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Supplement of

Harmonizing measurements of oxidative potential of PM: an interlaboratory comparison of the ascorbic acid assay

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S1. Overview of tests performed for designing the SOP

S1.1. Extraction fluid and AA preparation solvent

Several extraction fluid-AA preparation solvent pairs were tested with three samples: one blank, copper sulfate (0.22 µM in the well), and an ambient filter (11 µg/mL in the well). The extraction was tested in ultra-pure water (UP water, 18.2 MΩ cm, TOC<5ppb), potassium phosphate buffer (K-PO_4: KH_2PO_4, K_2HPO_4, 0.1M), Chelex-treated K-PO_4 buffer, and Gamble + 1,2-DPPC. AA was prepared in ultra-pure water (18.2 MΩ cm, TOC<5ppb), K-PO_4 buffer, and Chelex-treated K-PO_4 buffer. Criteria for selecting the extraction fluid-preparation solvent pair were the minimization of the variability and the limitation of time-consuming or error-prone steps. Gamble+DPPC extraction solution was only tested for comparison matter with the organizer's usual protocol, but was excluded from the possible matrices given the complexity of preparation and the potential errors it can induce.

Figure S1 shows that the UP-water/UP-water pair cannot be considered because AA consumption is very low for both samples. The highest values are obtained for the K-PO_4 (extraction)/UP-water (AA) pair, with a very low variability in the results. This pair was therefore selected for the SOP.

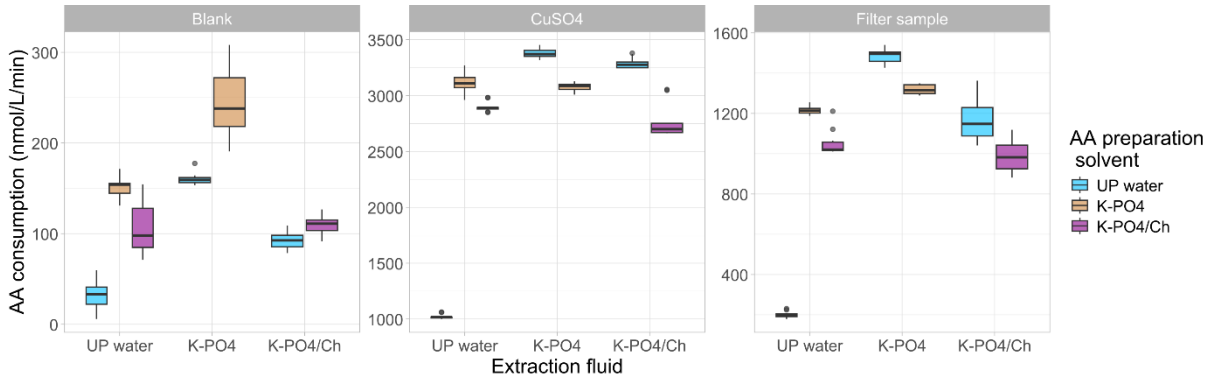


Figure S1. AA consumption slopes for each extraction fluid/AA preparation solvent pair.

S1.2. Impact of [AA]/[PM] ratios in the reaction medium

Participants reported [AA]/[PM] ratios ranging from 2 to 60, with some participants working at iso-concentrations (fixing PM concentrations in the wells), while others worked at iso-surface (fixing the filter portion to extract). This parameter was tested by modifying the initial concentration of PM in the well, diluting a 150 µg/mL extract to reach final concentrations in the wells ranging from 2.2 to 66.5 µg/mL and fixing [AA] concentration to 133 µM. Results showed a linear relationship for PM concentrations in the well that flattened for PM concentrations in the well above 20 µg/mL, supporting that extract concentrations should be fixed within this interval.

