Measurement Guidelines

for the determination of particulate organics

1st OGTAC-CC community meeting within the framework of the ECAC-CAIS CF 04/2024

Leibniz Association

TROPOS
Leibniz Institute for Tropospheric Research

Outlook Measurement Guidelines

Content:

1) About this document
2) Data Quality Objectives
3) Particle sampling protocol
   - 3.1 General considerations
   - 3.2 Handling aerosol particle sampler (offline)
   - 3.3 Sample pre-treatment, storage and transport
   - 3.4 Documentation of the procedure
   - 3.5 Cleaning and maintenance
   - 3.6 Quality management (field blanks)
4) Laboratory analysis protocol
   - 4.1 Sample preparation
   - 4.2 Analytical procedure
5) Data submission

Module dependent!

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Similar and identical to the technical requirements, respectively

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General recommendations from the CC that can be individually adjusted by the NF (proof of quality required)

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Particle sampling protocol

Contains:

- General aerosol particle sampling procedures given in the technical requirements, incl. documentation of experimental parameters (T, RH, flow rate, start end end time, batch numbers, etc.)
- Low-volume sampling following the EUSAAR OC/EC protocol
- High-volume sampling under discussion (cf. technical requirements)
- Filter/ substrate pre-treatment procedure
- Recommendation to minimize transfer steps, transport and storage times, *test experiments on the impact of sample storage currently ongoing (for the BB module)*
- *Maybe module dependent…*

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Particle sampling protocol

Contains:

- Maintenance and cleaning procedures
- System checks on a routine basis
- Field blanks (at least once a month if daily measurements are performed, preferably once a week) by following the full procedure unless placing the filter holder with the filter into the sampling unit and pump on

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Laboratory analysis protocol

- Recommended and supported analytical techniques and figures of merit to be met for the determination of particulate organics:

Target compound	Sum formula	IUPAC name	CAS number	Recommended and supported analytical technique	Analytical figures of merit
Levoglucosan	$C_6H_5O_{10}$	(1R,2S,3S,4R,5R)-6,8-dioxabicyclo[3.2.1]octane-2,3,4-triol	498-07-7	HPAEC-PAD (HPLC-PAD)	…
Mannosan	$C_6H_5O_{10}$	(1R,2S,3S,4S,5R)-6,8-dioxabicyclo[3.2.1]octane-2,3,4-triol	14168-65-1	HPAEC-PAD (HPLC-PAD)	…
Galactosan	$C_6H_5O_{10}$	(1R,2R,3S,4R,5R)-6,8-dioxabicyclo[3.2.1]octane-2,3,4-triol	644-76-8	HPAEC-PAD (HPLC-PAD)	…
…	…	…	…	…	…

- Other analytical methods applicable, participation in ILC will demonstrate capabilities (quality control)
- Intensive exchange between the NF and the CC for 1st time documentation

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Sample preparation / extraction procedure

Example BB module – overview current NFs:

NF	Birkenes	Zeppelin	Melpitz	Vielsalm	Sonnblick
Analytical technique	UPLC-Orbitrap MS	UPLC-Orbitrap MS	HPAEC-PAD	GC-MS	HPAEC-PAD
Extraction procedure	Filter sample (1.5 cm^2 or 3.0 cm^2) submerged by precleaned THF (2 mL) in a screw neck brown colored glassware vial, which is subjected to ultrasonic extraction (30 min). The solute is transferred to a centrifuge tube by pipetting. This step is performed twice. The solute is evaporated to 0.4 mL, spun (10 min; 2000 rpm) and transferred to a screw neck brown colored glassware vial to which Milli-Q water (450 µl) is added. The total volume is adjusted to 1 mL by precleaned THF. The sample is whirlmixed before analysis.		3 Spots (diameter 14mm) + 10ml ultrapure water 2h shaking (420rpm) filtration using a 0.45µm syringe filter (IC-Acrodisc, PALL)	We use the entire filter minus 1,5cm^2 for EC/OC. Add levoglucosan d7, Extraction with 5 ml 80/20 dichloromethane/methanol. Ultrasonication 2 times 15 minutes in a bath at 60°C. Add extraction IS at 1 ml extract. Evaporate to dryness, Derivatisation with BSTFA with 1% TMCS and anhydric pyridin, Incubation 1 hour at 80°C. Then add dodécane, Gently evaporation (40°C) and add cyclohexane to 1ml.	punches (PM10: 4,52 cm^2, PM1: 2,26 cm^2) are extracted with ultrapure water (Milli-Q) (PM10: 2 mL, PM1: 3 mL) by ultrasonic agitation (20 min), follwed by centrifugation

