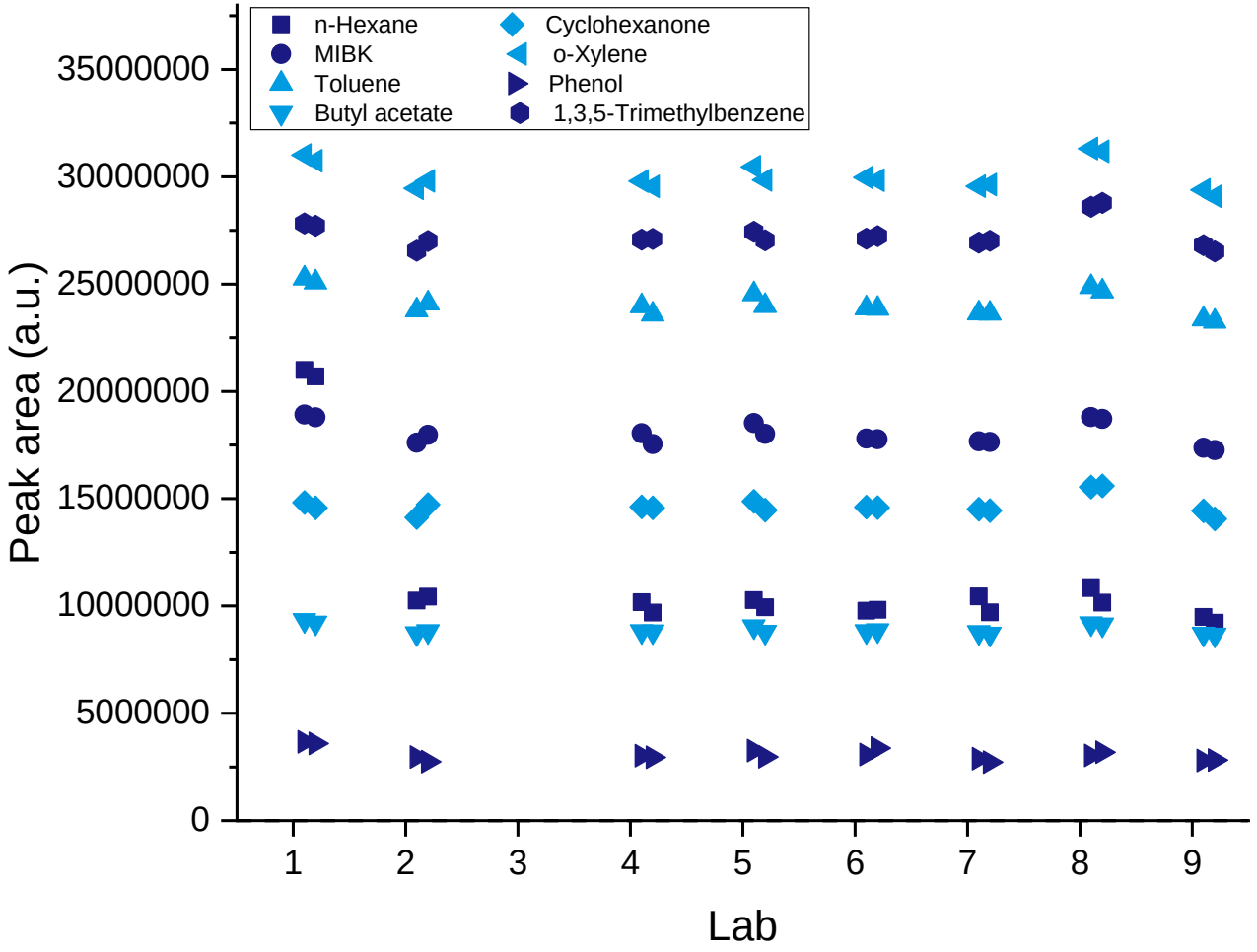
- Goal
  - Assess the participants capabilities in sampling and measuring VOCs
    - *n*-Hexane, MIBK, Toluene, Butyl acetate, Cyclohexanone, *o*-Xylene, Phenol, 1,3,5-Trimethylbenzene
  - External validation gCRM

- Workshop
  - Participants sample at least 3 tubes with dynamic gas mixture of VOCs in air at VITO
  - VSL determined the reference value
  - 4 participants

- Interlaboratory comparison
  - VITO sampled 3 participants tubes with dynamic gas mixture
  - VSL determined the reference value
  - 8 participants

Homogeneity samples interlaboratory comparison

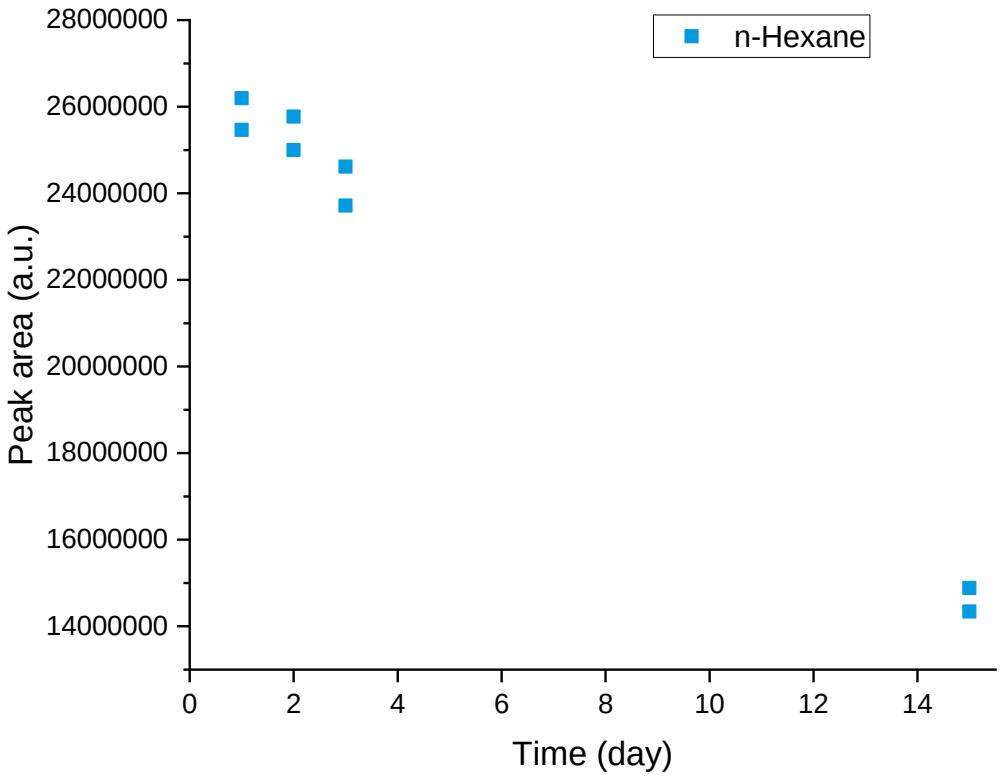
- Lab 1
  - Tubes were resampled
  - Different reference value
- Lab 3
  - Only participated in the workshop
- Results other labs
  - comparable within the uncertainty of 5 %
- n-Hexane
  - Results to low