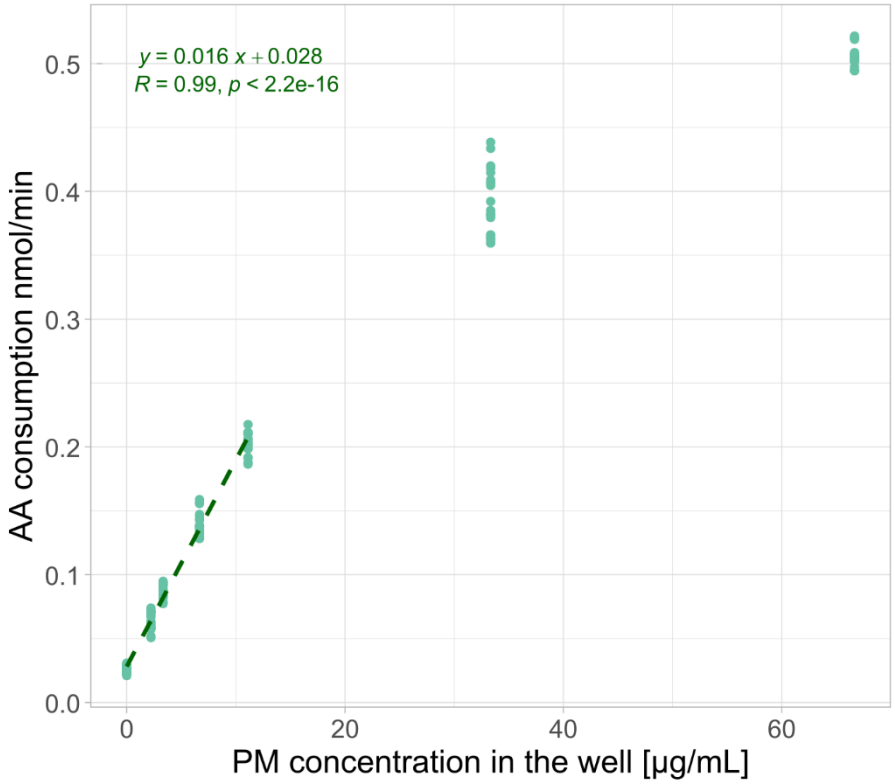


Figure S2. Effect of PM concentration in the reaction medium on AA consumption slope, with fixed initial concentration of AA of 133µM.

S1.3. Impact of extract filtration

The impact of the extract filtration prior to their introduction in the well was tested at different PM concentrations (Figure S3). There was no difference in the impact of the filtration step depending on the concentration, with slightly higher AA consumption slopes and lower variability in the results for unfiltered extracts compared to filtered extracts. Not filtering the extracts could lead to more variability in the framework of an ILC, depending on lab workers' difficulty to pipet the samples, however it has to be balanced with the potential contamination that can be induced by the filtration step.

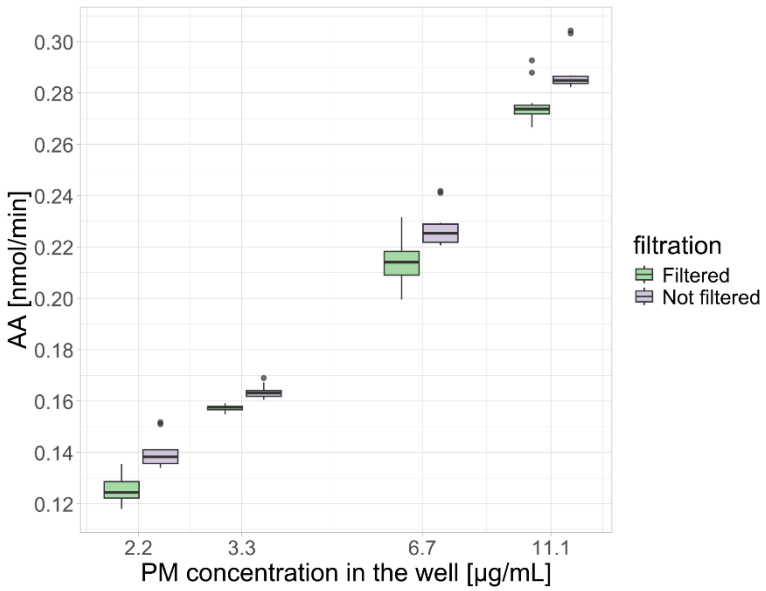


Figure S3. Impact of the extract filtration on AA consumption slope at different PM concentrations.

S1.4. pH-dependence of AA's λ_{max}

The pH-dependence of AA's maximum absorption wavelength (λ_{max}) was tested at different AA concentrations, diluting the solutions in UP-water and in K-PO_4. Results showed a shift in λ_{max} when AA was not buffered, caused by the coexistence of both AA and AH^- with pH modifications (pKa_1 = 4.1, pKa_2 = 11.8), therefore impacting the slope of the calibration curve (Figure S4). It was therefore recommended to perform the calibration curve by diluting AA in K-PO_4, with the final volume of each calibration point equal to the total reaction volume for samples.

