Supplementary material to

External quality assurance schemes (EQUASs) and interlaboratory comparison investigations (ICIs) for the human biomonitoring of aromatic amines in urine as part of the quality assurance programme under HBM4EU

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Suppl. Table 1 Countries and numbers of participants

Country	Number of participants
Germany	7
UK	1
France	2
Switzerland	1[#]

[#]only registered

Suppl. Table 2 Final concentrations of the control materials (CMs)

Aromatic amine$_{CM}$	Final concentration (ng/mL)		
	Round 1	**Round 2**	**Round 3**
TOL$_{low}$	0.3	0.3	0.5
TOL$_{high}$	1.5	1.5	2
Aniline$_{low}$	2.7[#]	1.5[#]	4.4
Aniline$_{high}$	10	10	20
MOCA$_{low}$	10	13	13
MOCA$_{high}$	100	120	50
2,4-TDA$_{low}$	50	52	48
2,4-TDA$_{high}$	180	180	80
2,6-TDA$_{low}$	50	48	52
2,6-TDA$_{high}$	200	220	80
MDA$_{low}$	5	5.5	2.5
MDA$_{high}$	90	95	10

[#]No additional spiking was conducted as the native concentrations in the pooled urine were sufficiently high to reach the range of the expected exposure levels in the general population.

Analytical procedure for testing the control materials used in the QA/QC programme

Determination of aniline and TOL

First, 5 mL of urine was spiked with 30 µL of the internal standard solution (75.5 µg/L TOL-D_9 and 742 µg/L aniline-$^{13}C_6$ in ACN) and 1 mL HCl (37%). The sample was hydrolysed for 1 h at 80–85 °C and subsequently cooled in an ice bath, followed by the addition of 750 µL 10M NaOH, 3 mL 0.5M MES buffer (pH 6), and another 500 µL 10M NaOH. The pH was adjusted to 6.2 ± 0.2 by adding either 10M NaOH or acetic acid. The sample was then extracted twice on the multi-tube mixer, using 5 mL *n*-hexane for 15 min each time. Phase separation was achieved by centrifugation (10 min, 2200 *g*, approx. 10 °C). The hexane phase was transferred into a fresh tube through an intermediate Na_2SO_4 filter. The filter was rinsed with 2 mL *n*-hexane. Subsequently, 25 µL pyridine and 50 µL pentafluoropropionic anhydride (PFPA) were added to the combined organic phase for derivatisation, which was carried out in a water bath for 1 h at 80–85 °C. The sample was cooled to room temperature followed by the extraction with 3 mL phosphate buffer (pH 8). The sample was then centrifuged for phase separation (5 min, approx. 2000 *g*, approx. 10 °C). After that, 200 µL toluene were added to the organic phase, which was then concentrated in a vacuum concentrator to approx. 50–80 µL. The sample was transferred into a vial and analysed by GC-MS (negative chemical ionization). Sample analysis was performed with an Rxi-5MS (30 m, 0.25 mm ID, 0.25 µm df) at an injector temperature of 280 °C, a constant helium flow of 1.1 mL/min, and the following temperature program: initial temperature of 100 °C was held for 1 min. The temperature was then increased to 117 °C at a rate of 3 °C/min, to 200 °C at a rate of 8 °C/min, and further to 300 °C at a rate of 25 °C/min. The source temperature was set to 180 °C, interface temperature was 280 °C, and the solvent delay was 4.5 min. The limits of quantification (LOQ) and detection (LOD) for aniline were 0.200 ng/mL and 0.0667 ng/mL, for TOL 0.0100 ng/mL and 0.00333 ng/mL.

Determination of 2,4-TDA, 2,6-TDA, MDA, and MOCA

100 µL 6 N HCl and 50 µL of the internal standard solution (1 µg/mL 2,4-TDA-$^{13}C_6$, 1 µg/mL 2,6-TDA-$^{13}C_6$, and 0.2 µg/mL 4,4‘-MDA-D_8 in H_2O) were added to a 250 µL urine sample, mixed properly and hydrolysed for 4 h at 80 °C. The sample was cooled down, and 500 µL 1 N NaOH were added before solid phase extraction (SPE). SPE cartridges (Strata XC, 30 mg, 3 mL, Phenomenex Ltd. Deutschland, Aschaffenburg, Germany) were conditioned with 1 mL MeOH and 1 mL water. Afterward loading the sample, the cartridge was washed with 1 mL 0.1 N HCl and 2 mL MeOH. The sample was eluted with 2× 500 µL MeOH/isopropanol/NH_4OH (63:17:20), evaporated to dryness using a vacuum concentrator, reconstituted in 250 µL NH_4OAc/ACN (9:1, pH 9.2), and finally analysed by LC-MS/MS. A Gemini C18 column (3 µm, 3 × 150 mm, 110 Å, Phenomenex Ltd. Deutschland, Aschaffenburg, Germany) was used for chromatographic separation with a flow rate of 1 mL/min and the following gradient applied: Starting conditions were 10% B; this proportion increased over 30% B over the course of 1 min. Over the next minute, the gradient further increased to 90% B, which was held constant for the next 2 min. The B-content decreased over the course of 1 min to the starting condition of 10 %, under which the column was re-equilibrated for the next 3 min. Injection volume was 5 µL and column oven was kept at 35 °C. The MS was operated in positive-ion mode with the following parameters applied: Collision Gas (CAD) 5, Source Gas 1 (GS1) 45, Source Gas 2 (GS2) 55, Curtain Gas (CUR) 30, Ion Source (IS) 5500, Temperature (TEM) 650, Entrance Potential (EP) 10. The LOQ (and LOD) were as follows: 2,4-TDA 25.0 ng/mL (8.33 ng/mL), 2,6-TDA 25.0 ng/mL (8.33 ng/mL), MDA 0.100 ng/mL (0.0333 ng/mL), MOCA 10 ng/mL (3.33 ng/mL).