Data processing

- Zeta scores for the assessment of laboratory results according to ISO 13528
- $\zeta_{lab(i)} = \frac{m_{lab(i)} - m_{ref(i)}}{\sqrt{u^2_{lab(i)} + u^2_{ref(i)}}}$
- $m_{ref(i)}$ → reference value VSL

- *n*-Hexane
  - Interlaboratory comparison: Consensus value
  - Workshop: Reference value



Consensus values

Workshop

Component	m	u(m)	m_{ref}	$U(m_{ref})$	τ
n-Hexane	122	21	107	5	28
MIBK	134	15	138	7	22
Toluene	124	14	128	6	20
Butyl acetate	84	9	86	4	12
Cyclohexanone	114	8	122	6	0.0
o-Xylene	154	10	162	8	7
Phenol	69	4	99	5	0.0
1,3,5-TMB	131	11	138	7	13

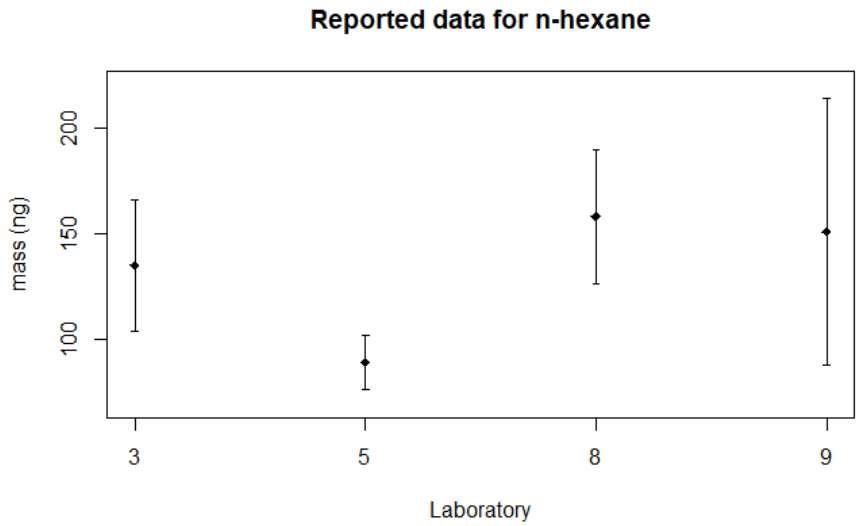
Interlaboratory comparison

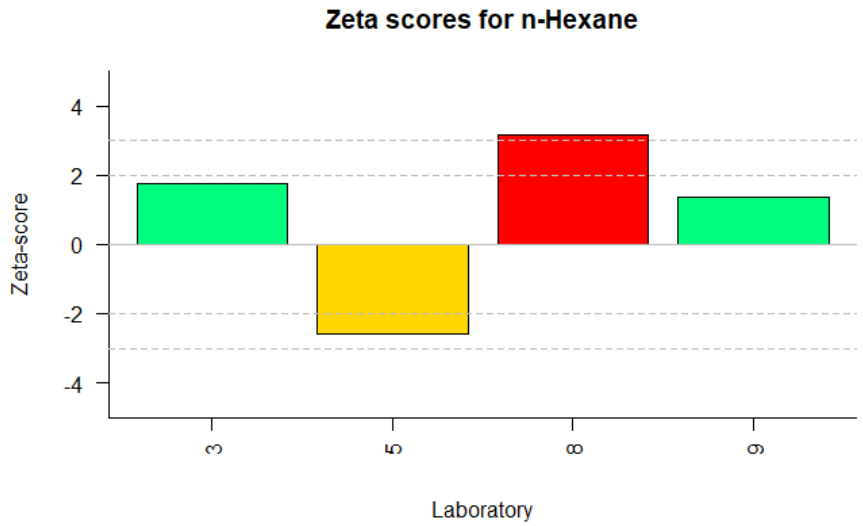
Component	m	u(m)	M_{ref} [1]	$U(m_{ref})$	τ
n-Hexane	98	6	49.5 [2]	2.5 [2]	8
MIBK	99	7	119	6	15
Toluene	97	7	110	5	14
Butyl acetate	101	7	74	4	14
Cyclohexanone	99	8	106	5	17
o-Xylene	107	4	139	7	4
Phenol	26	7	61	3.0	13
1,3,5-TMB	94	6	119	6	9