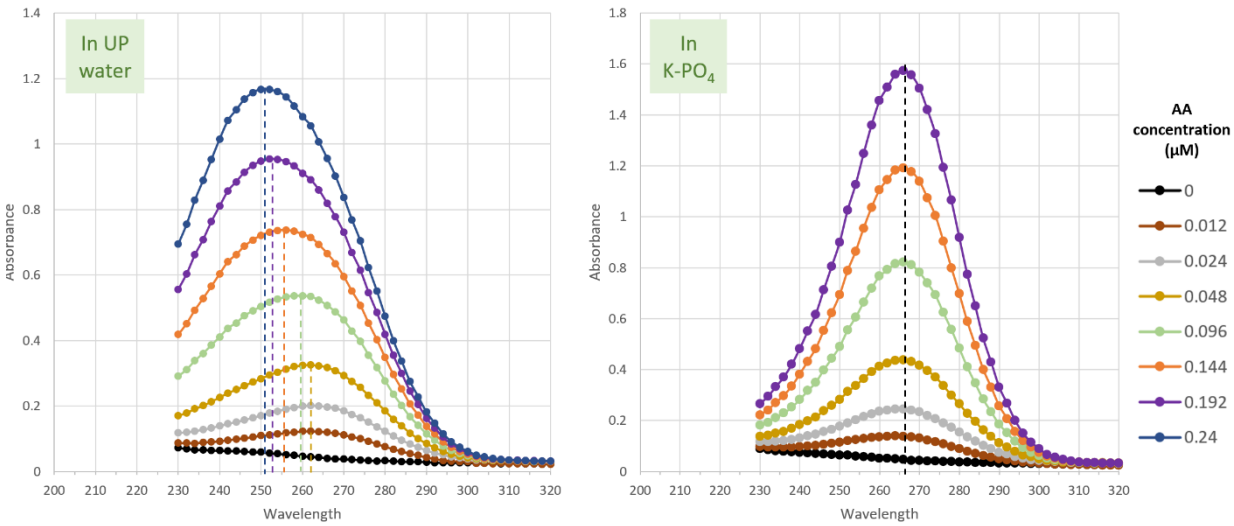


Figure S4. Comparison of AA's maximum absorption wavelength at different concentrations when diluted in ultra-pure water (left) or in potassium phosphate buffer (right).

S2. Figures

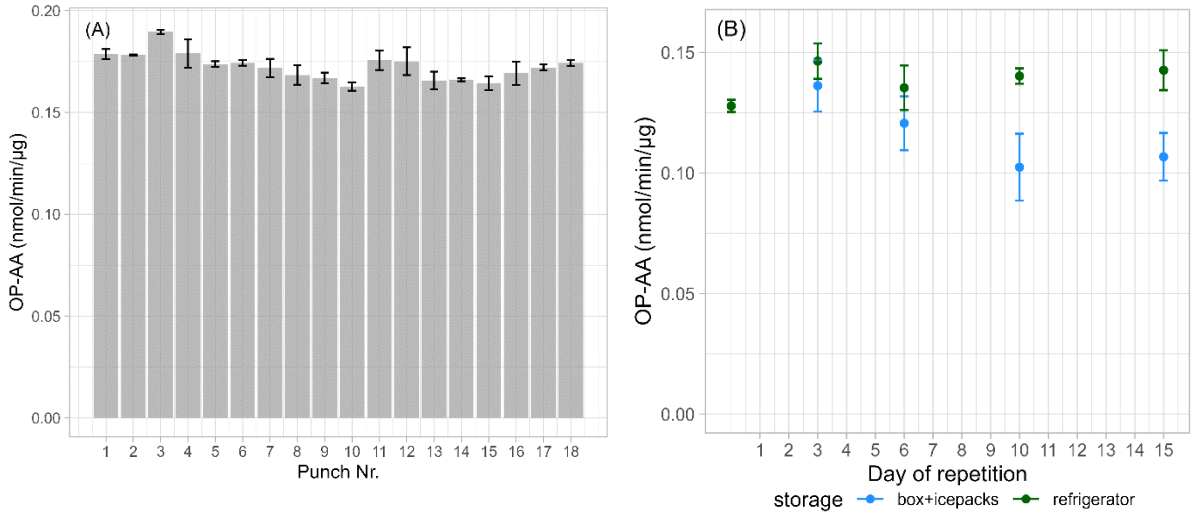


Figure S5. Results of the homogeneity (A) and stability (B) tests.