Suppl. Table 3 Method information for measuring the homogeneity and stability of aniline and TOL

ISO17025 accredited		Yes
Sample preparation	Sample amount extracted	5 mL
Extraction	pH adjustment	6–6.4
	LLE	2× 5 mL Hexane (15 min)
Derivatisation	Reagent	PFPA
Instrument	Separation	GC
	Detection	MS single quadrupole
Quantification	Use of internal standard (ISTD)	Yes
	Isotopic label	Yes
	Moment of addition	Before hydrolysis
	Response normalised to ISTD	Yes
Calibration	Matrix-matched	Addition to blank matrix before extraction
	Multilevel	Yes
Correction for recovery	No	
Identification criteria	Retention-time tolerance	Identification via retention time of isotopically labelled standard

Suppl. Table 4 Method information for measuring the homogeneity and stability of 2,4-TDA, 2,6-TDA, MDA, and MOCA

ISO17025 accredited		No
Sample preparation	Sample amount extracted	0.25 mL
Extraction	pH adjustment	1
	SPE	
Derivatisation	No	
Instrument	Separation	HPLC
	Detection	MS triple quadrupole
Quantification	Use of internal standard (ISTD)	Yes
	Isotopic label	Yes
	Moment of addition	Before hydrolysis
	Response normalised to ISTD	Yes
Calibration	Matrix-matched	Addition to blank matrix before extraction
	Multilevel	Yes
Correction for recovery	No	
Identification criteria	Retention-time tolerance	Identification via retention time of isotopically labelled standard

Suppl. Table 5 Obtained values of homogeneity measurements (n = 10)

Aromatic amine$_{CM}$	Round 1		Round 2		Round 3		Over all rounds
	Mean (ng/mL)	RSD (%)	Mean (ng/mL)	RSD (%)	Mean (ng/mL)	RSD (%)	Mean RSD (%)
TOL$_{low}$	0.31	3.2	0.29	3.4	0.5	4.0	**3.6**
TOL$_{high}$	1.48	2.7	1.4	2.9	1.96	2.0	**2.5**
Aniline$_{low}$	2.7	14.8	1.5	13.3	4.4	9.1	**12.4**
Aniline$_{high}$	11.8	3.4	9.7	3.1	18.8	2.1	**2.9**
MOCA$_{low}$	13.7	24.8	10.5	21.9	22.1	18.1	**21.6**
MOCA$_{high}$	138.2	17.5	116	14.4	67.7	13.9	**15.3**
2,4-TDA$_{low}$	53.1	8.5	38.1	5.8	41.8	6.0	**6.7**
2,4-TDA$_{high}$	195.6	5.0	135.7	4.7	70.2	5.4	**5.0**
2,6-TDA$_{low}$	52.3	6.7	46	3.7	47	6.4	**5.6**
2,6-TDA$_{high}$	212.9	6.1	205	4.1	74.3	5.8	**5.3**
MDA$_{low}$	5.2	5.8	6.6	6.1	2.2	9.1	**7.0**
MDA$_{high}$	0.31	3.2	0.29	3.4	0.5	4.0	**4.9**

CM = control material; RSD = relative standard deviation

Suppl. Table 6 Obtained values of stability measurements (n = 3)