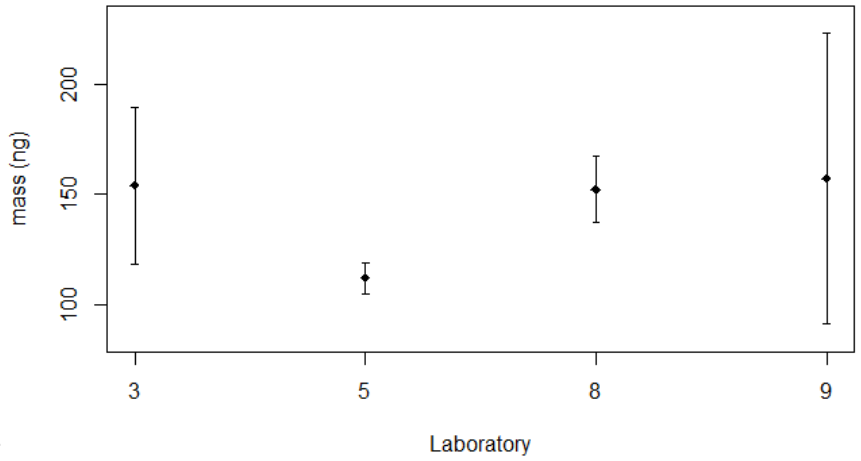
[1] Save for Lab 1

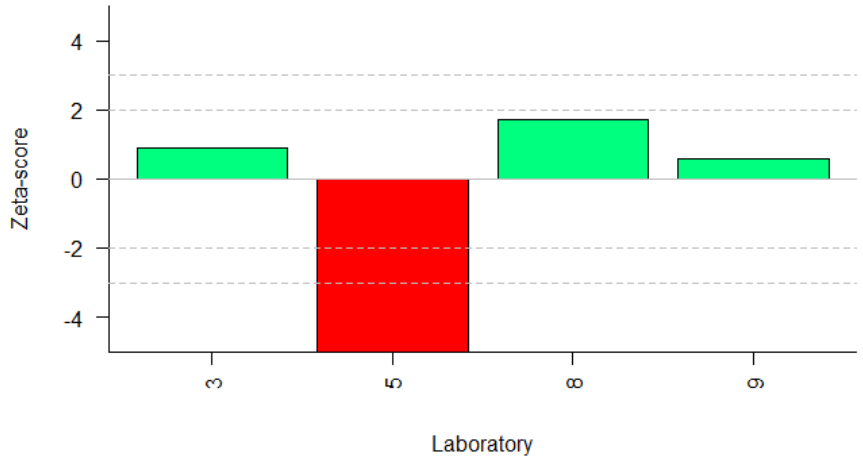
[2] Consensus value used

Preliminary results workshop









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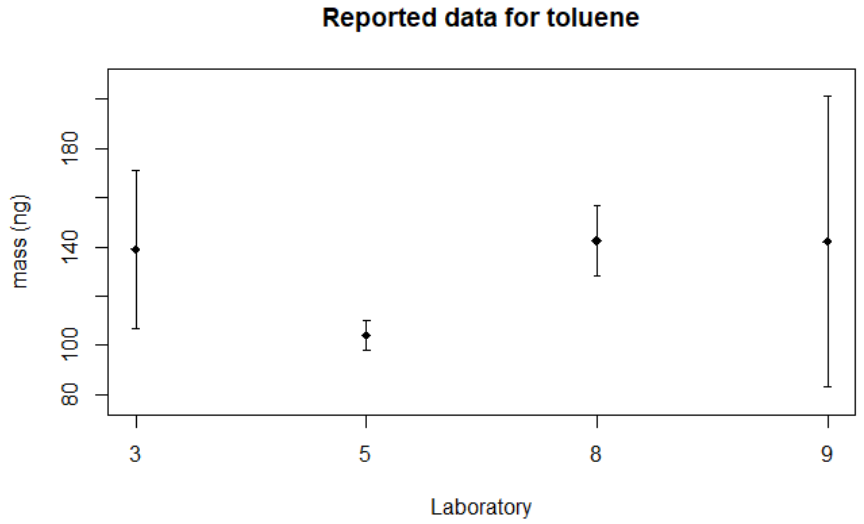