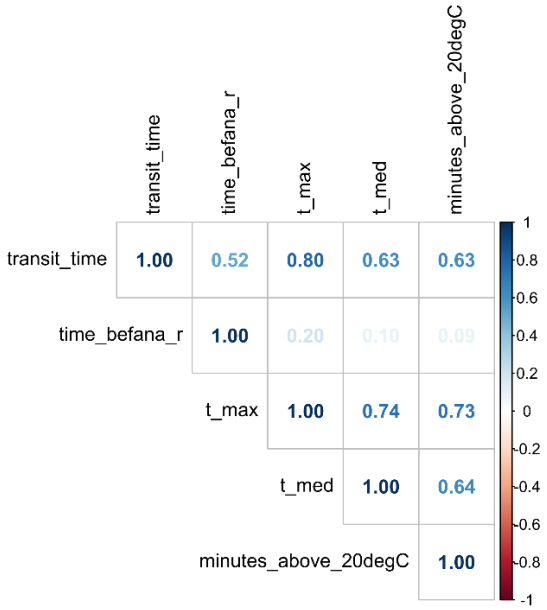


Figure S6. Correlation coefficients between technical variables and OP

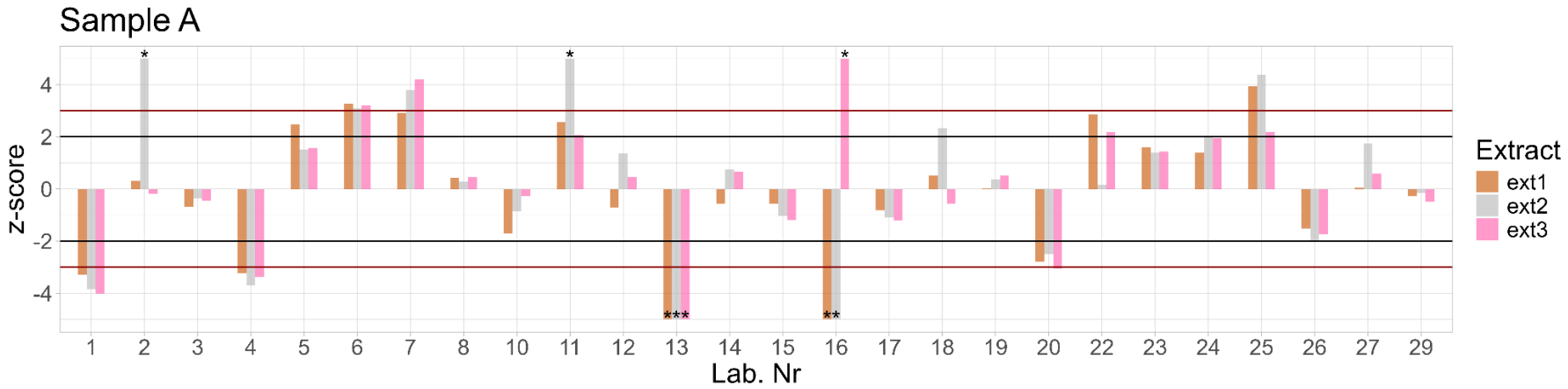


Figure S7. Evaluation of participants' performance in the interlaboratory comparison, with representation of z-score per extract in sample A. Results were cropped for $|z| \leq 5$, and stars represent bars that exceed this value.

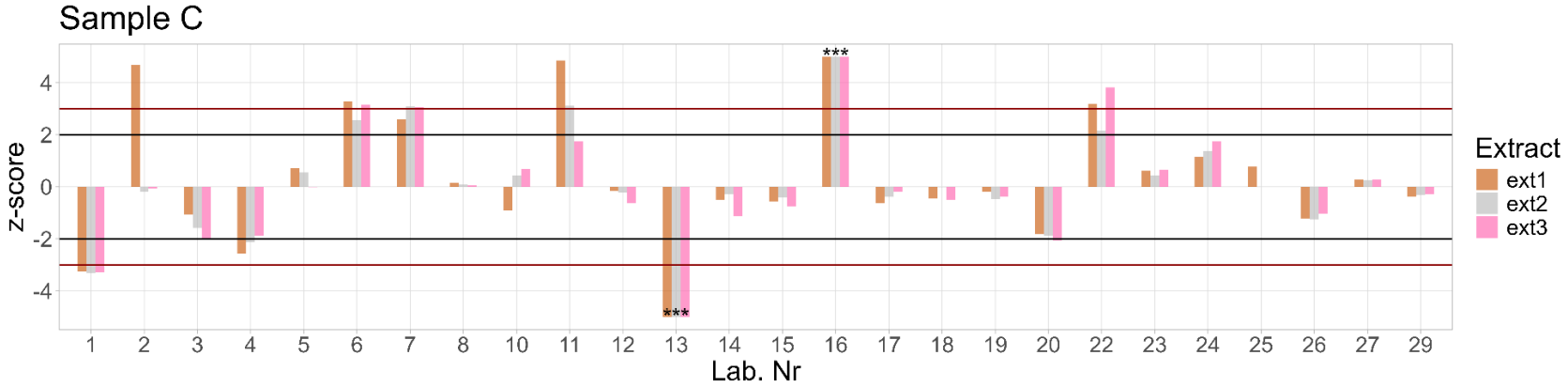


Figure S8. Evaluation of participants' performance in the interlaboratory comparison, with representation of z-score per extract in sample C. Results were cropped for $|z| \leq 5$, and stars represent bars that exceed this value.

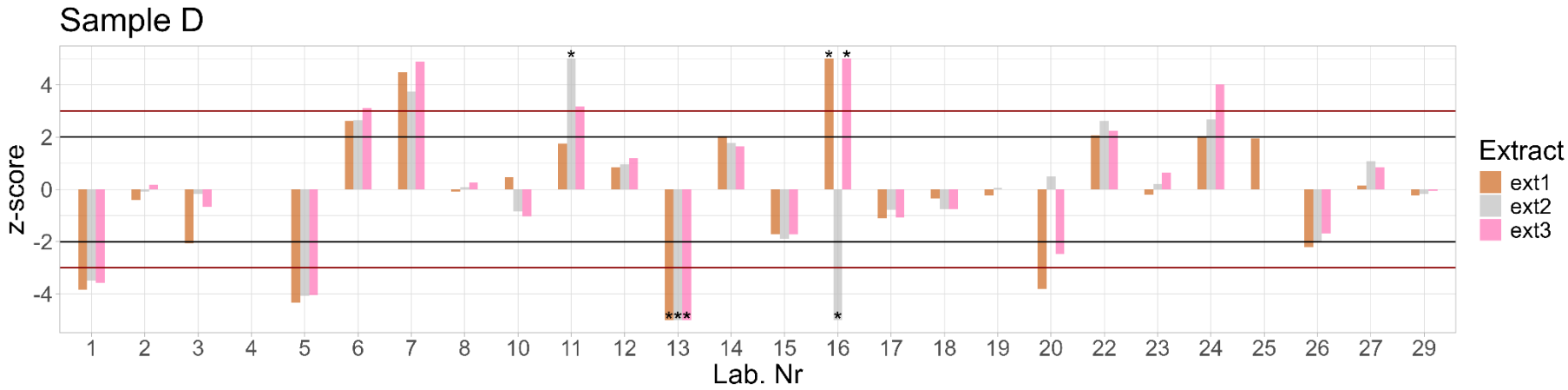


Figure S9. Evaluation of participants' performance in the interlaboratory comparison, with representation of z-score per extract in sample D. Results were cropped for $|z| \leq 5$, and stars represent bars that exceed this value.