Aromatic amine$_{CM}$	Round 1			Round 2			Round 3			Over all rounds
	Mean ± SD (ng/mL)		Relative difference between day 0 and day 46 (%)	Mean ± SD (ng/mL)		Relative difference between day 0 and day 46 (%)	Mean ± SD (ng/mL)		Relative difference between day 0 and day 46 (%)	Mean relative difference
	t = 0 d	t = 46 d at -20°C		t = 0 d	t = 60 d at -20°C		t = 0 d	t = 40 d at -20°C		
TOL$_{low}$	0.32 ± 0.01	0.30 ± 0.00	6.3	0.29 ± 0.01	0.30 ± 0.02	3.4	0.50 ± 0.02	0.46 ± 0.00	8.0	5.9
TOL$_{high}$	1.50 ± 0.04	1.39 ± 0.01	7.3	1.40 ± 0.05	1.45 ± 0.02	3.6	2.00 ± 0.02	1.83 ± 0.02	8.5	6.5
Aniline$_{low}$	2.8 ± 0.2	3.2 ± 0.2	14.3	1.6 ± 0.3	1.6 ± 0.1	0.0	4.6 ± 0.2	4.3 ± 0.3	6.5	6.9
Aniline$_{high}$	11.5 ± 0.2	11.3 ± 0.2	1.7	10.1 ± 0.3	9.9 ± 0.1	2.0	18.8 ± 0.0	18.4 ± 0.5	2.1	1.9
MOCA$_{low}$	16.6 ± 2.2	13.9 ± 2.9	16.3	12.2 ± 4.6	7.6 ± 0.6	37.7	21.1 ± 0.7	17.5 ± 4.6	17.1	23.7
MOCA$_{high}$	145.7 ± 39.6	144.3 ± 18.8	1.0	107.1 ± 6.8	104.4 ± 17.2	2.5	63.0 ± 0.6	63.2 ± 13.6	0.3	1.3
2,4-TDA$_{low}$	52.5 ± 1.4			39.2 ± 2.5	42.2 ± 2.2	7.7	42.2 ± 2.7	41.7 ± 0.5	1.2	4.4
2,4-TDA$_{high}$	186.7 ± 6.7	184.7 ± 9.7	1.1	141.7 ± 2.9	149.3 ± 6.4	5.4	71.2 ± 4.1	70.9 ± 2.9	0.4	2.3
2,6-TDA$_{low}$	54.8 ± 2.0	50.5 ± 3.4	7.8	45.2 ± 2.0	46.3 ± 5.4	2.4	44.2 ± 2.0	47.8 ± 3.8	8.1	6.1
2,6-TDA$_{high}$	204.3 ± 10.0	203.0 ± 3.6	0.6	209.3 ± 10.0	225.7 ± 7.6	7.8	72.8 ± 5.2	75.9 ± 0.9	4.3	4.2
MDA$_{low}$	5.1 ± 0.6	5.8 ± 0.5	13.7	6.8 ± 0.5	6.9 ± 0.3	1.5	2.4 ± 0.3	2.5 ± 0.3	4.2	6.5
MDA$_{high}$	101.1 ± 6.8	95.0 ± 7.0	6.0	104.0 ± 6.1	113.7 ± 3.2	9.3	10.2 ± 0.3	11.0 ± 0.7	7.8	7.7

SD = standard deviation

Suppl. Table 7 Overview of evaluation scheme, evaluation results and Z-scores

Evaluation scheme					Evaluation results						Z-scores		
Aromatic amine	**R**	**CM**	**Number of P (including E)**	**Evaluation as**	**A (ng/mL)**	**Uncertainty of A or of C when A was not available (%)**	**C (ng/mL)**	**$RSD_{experts}$ (%)**	**Study RSD_R (%)**	**$\frac{C-A}{A}$ (%)**	**Satis (%)**	**Quest (%)**	**Unsat (%)**
TOL	**1**	low	4 (3)	EQUAS	0.32	2.2	0.30	8.4	11.0	−6%	4 (100%)	0 (0%)	0 (0%)
		high	4 (3)	EQUAS	1.40	2.1	1.32	8.1	12.5	−6%	4 (100%)	0 (0%)	0 (0%)
	2	low	5 (3)	EQUAS	0.28	1.0	0.29	3.7	9.0	4%	5 (100%)	0 (0%)	0 (0%)
		high	5 (3)	EQUAS	1.36	1.1	1.33	4.3	8.1	−2%	5 (100%)	0 (0%)	0 (0%)
	3	low	6 (3)	EQUAS	0.54	4.9	0.55	18.3	33.0	2%	5 (83.3%)	0 (0%)	1 (16.7%)
		high	6 (3)	EQUAS	1.75	3.4	1.61	12.7	18.1	−8%	5 (83.3%)	1 (16.7%)	0 (0%)
TOL mean	**1–3**	low	6 (3)	–	–	2.7	–	10.1	17.7	–	94.4%	0%	5.6%
		high	6 (3)	–	–	2.2	–	8.4	12.9	–	94.4%	5.6%	0%
		low and high	6 (3)	–	–	2.5	–	9.25	15.3	–	94.4%	2.8%	2.8%
Aniline	**1**	low	4 (3)	np	na	na	na	na	na	na	na	na	na
		high	4 (3)	np	na	na	na	na	na	na	na	na	na
	2	low	5 (3)	np	na	na	na	na	na	na	na	na	na
		high	5 (3)	np	na	na	na	na	na	na	na	na	na
	3	low	5 (3)	np	na	na	na	na	na	na	na	na	na
		high	5(3)	EQUAS	15.5	5.9	17.5	22.2	22.5	13%	5 (100%)	0 (0%)	0 (0%)
Aniline mean	**1–3**	low	5 (3)	–	–	–	–	–	na	–	na	na	na
		high	5 (3)	–	–	–	–	–	22.5	–	100%	0%	0%
		low and high	5 (3)	–	–	–	–	–	22.5	–	100%	0%	0%