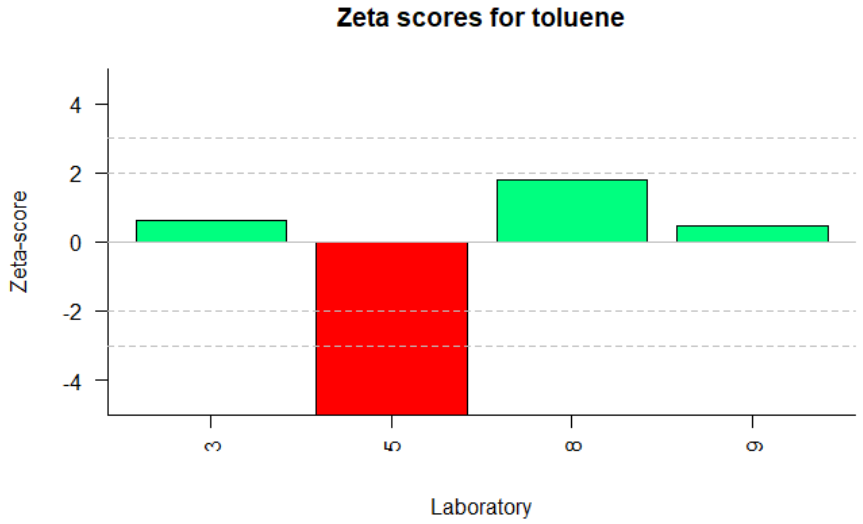

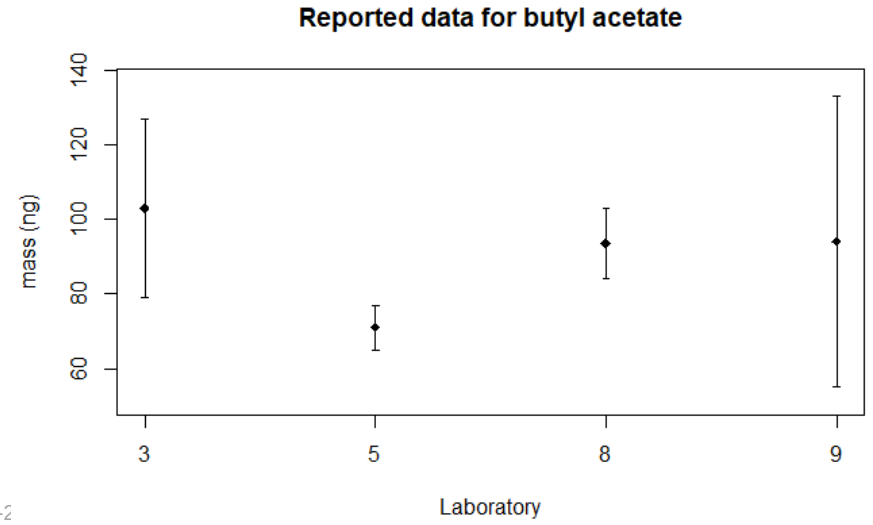

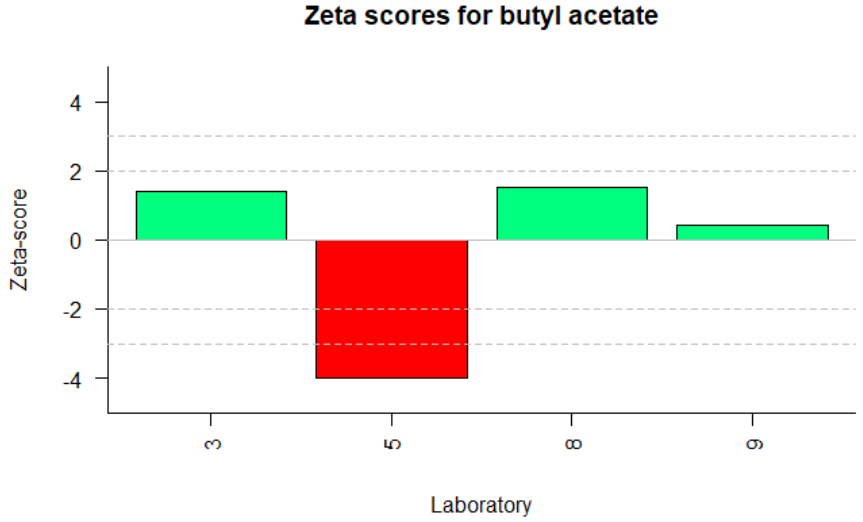

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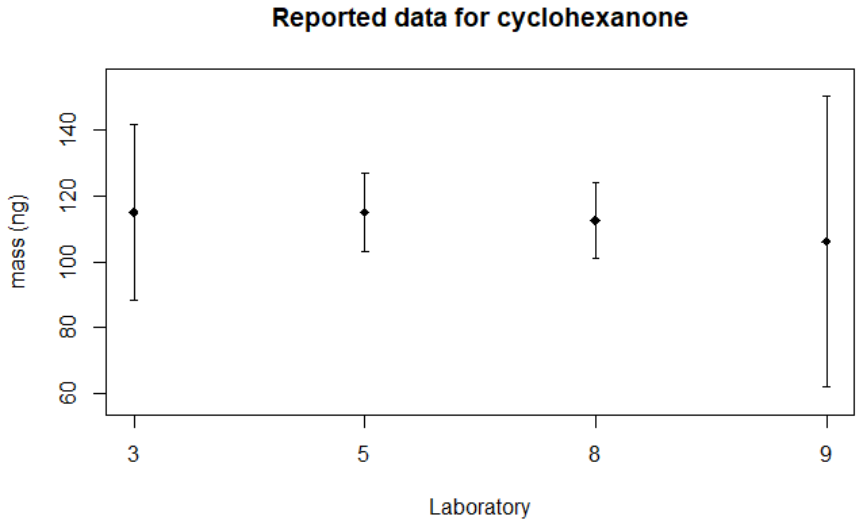

