



Supplement of

Performance evaluation of four cascade impactors for airborne ultrafineparticle (UFP) collection: the influence of particle type, concentration, mass, and chemical nature

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Parameter	HPLC-MS neg	HPLC-MS pos	HPLC-FLD		
Analytical column	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 μm)	Gemini 5u C18 110A (150 mm x 4.6 mm, 5 μm)	EC 125/4 Nucleosil 100-5 C18 HD (125 mm x 4 mm, 5 μm)		
Column temperature	40 °C	30 °C	30 °C		
Injection volume	20 µL	20 µL	25 μL		
Autosampler temperature	_	_	-5 °C		
Flow rate	0.5 mL/min	0.3 - 0.5 mL/min	1 mL/min		
Gradient	A) 80% ACN, B) 4 mM HCOOH 0 min 5% A 1 min 5% A 18 min 50% A 21 min 100% A 29 min 100% A 31 min 5% A	A) 80%MeOH, B) 4 mM HCOOH 0 min 50% A 3 min 80% A 12 min 100% A 18 min 90% A 20 min 50% A 25 min 75% A	A) ACN, B) H ₂ O (Milli-pore) 0 min 60% A 5 min 70% A 8 min 70% A 12 min 80% A 15 min 80% A 19 min 90% A 22 min 60% A		
Detector	MSD Time ESI(-)-m/z-ions 0 min 207 8 min 111, 157, 171, 185 18 min 121, 135, 183 25 min 193, 217	MSDTimeESI(+)-m/z-ions0 min212, 227, 26912 min257, 261, 299	FLDTime $\lambda_{ex} / \lambda_{em}$ [nm]0 min259 / 3863.3 min242 / 3885.8 min250 / 3707.5 min270 / 39013 min290 / 430		

Table S1: Overview of HPLC methods applied for mass based chemical analysis applied on the environmental UFP samples.

Table S2: Summary of Considered Uncertainties and Their Contributions

Source of Uncertainty	Relative Uncertainty (%)		
Relative Standard Deviation of Repeated	2		
Analysis			
Errors from Reference Material	0.5		
Errors from Self-Prepared Stock Solutions	5		
Dilution Errors	5		
Calibration Uncertainty	5		
Inaccuracies from Balance and Pipette	1		

Table S3: Specifications regarding the different marker compounds that were analyzed and chosen for this study.

Marker	Method	Recovery	LOD _{Air}		LODIschumment	External standard	
			[pg/m ³]			calculation	
			43.2 m ³	5.76 m ³	[pg]	Response	
						factor	\mathbb{R}^2
						[AU/µg/L]	
Levo	HPLC-MS	$86 \pm 9\%$	130.09	975.67	5619.89	442.68	0.99
	neg						
РА	HPLC-MS	84±6%	186.57	1399.28	8059.82	4415.4	0.99
	neg						
ТА	HPLC-MS	85±6%,	171.76	1288.20	7420.03	3352.9	0.99
	neg						
6PPD	HPLC-MS	75±7%	40.17	301.26	1735.34	26766	0.98
	pos						
BaP	HPLC-	78±5%	1.62	12.15	69.98	10.116	1.00
	FLD/UV						
BbF	HPLC-	74 <u>+</u> 4%	1.16	8.70	50.11	12.15	1.00
	FLD/UV						



Figure S1: logarithmic representation of Fig. 6b.



Sect.S1.1 Estimation of Impactor Uncertainties

To accurately assess the overall measurement uncertainty associated with the various impactors used in our study, we applied Gaussian error propagation. The overall chemical analysis error was 9% for all impactors. For the Ultra MOUDI impactor, in addition to the analysis error, the flow error was 10% and the handling error was increased to 10%. This adjustment leads to a total measurement uncertainty for the Ultra MOUDI of approximately 16.76%. The ELPI impactor had a flow error of 3% and an increased handling error of 15%, resulting in a total measurement uncertainty of around 17.75%. For the 120R MOUDI impactor, the flow error was 3% and the handling error was increased to 10%, leading to a total measurement uncertainty of approximately 13.78%. For the PENS impactor, the flow error was 5% and the handling error was increased to 10%, resulting in a total measurement uncertainty of approximately 14.35%.

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