Evaluation scheme					Evaluation results						Z-scores		
Aromatic amine	**R**	**CM**	**Number of P (including E)**	**Evaluation as**	**A (ng/mL)**	**Uncertainty of A or of C when A was not available (%)**	**C (ng/mL)**	**$RSD_{experts}$ (%)**	**Study RSD_R (%)**	$\frac{C-A}{A}$ (%)	**Satis (%)**	**Quest (%)**	**Unsat (%)**
MOCA	**1**	low	8 (4)	ICI	na	6.0	8.5	–	59.0	na	6 (75%)	1 (12.5%)	1 (12.5%)
		high	8 (4)	EQUAS	107.6	6.0	72.9	21.8	42.7	−32%	5 (62.5%)	2 (25%)	1 (12.5%)
	2	low	8 (3)	ICI	na	14.8	13.3	–	39.3	na	7 (87.5%)	1 (12.5%)	0 (0%)
		high	8 (3)	EQUAS	127.2	3.6	130.1	13.7	16.1	2%	8 (100%)	0 (0%)	0 (0%)
	3	low	9 (5)	EQUAS	9.3	3.8	9.6	14.8	59.0	3%	8 (89%)	0 (0%)	1 (11%)
		high	9 (5)	EQUAS	42.7	6.5	40.6	25.4	44.5	−5%	8 (89%)	0 (0%)	1 (11%)
MOCA mean	**1–3**	low	9 (5)	–	–	8.2	–	-	52.4	–	83.8%	8.3%	7.8%
		high	9 (5)	–	–	5.4	–	20.3	34.4	–	83.8%	8.3%	7.8%
		low and high	9 (5)	–	–	6.8	–	-	43.4	–	83.8%	8.3%	7.8%
2,4-TDA	**1**	low	7 (4)	EQUAS	49.1	1.3	47.1	4.9	34.0	−4%	5 (72%)	1 (14%)	1 (14%)
		high	7 (4)	EQUAS	178.3	2.8	147.1	10.4	34.2	−17%	5 (72%)	1 (14%)	1 (14%)
	2	low	8 (3)	ICI	na	9.2	40.7	–	22.2	na	7 (87.5%)	0 (0%)	1 (12.5%)
		high	8 (3)	ICI	na	8.2	138.7	–	17.4	na	7 (87.5%)	0 (0%)	1 (12.5%)
	3	low	8 (5)	EQUAS	41.5	1.5	39. 6	7.1	10.0	na	8 (100%)	0 (0%)	0 (0%)
		high	8 (5)	EQUAS	69.6	1.1	66.0	5.3	9.7	−5%	8 (100%)	0 (0%)	0 (0%)
2,4-TDA mean	**1–3**	low	8 (5)	–	–	4.0	–	–	22.1	–	86.5%	4.7%	8.8%
		high	8 (5)	–	–	4.0	–	–	20.4	–	86.5%	4.7%	8.8%
		low and high	8 (5)	–	–	4.0	–	–	21.3	–	86.5%	4.7%	8.8%

Evaluation scheme					Evaluation results						Z-scores		
Aromatic amine	**R**	**CM**	**Number of P (including E)**	**Evaluation as**	**A (ng/mL)**	**Uncertainty of A or of C when A was not available (%)**	**C (ng/mL)**	**$RSD_{experts}$ (%)**	**Study RSD_R (%)**	**$\frac{C-A}{A}$ (%)**	**Satis (%)**	**Quest (%)**	**Unsat (%)**
2,6-TDA	**1**	low	7 (4)	EQUAS	51.8	3.2	46.4	12.1	37.0	−10%	5 (71%)	0 (0%)	2 (29%)
		high	7 (4)	ICI*	na	5.4	196.2	–	40.1	na	5 (72%)	1 (14%)	1 (14%)
	2	low	8 (3)	ICI	na	2.3	45.5	–	25.1	na	6 (75%)	1 (12.5%)	1 (12.5%)
		high	8 (3)	ICI	na	12.3	192.9	–	25.1	na	7 (87.5%)	0 (0%)	1 (12.5%)
	3	low	8 (5)	EQUAS	48.5	2.7	49.1	12.6	122.0	1%	7 (87.5%)	0 (0%)	1 (12.5%)
		high	8 (5)	EQUAS	77.4	3.0	78.8	13.8	70.2	2%	7 (87.5%)	0 (0%)	1 (12.5%)
2,6-TDA mean	**1–3**	low	8 (5)	–	–	2.7	–	–	61.4	–	77.8%	4.2%	18.0%
		high	8 (5)	–	–	6.9	–	–	45.1	–	82.3%	4.7%	13.0%
		low and high	8 (5)	–	–	4.8	–	–	53.3	–	80.1%	4.4%	15.5%
MDA	**1**	low	8 (4)	EQUAS	4.9	2.9	4.5	12.2	18.0	–8%	8 (100%)	0 (0%)	0 (0%)
		high	8 (4)	EQUAS*	95.2	1.7	80.7	6.3	24.8	–15%	7 (87.5%)	1 (12.5%)	0 (0%)
	2	low	9 (3)	ICI	na	9.5	5.6	–	20.1	na	8 (89%)	0 (0%)	1 (11%)
		high	9 (3)	ICI	na	7.1	91.7	–	12.4	na	8 (89%)	0 (0%)	1 (11%)
	3	low	10 (5)	EQUAS	2.2	2.0	2.2	9.1	12.0	0%	10 (100%)	0 (0%)	0 (0%)
		high	10 (5)	EQUAS	10.3	2.3	9.3	10.9	12.5	–10%	10 (100%)	0 (0%)	0 (0%)
MDA mean	**1–3**	low	10 (5)	–	–	4.8	–	–	16.7	–	96.3%	0%	3.7%
		high	10 (5)	–	–	3.7	–	–	16.6	–	92.2%	4.2%	3.7%
		low and high	10 (5)	–	–	4.3	–	–	16.6	–	94.3%	2.1%	3.7%