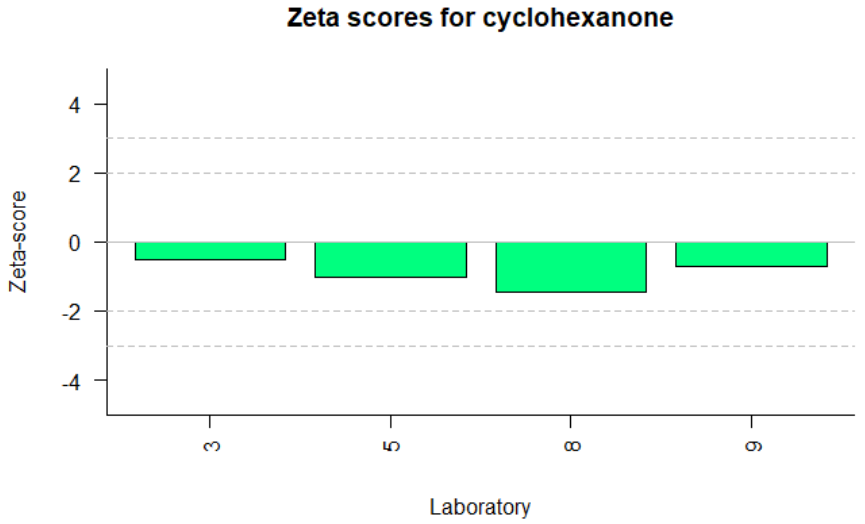

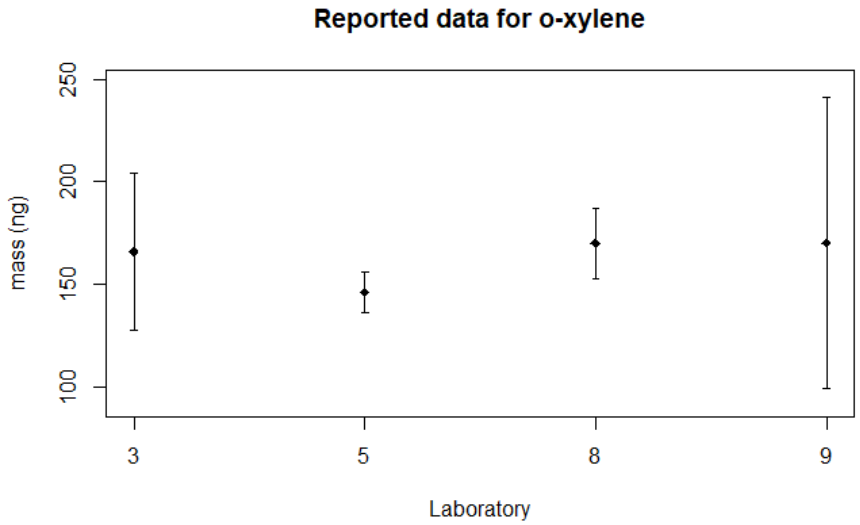

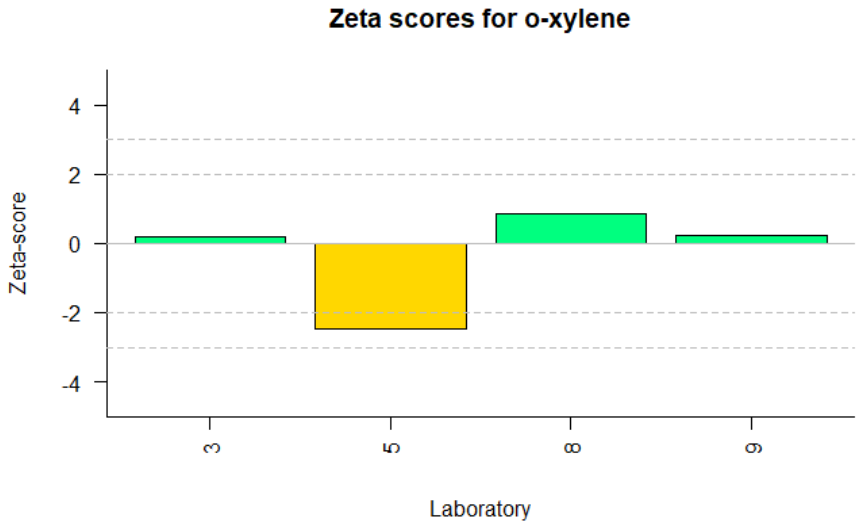

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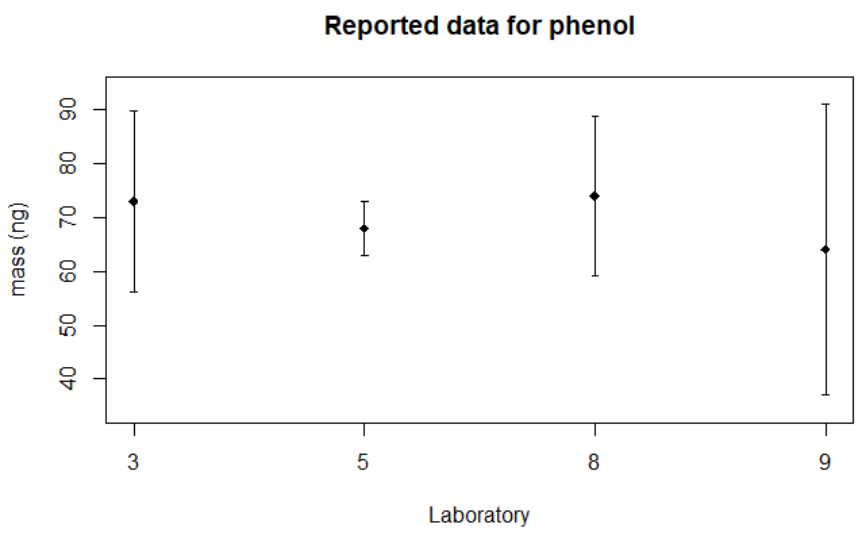
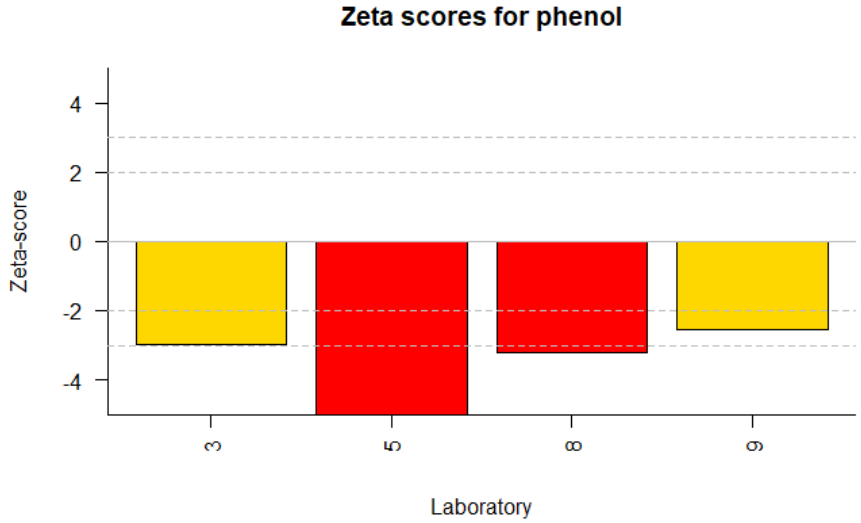
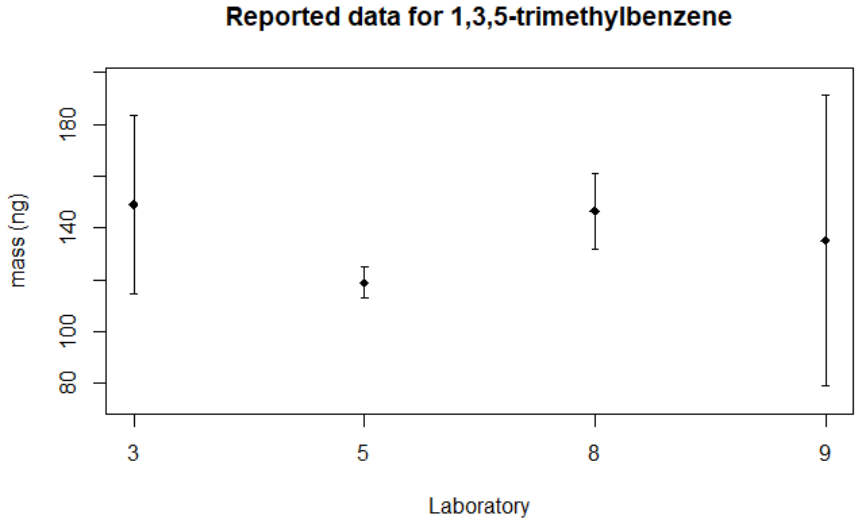
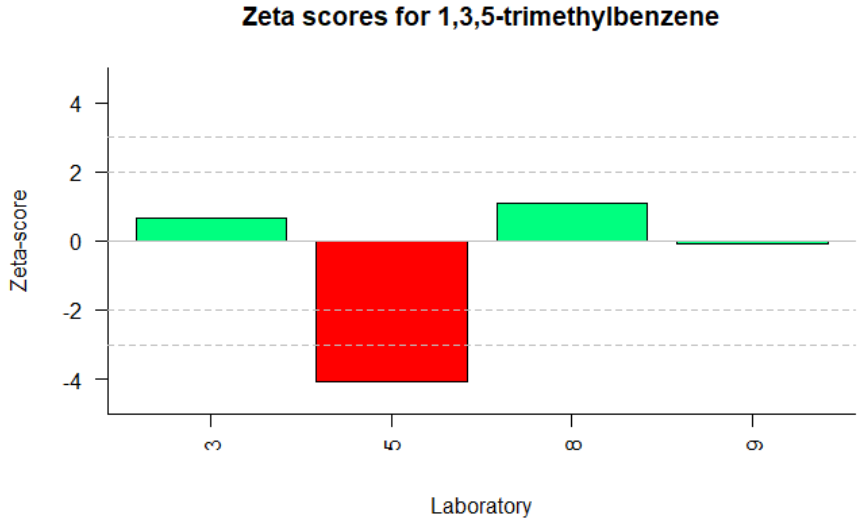
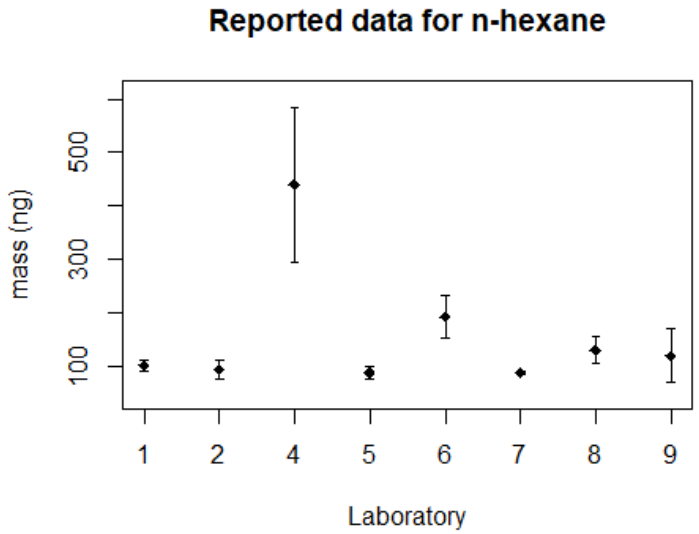