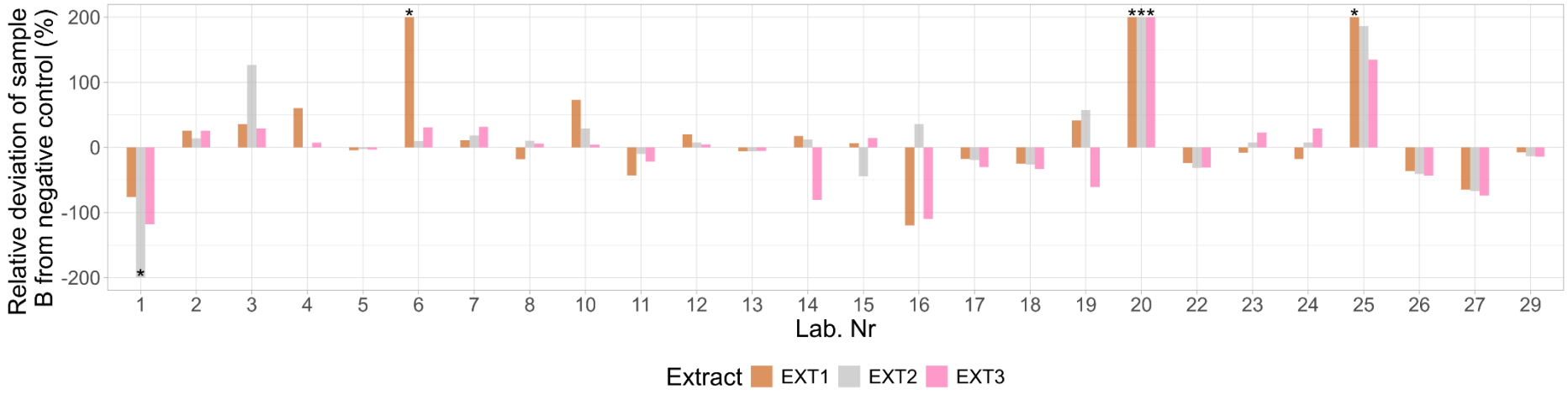


Figure S10. Relative deviation of sample B's slope from the average slope of the negative controls. Black stars represent the discarded replicates to calculate the LOD per laboratory. Results were cropped for deviations exceeding 200% or below -200%, and stars represent bars that exceed this value.

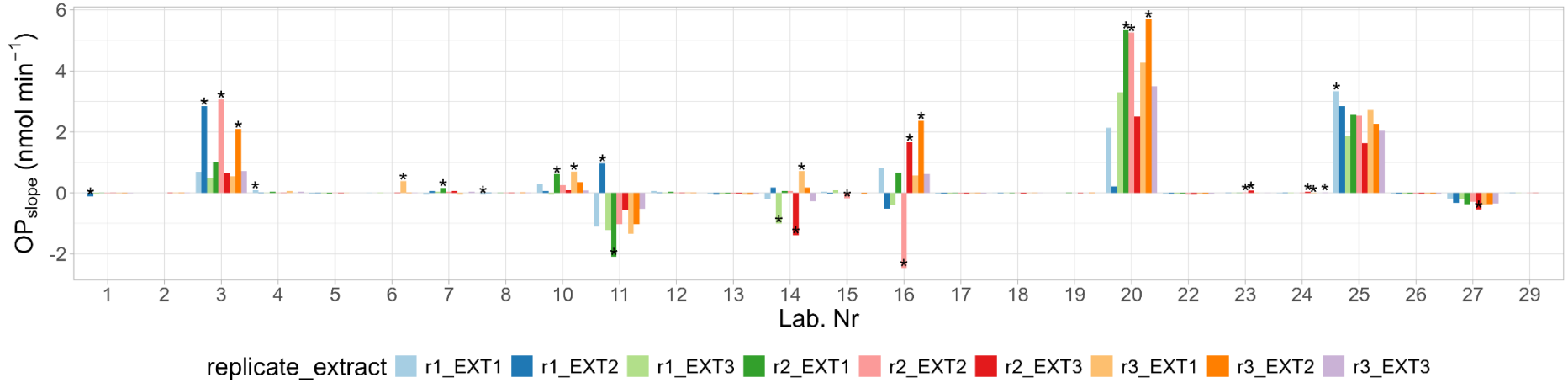


Figure S11. Sample B's OP_{slope} for each extract and each replicate. Black stars represent the discarded replicates to calculate the LOD per laboratory.