Evaluation scheme					Evaluation results						Z-scores		
Aromatic amine	**R**	**CM**	**Number of P (including E)**	**Evaluation as**	**A (ng/mL)**	**Uncertainty of A or of C when A was not available (%)**	**C (ng/mL)**	**$RSD_{experts}$ (%)**	**Study RSD_R (%)**	$\frac{C-A}{A}$ (%)	**Satis (%)**	**Quest (%)**	**Unsat (%)**
Aromatic amines mean	**1-3**	**low and high**	–	–	–	–	–	–	–	–	**89.9%**	**3.7%**	**6.4%**

A = assigned value; C = consensus value; CM = control material; E = experts; na = not available; np = no evaluation was possible because EQUAS requirements did not meet the criterion (u > 0.7 σT) and the number of participants was too low to calculate a reliable ICI consensus value; EQUAS* = EQUAS evaluation with results from only 2 experts; ICI* = ICI evaluation with results from only 5 participants; P = participants; Quest = questionable; R = round; $RSD_{experts}$ = relative standard deviation of experts' results; Satis = satisfactory; Study RSD_R= robust relative standard deviation of participants' results; Unsat = unsatisfactory;

Suppl. Table 8 Range of LOQs reported by participants and experts for aromatic amines

	Participants	Round 1	Round 2	Round 3	Over all rounds
TOL	lowest LOQ (ng/mL)	0.010	0.010	0.010	**0.010**
	highest LOQ (ng/mL)	0.600	0.200	1.000	**1.000**
	mean LOQ (ng/mL)	0.162	0.102	0.260	**0.175**
	total number of reported LOQs	5	6	6	**17**
	Experts	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
	lowest LOQ (ng/mL)	0.010	0.010	0.010	**0.010**
	highest LOQ (ng/mL)	0.100	0.100	0.100	**0.100**
	mean LOQ (ng/mL)	0.053	0.053	0.053	**0.053**
	total number of reported LOQs	3	3	3	**9**

	Participants	Round 1	Round 2	Round 3	Over all rounds
Aniline	lowest LOQ (ng/mL)	0.100	0.100	0.100	**0.100**
	highest LOQ (ng/mL)	2.00	2.00	2.00	**2.00**
	mean LOQ (ng/mL)	0.960	0.967	1.26	**1.06**
	total number of reported LOQs	5	6	5	**16**
	Experts	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
	lowest LOQ (ng/mL)	0.100	0.100	0.100	**0.100**
	highest LOQ (ng/mL)	2.00	2.00	2.00	**2.00**
	mean LOQ (ng/mL)	0.767	0.767	0.767	**0.767**
	total number of reported LOQs	3	3	3	**9**

	Participants	Round 1	Round 2	Round 3	Over all rounds
MOCA	lowest LOQ (ng/mL)	0.050	0.050	0.050	**0.050**
	highest LOQ (ng/mL)	10.0	10.0	2.00	**10.0**
	mean LOQ (ng/mL)	2.35	1.78	1.02	**1.72**
	total number of reported LOQs	8	8	8	**24**
	Experts	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
	lowest LOQ (ng/mL)	0.050	0.050	0.050	**0.050**
	highest LOQ (ng/mL)	10.0	10.0	10.0	**10.0**
	mean LOQ (ng/mL)	2.38	2.37	2.38	**2.38**
	total number of reported LOQs	5	5	5	**15**

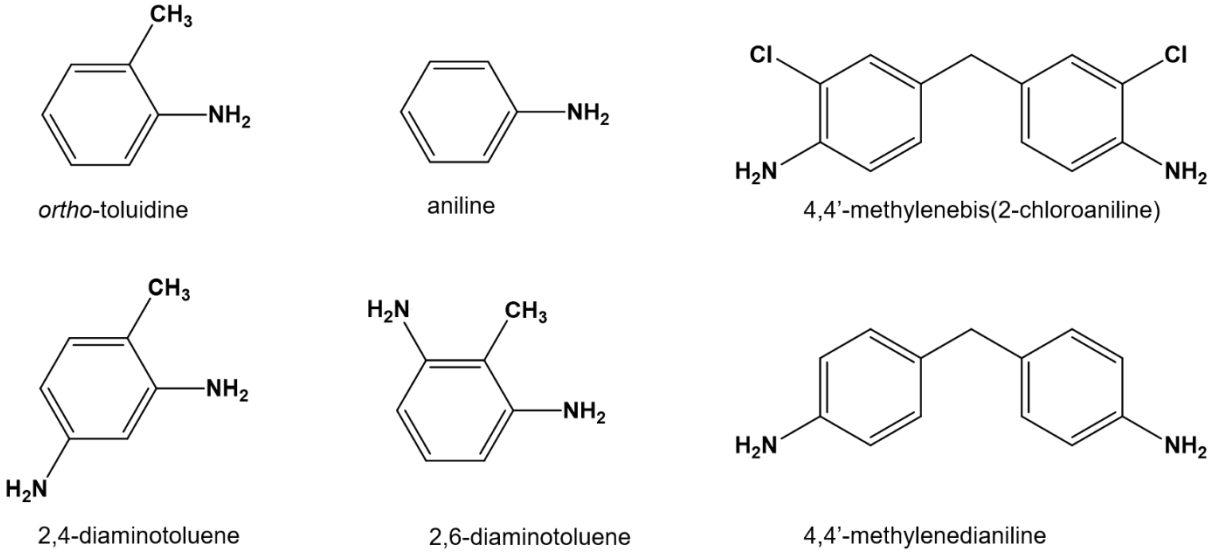
	Participants	Round 1	Round 2	Round 3	Over all rounds
2,4-TDA	lowest LOQ (ng/mL)	0.050	0.050	0.050	**0.050**
	highest LOQ (ng/mL)	25.0	25.0	25.0	**25.0**
	mean LOQ (ng/mL)	4.02	3.64	3.77	**3.80**
	total number of reported LOQs	7	8	8	**23**
	Experts	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
	lowest LOQ (ng/mL)	0.050	0.050	0.050	**0.050**
	highest LOQ (ng/mL)	25.0	25.0	25.0	**25.0**
	mean LOQ (ng/mL)	5.23	5.23	5.23	**5.23**
	total number of reported LOQs	5	5	5	**15**