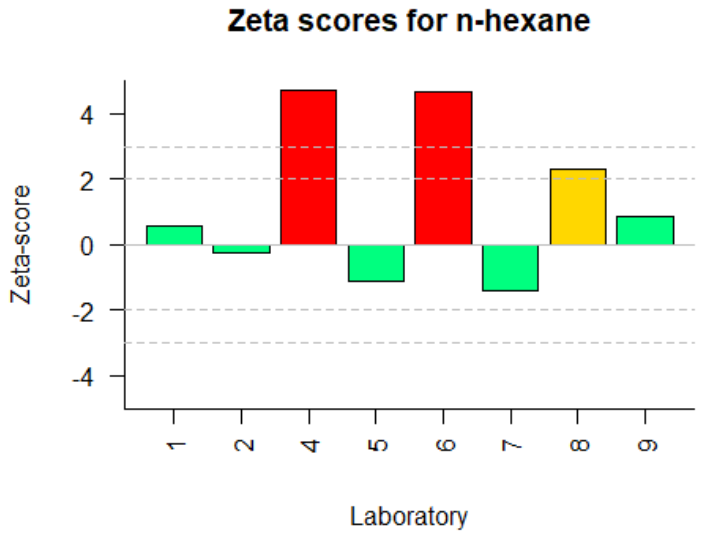


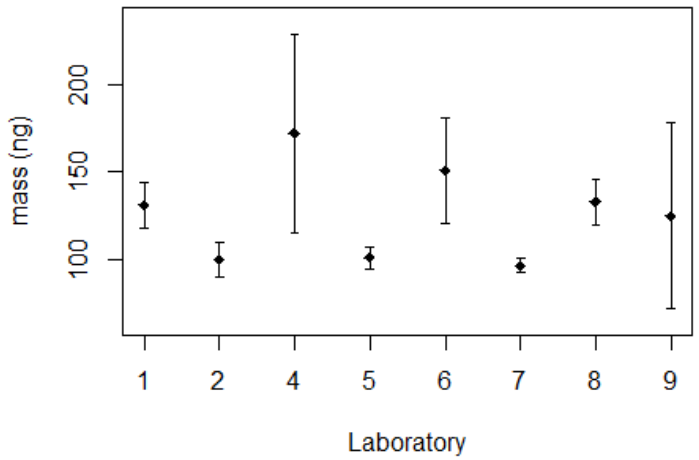


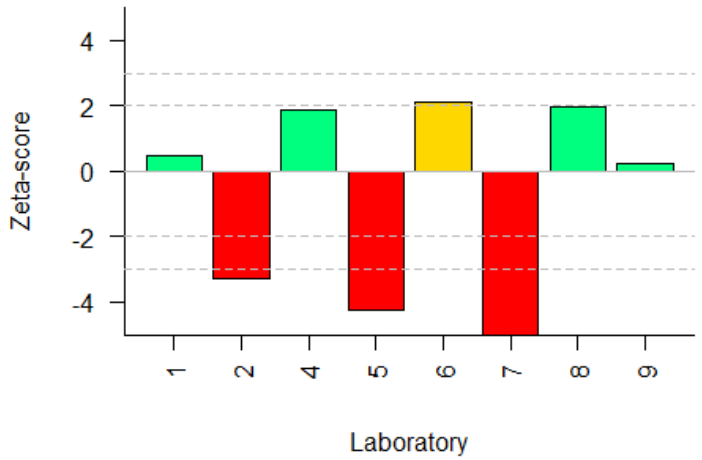


Preliminary results interlaboratory comparison









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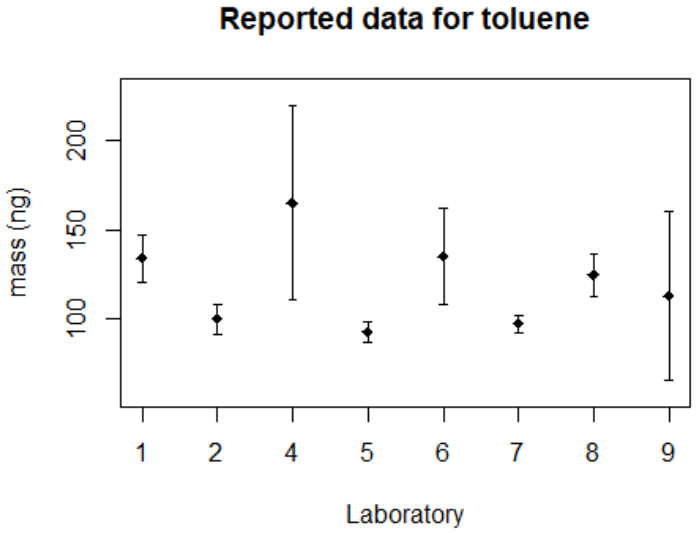