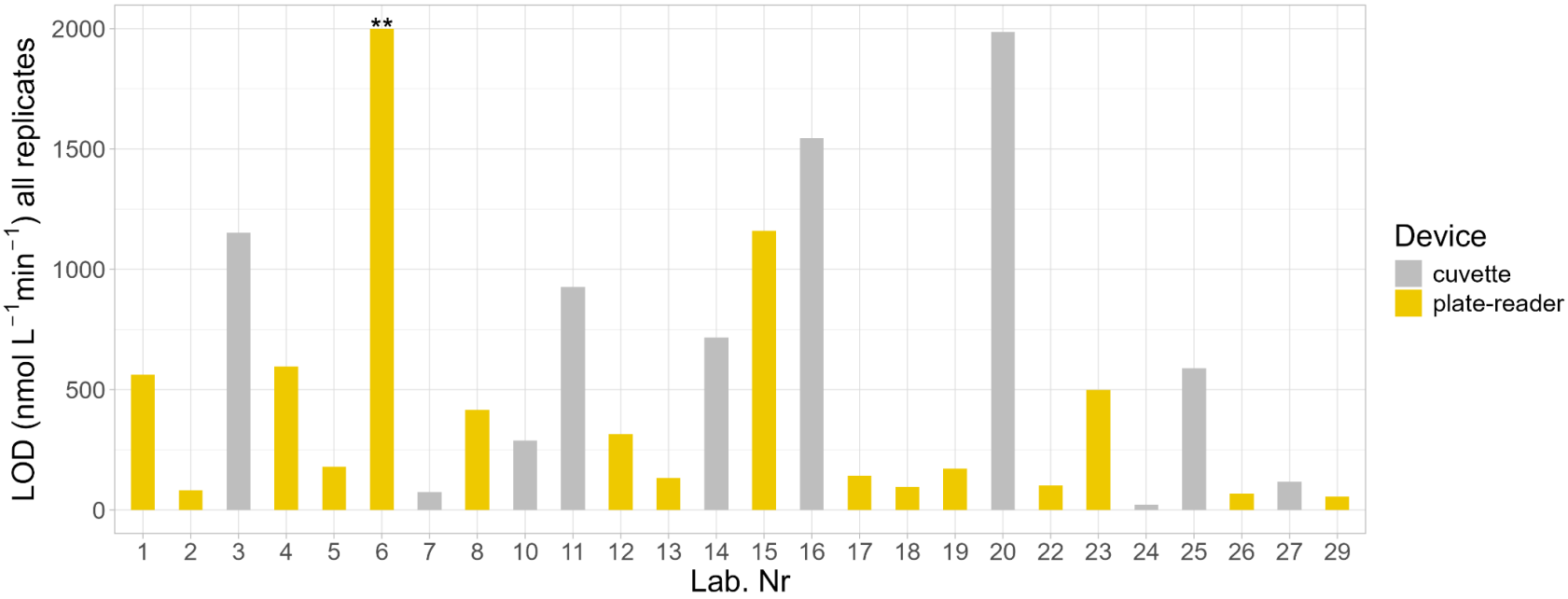


Figure S 12. Theoretical limits of detection based on the standard deviation of all replicates of sample B. Results were cropped at LOD≤ 2000 nmol L^{-1} min^{-1}, and stars represent bars that exceed this value.