Suppl. Table 8 Range of LOQs reported by participants and experts for aromatic amines (continued)

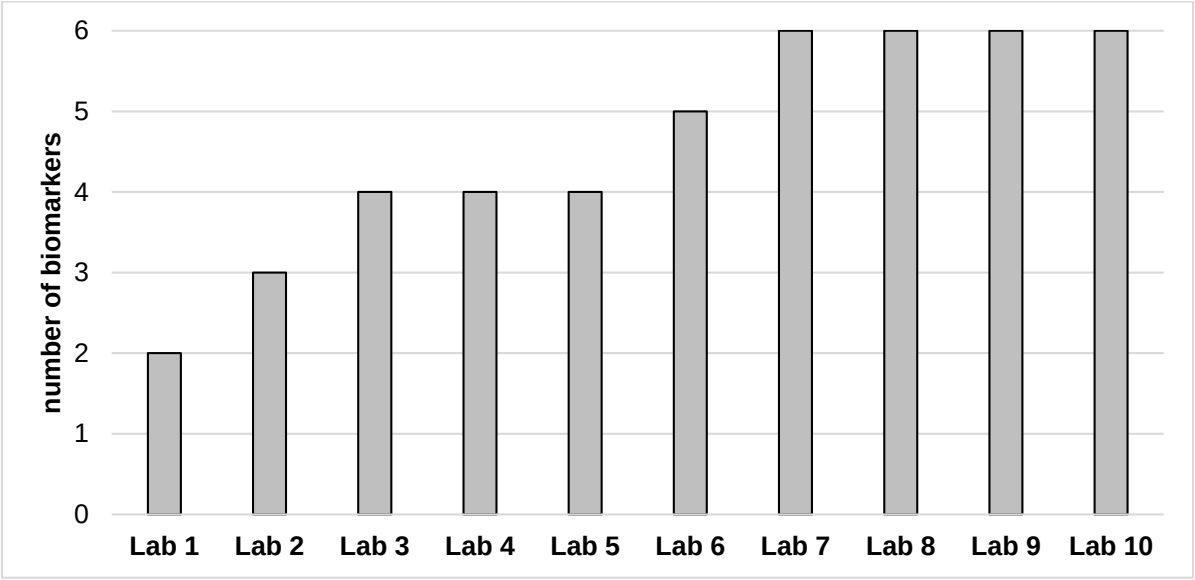
	Participants	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
2,6-TDA	lowest LOQ (ng/mL)	0.050	0.050	0.050	**0.050**
	highest LOQ (ng/mL)	25.0	25.0	25.0	**25.0**
	mean LOQ (ng/mL)	4.02	3.64	3.77	**3.80**
	total number of reported LOQs	7	8	8	**23**
	Experts	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
	lowest LOQ (ng/mL)	0.050	0.050	0.050	**0.050**
	highest LOQ (ng/mL)	25.0	25.0	25.0	**25.0**
	mean LOQ (ng/mL)	5.23	5.23	5.23	**5.23**
	total number of reported LOQs	5	5	5	**15**

	Participants	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
MDA	lowest LOQ (ng/mL)	0.030	0.030	0.030	**0.030**
	highest LOQ (ng/mL)	1.00	1.00	1.00	**1.00**
	mean LOQ (ng/mL)	0.496	0.353	0.507	**0.453**
	total number of reported LOQs	8	9	10	**27**
	Experts	**Round 1**	**Round 2**	**Round 3**	**Over all rounds**
	lowest LOQ (ng/mL)	0.030	0.030	0.030	**0.030**
	highest LOQ (ng/mL)	1.00	1.00	1.00	**1.00**
	mean LOQ (ng/mL)	0.474	0.296	0.294	**0.355**
	total number of reported LOQs	5	5	5	**15**