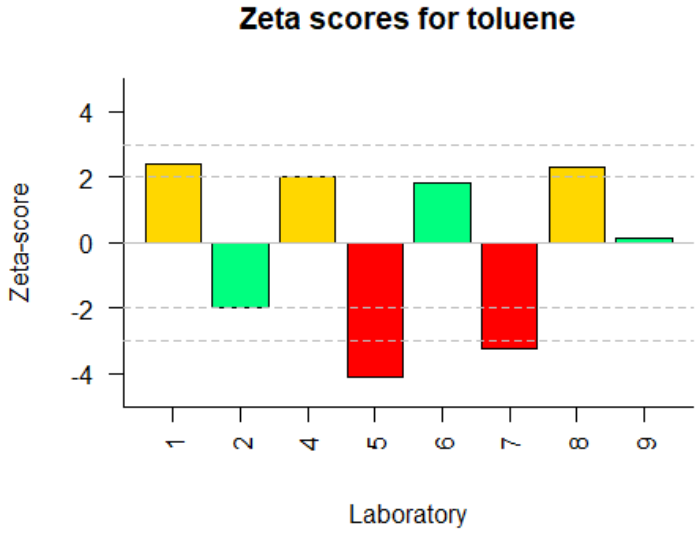

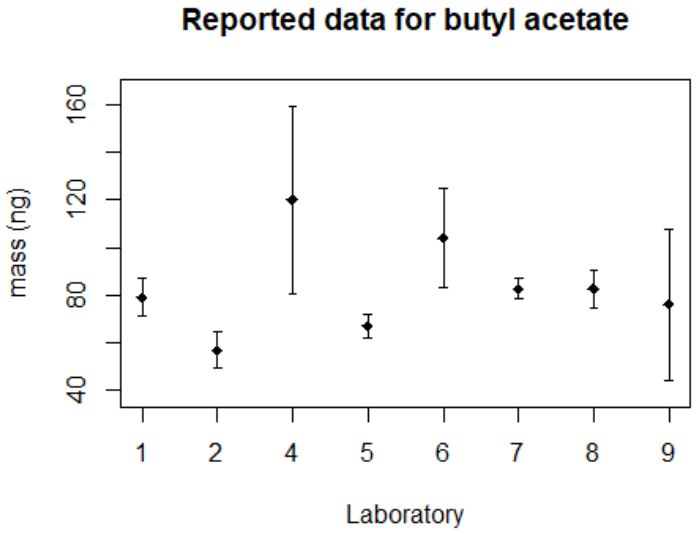

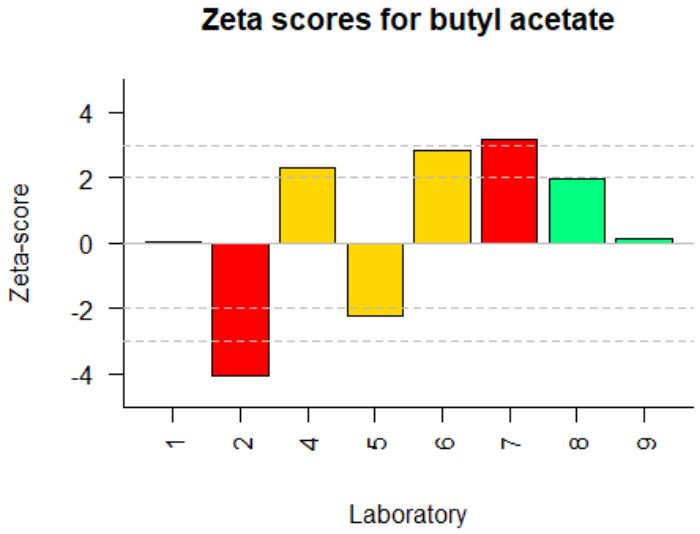

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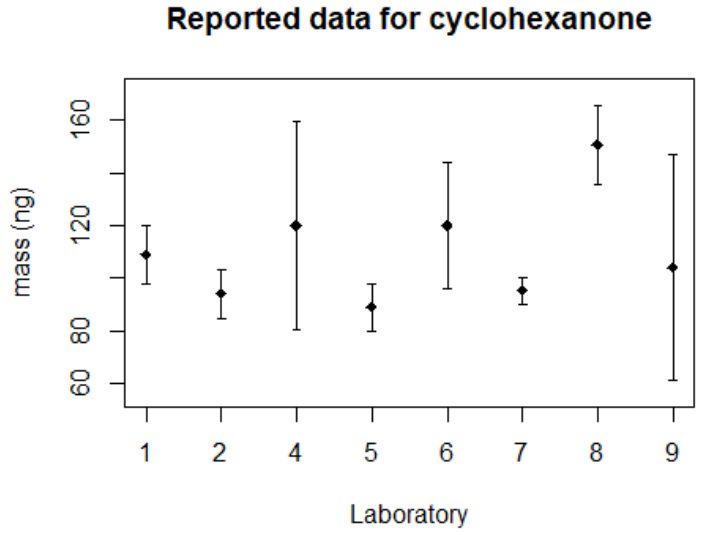