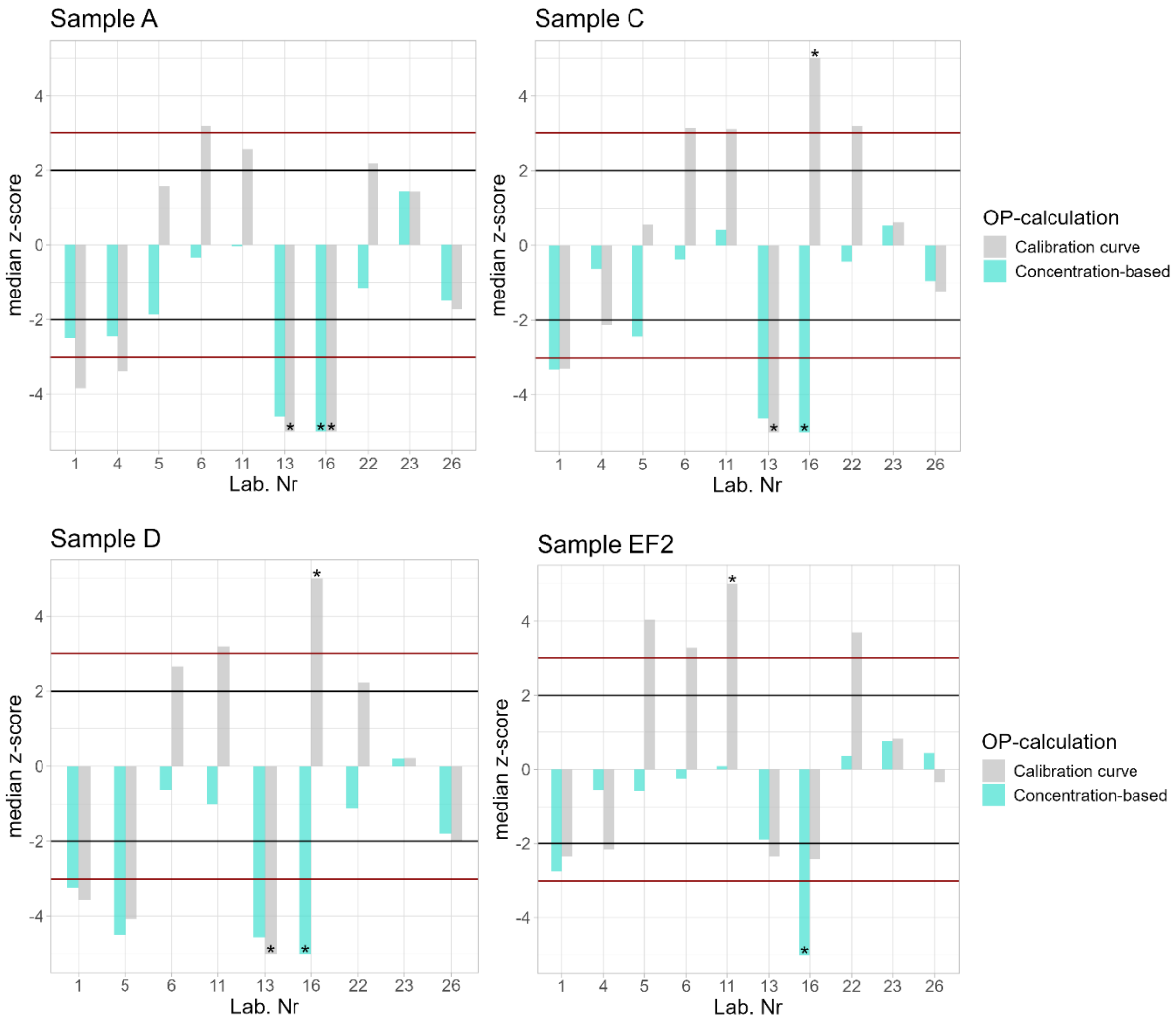


Figure S13. Comparison of participants' performances depending on OP calculation (i.e. using the concentration-based vs. the calibration curve) for participants outside the $[AA]_{th}$ range (i.e. $[AA]_0$ < 119.7 µM or $[AA]_0$ > 146.3 µM)

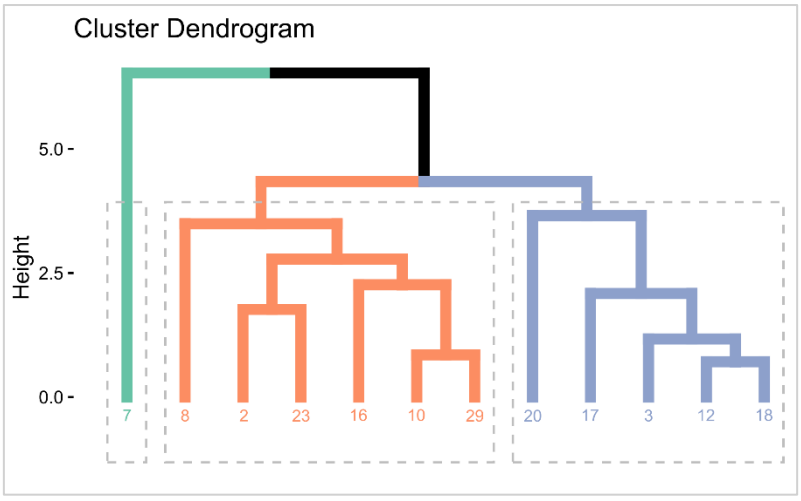


Figure S14. Clustering analysis on the difference between home and SOP results within each laboratory.

S3. Tables

Table S1. Summary statistics over all laboratories of the percentage deviations by sample for all extracts (based on the average of replicates per extract).

Sample	Minimum	Mean	Median	Maximum
A	-119.0	5.06	6.09	203.0
B	-1.52	0.25	0.00	3.91
C	-116.0	-1.98	-4.49	97.1
D	-118.0	-1.25	-0.47	114.0
EF2	-46.9	10.70	3.15	146.0

Note: Exclusion of laboratory 16 for statistics calculations.

Table S2. Summary statistics over all laboratories of the z-scores by sample for all extracts (based on the average of replicates per extract).

Sample	Minimum	Mean	Median	Maximum
A	-5.96	0.23	0.29	10.20
C	-5.80	-0.08	-0.20	4.85
D	-5.92	-0.09	-0.06	5.70
EF2	-2.34	0.53	0.16	7.31

Note: Exclusion of laboratory 16 for statistics calculations.

Sample	Minimum	Mean	Median	Maximum
A	-25.7	0.04	0.22	20.3
C	-5.80	0.51	-0.19	25.1
D	-18.8	0.14	-0.06	26.7
EF2	-2.41	0.42	0.05	7.31

Note: with all laboratories

Table S3. Contingency table of z-scores and participation to the OP-DTT ILC1.