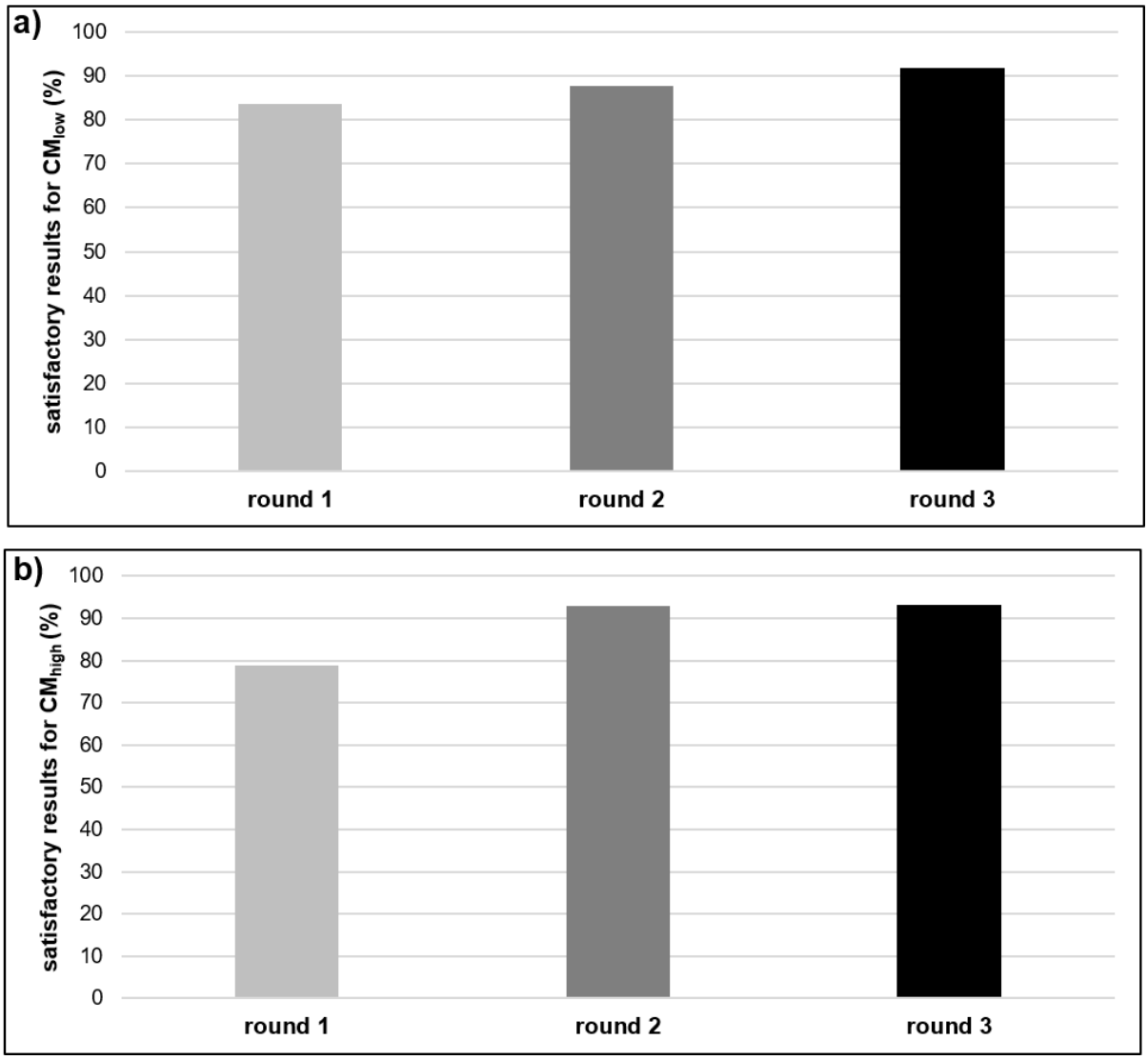
Supplementary Figures



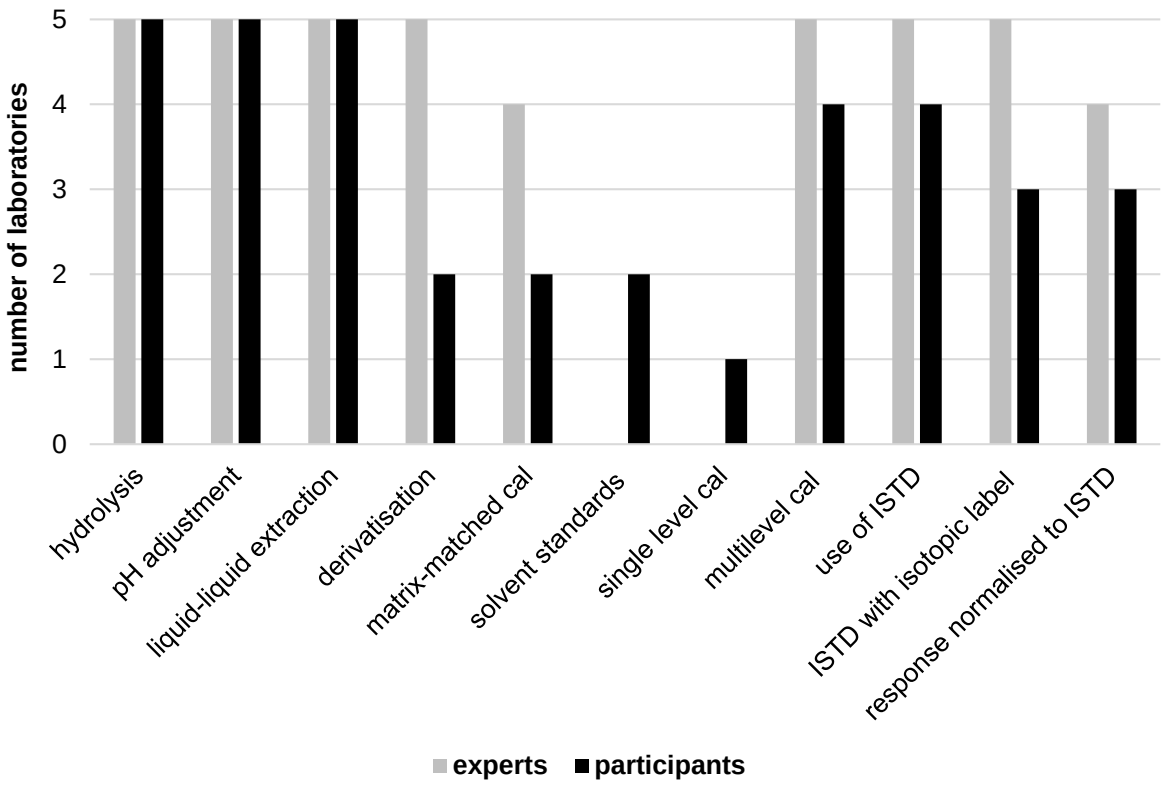
Suppl. Fig. 1 Structures of the analysed aromatic amines in the HBM4EU QA/QC programme



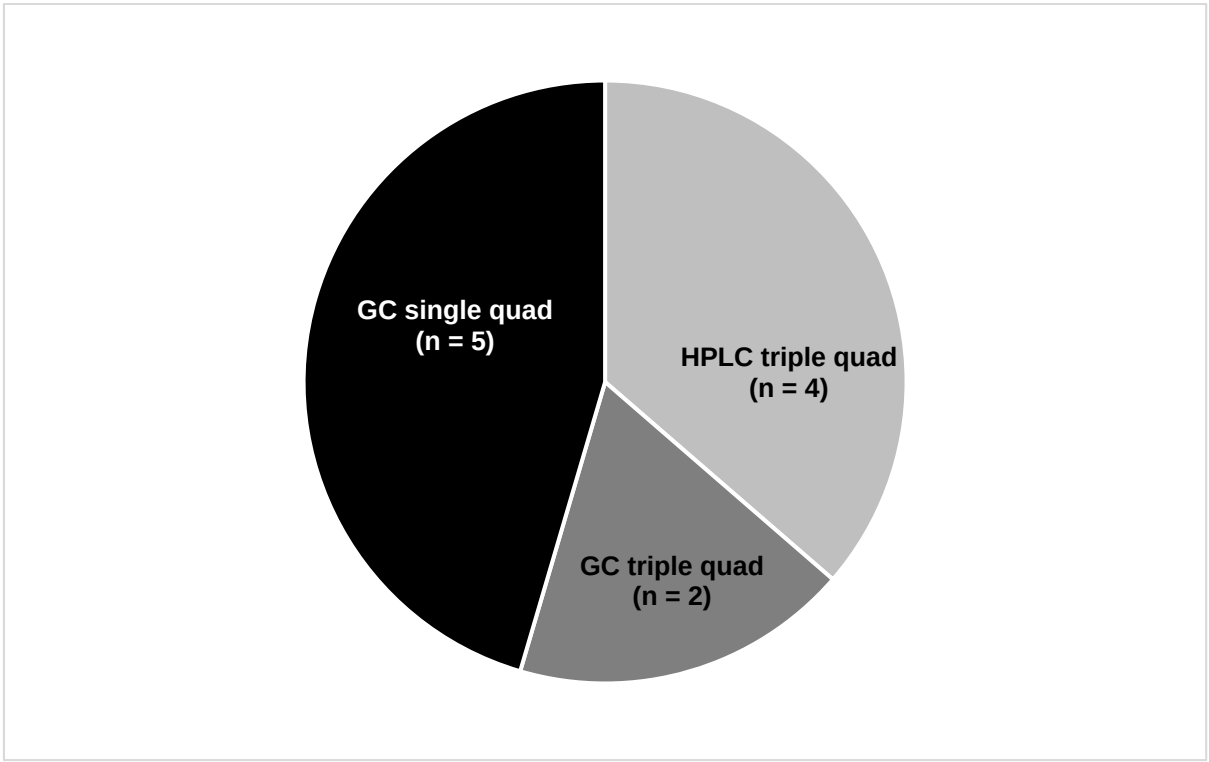
Suppl. Fig. 2 Number of biomarkers for which quantitative results were reported



Suppl. Fig. 3 Average of satisfactory results for the evaluable biomarkers in CM_{low} (a) and CM_{high} (b)



Suppl. Fig. 4 Method features of experts (n = 5) and participants (n = 5)
cal = calibration, ISTD = internal standard



Suppl. Fig. 5 Applied instruments and detection techniques by participants (including experts)