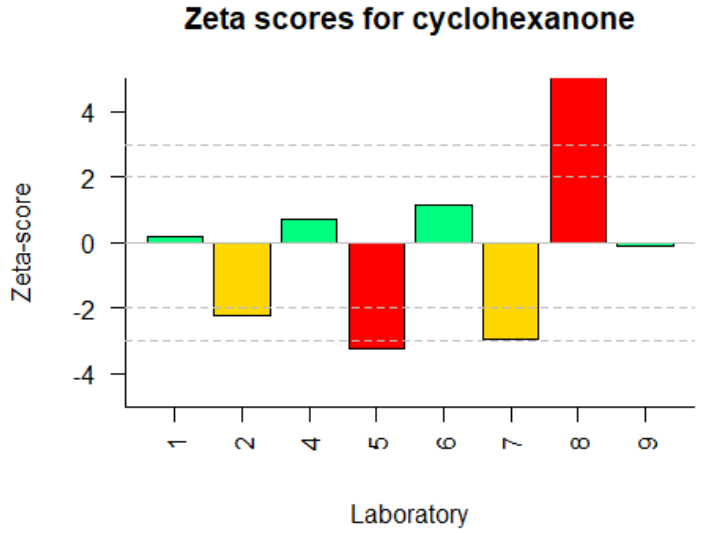

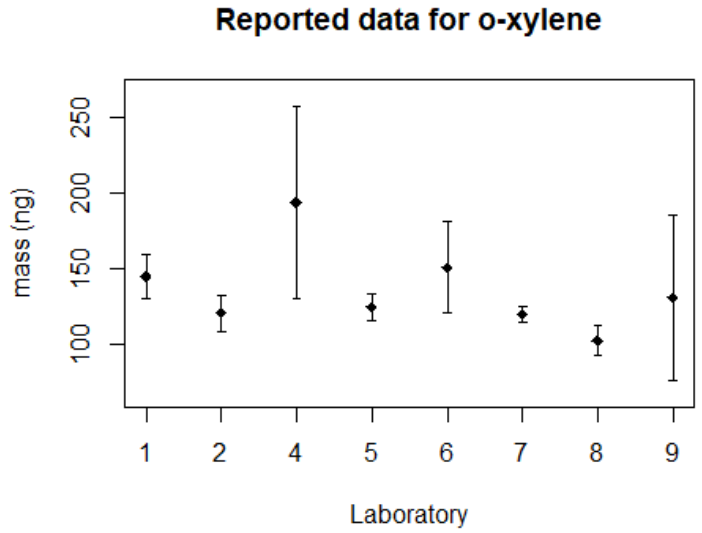

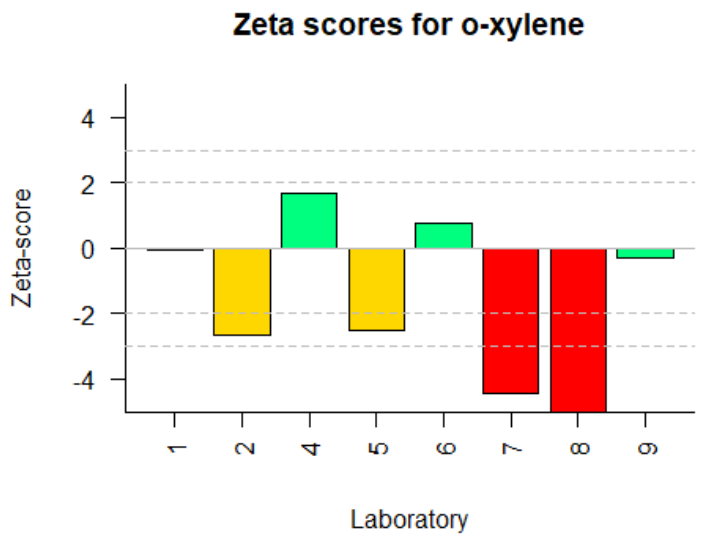

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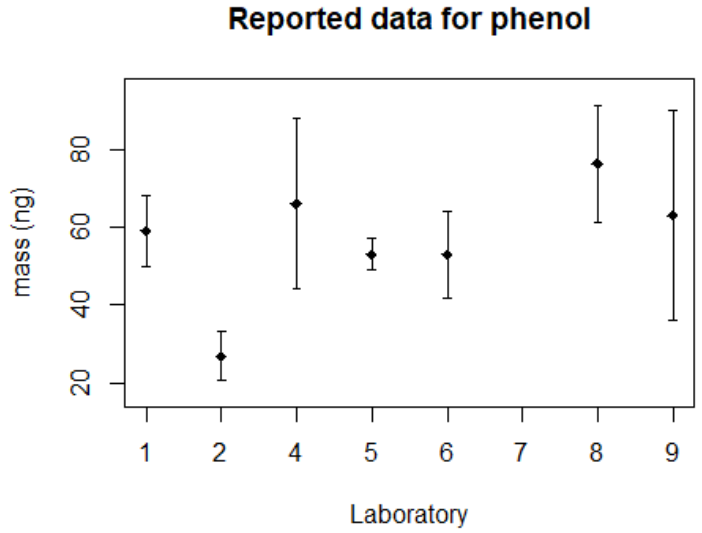

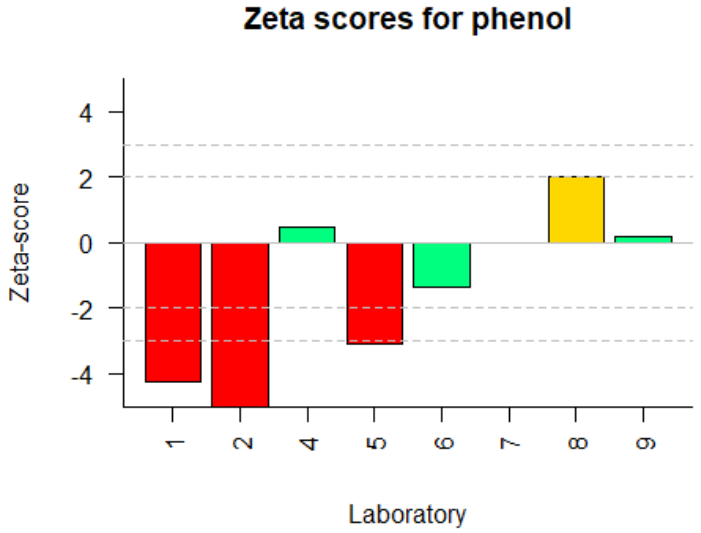

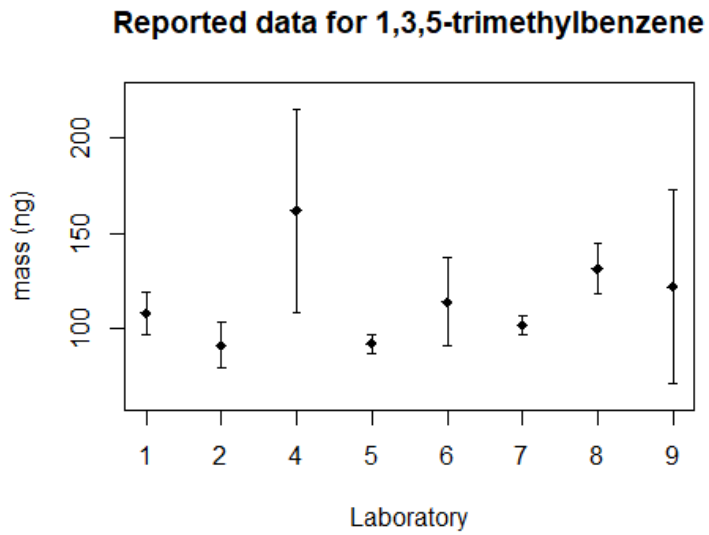

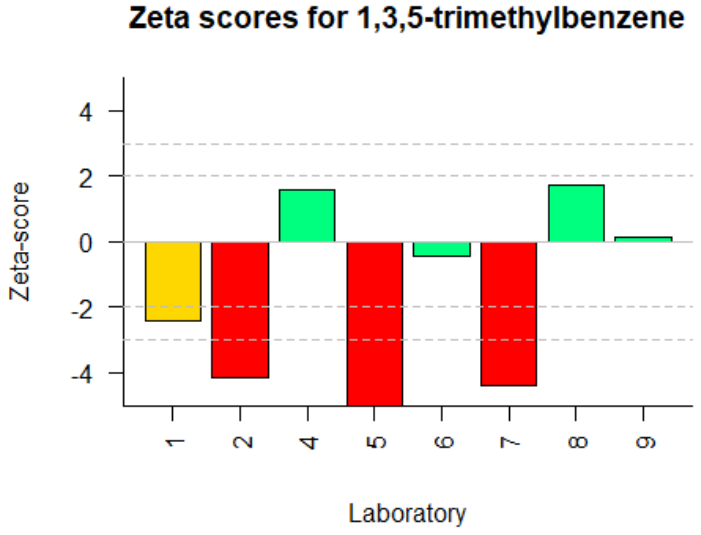

Conclusion

- The results highlight the complexity of these measurements

- Workshop:
  - Satisfactory results for labs 3, 8 and 9
  - Lab 5 reported biased results for most VOC

- Interlaboratory comparison
  - Lab 9 performed satisfactory for all VOCs
  - Labs 1, 4 and 6 perform satisfactory for most VOCs and questionable for a few components
  - Lab 2, 5, 7 and 8 report biased results for most VOCs

Reports

- Available in the coming months
  - ***D5**: "Summary report on the evaluation of the inter-laboratory comparison performed with the ERM and gCRMs: including information on the repeatability and reproducibility of the data and an evaluation of the major uncertainty sources in sampling, analysis and reporting, according to the EN 16516 test method".*
  - ***D6**: "Report on the preparation and measurement uncertainty of ERMs, gPRM and gCRMs"*

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