Characteristic	N	Did not participate to the OP-DTT ILC1 (n=10)	Participated to the OP-DTT ILC1 (n=16)	*p*-value[1]
Sample A	**26**			**>0.9**
Satisfactory	**16**	**6 (60%)**	**10 (63%)**	
Not satisfactory	**10**	**4 (40%)**	**6 (38%)**	
Warning signal		1 (10%)	2 (13%)	
Action signal		3 (30%)	4 (25%)	
Sample C	**26**			**0.6**
Satisfactory	**15**	**4 (40%)**	**11 (69%)**	
Not satisfactory	**11**	**6 (60%)**	**5 (31%)**	
Warning signal		1	0	
Action signal		2	5	
Sample D	**26**			**0.5**
Satisfactory	**14**	**6 (67%)**	**8 (50%)**	
Not satisfactory	**12**	**4 (40%)**	**8 (50%)**	
Warning signal		2	3	
Action signal		1	5	
Missing		1	0	
Sample EF2	**26**			**0.7**
Satisfactory	**18**	**8 (80%)**	**10 (63%)**	
Not satisfactory	**8**	**2 (20%)**	**6 (38%)**	
Warning signal		1	3	
Action signal		1	3	

[1]*Fisher's exact test for the difference between counts of satisfactory and not satisfactory z-scores in participants who participated to the ILC1 vs. "new" participants.*

Table S4. Description of the physical and analytical parameters evaluated in the multiple regression models.

Characteristics	**N (%)**		
Device			
Cuvette	10 (38%)		
Plater-reader	16 (62%)		
Consumables washed with HNO_3			
Yes	21 (81%)		
No	5 (19%)		
Duration above 20°C (minutes)			
0	19 (76%)		
10	2 (8.0%)		
340	1 (4.0%)		
≥ 680	3		
Unknown	1		
	Minimum	**Median (Q1, Q3)**	**Maximum**
Transit time (days)	0.00	1.60 (0.90, 2.90)	10.60
Time before analysis (days)	2	19 (9, 28)	48
Maximum temperature reached during the transit (°C)	1.6	14.3 (10.0, 19.9)	27.7
Unknown	1	1	1
Median temperature reached during the transit (°C)	-1.3	5.4 (3.1, 8.4)	19.4
Unknown	1	1	1
Average $[AA]_0$ (µM)	-421	130 (123, 137)	12 511
Average slope of the negative control (nM/min)	-3 177	490 (190, 778)	4 058

Table S5. Comparison of LOD (nmol L-1 min-1) in participants in the satisfactory vs. warning or action z-score zones for each sample.

Characteristic	**Satisfactory**	**Warning or Action**	***p*-value⁺**
Sample A			
LOD (nmol L^{-1} min^{-1})*	153 (80, 196)	251 (133, 479)	**0.2**
N	16	10	
Sample C			
LOD (nmol L^{-1} min^{-1})*	165 (82, 212)	145 (118, 402)	**0.8**
N	18	8	
Sample D			
LOD (nmol L^{-1} min^{-1})*	165 (85, 212)	145 (85, 402)	**>0.9**
N	14	12	

*+Wilcoxon rank sum exact test for the difference between LOD in the participants in the satisfactory vs. warning or action z-score zones; *Median (25th percentile, 75th percentile).*

Table S6. Reported AA depletion slopes and corresponding OP_m^{AA} for different concentrations of $CuSO_4$, $5H_2O$.

Reference	Reagent used	$[AA]_0$	Concentration in reactive medium	Reported slope (corrected for reagent blank)	Calculated OP_m (nmol min^{-1} μg^{-1})	Information/assumptions used for calculations*
Assigned value of EF2 in this study	$CuSO_4$, $5H_2O$, ≥99%	133 µM	0.2 µM in K-PO_4 buffer 0.1M	/	78.49	/
(Expósito et al., 2024)	$CuSO_4$, analytical grade	200 µM	0.34 µM in PBS1X	0.47 µM min^{-1}	5.53 10^{-3}	M($CuSO_4$, $5H_2O$) = 249.68 g mol^{-1} Final volume = 200 µL
			1 µM in PBS1X	1.29 µM min^{-1}	5.17 10^{-3}	
(Pietrogrande et al., 2019)	$CuSO_4$, $5H_2O$, 98%	100 µM	0.1 µM in Na-PO_4 buffer 0.1M	2.33 nmol min^{-1}	30.79	M($CuSO_4$, $5H_2O$) = 249.68 g mol^{-1} Final volume = 3.03 mL
(Pietrogrande et al., 2022)			0.05 µM in Na-PO_4 buffer 0.1M	1.20 nmol min^{-1}	31.72	
			0.10 µM in Na-PO_4 buffer 0.1M	2.28 nmol min^{-1}	30.13	
			0.17 µM in Na-PO_4 buffer 0.1M	5.31 nmol min^{-1}	41.23	
(Visentin et al., 2016)	Cu(II)	100 µM	0.17 µM in Na-PO_4 buffer 0.1M	3.52 µM min^{-1}	32.32	
(Sekine et al., 2025)	$CuSO_4$, $5H_2O$, 99.5+%	99 µM	0.1 µM in MilliQ water	1.8 µM min^{-1}	72.09	M($CuSO_4$, $5H_2O$ = 249.68 g mol^{-1} Final volume = 10.1 mL
			0.2 µM in MilliQ water	2.9 µM min^{-1}	58.07	
			0.3 µM in MilliQ water	3.8 µM min^{-1}	50.73	
			0.5 µM in MilliQ water	4.8 µM min^{-1}	38.44	

*This information was used to calculate OP_m^{AA} in nmol min^{-1} μg^{-1} because the unit of the reported data varied.