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Sample preparation / extraction procedure

Example BB module – recommendation for HPAEC-PAD:

- Use the minimum required filter area to minimize the amount of extraction solvent plus use appropriate labware (e.g., extraction in small Eppendorf vials, plastic labware need to be borate free)
- Document the filter area and the amount of extraction solvent
- Extraction solvent: ultrapure water
- Sample shaking (no ultrasonication), 2h / 420rpm
- *Impact ultrasonication on anhydrosugars - any experience? TROPOS ACD test experiments ongoing together with the federal agency for the environment in Saxony – work in progress!*
- Filtration via 0.45µm PTFE filter (e.g., syringe filter), avoid cellulose filters

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Analytical procedure

Instrument information:

- General type
- Autosampler type
- Injector (amount of injected volume)
- Detection unit
- All linked to the instrument database!
- Separation column (stationary phase)
- Mobile phase

Analytical conditions:

- Flow rate
- Temperature program
- Gradients
- Oven temperature
- Concentrations/mixtures

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Analytical procedure

Calibration:

- External calibration
- Standards; purity and concentration
- Number of standards and repetitions is not yet decided – Should be done for each analytical sequence

Quality management:

- Solvents, Eluents, derivatization reagents and water in sufficient purity
- Gases in sufficient purity

→ Input from the NFs through the ILC

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QA/QC and maintenance of the analytical setup

- QA/QC tests are part of the annual ILC but should be done routinewise minimum 4 times a year in total, including:
  - Recovery control for evaluation of the extraction
  - Repeatability
  - (Reproducibility)

  } *DQOs*

- Data checks on a routine basis

Maintenance example HPAEC-PAD:

- Polishing of the working electrode and rigorous cleaning of the instrument to avoid electrode surface poisoning, e.g. if before high salt containing samples have been analyzed
- Cleaning should include also tubing and fittings

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Data aquisition and processing

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Data aquisition and processing

General:

- Sequence table shall include a defined set of samples, blanks and control standards, e.g. one control standard every 10 samples
- Peak integration should preferably be done automatically (e.g. Chromeleon software)
- Sample results need to be in the calibrated concentration range of the target compound, if not samples need to be diluted
- *Offline data workflow includes preparation, exposure, extraction and analysis protocol (machine readable protocol database)*
  → *see presentation by Markus Fiebig*
- Data provision always as 1) raw data plus the corresponding calibration curves, 2) processed to the level of mass per volume extraction solvent and 3) processed to the level of atmospheric concentration in mass per volume air

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2) Calibration Centre Activities – task chain

- Definition of target compounds, e.g., biomass burning or on secondary organic aerosol constituents of biogenic and anthropogenic origin
- Set up technical requirements, for all steps from sampling to the quantitative result, set Data Quality Objectives (DQO)
- Development of measurement guidelines based on the technical requirements and Interlaboratory Comparisons (ILCs)

Future activities:

- SOP templates needs to be finalized by each NF individually together with the calibration centre containing step by step instructions for a specific sampler/analytical method combination at the respective NF (max. level of detail)
- NF individual SOP will finally need approval by the calibration centre
- Define QA/QC procedures, e.g., performance test by ILCs
- Develop workflow for offline data submission

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Agenda

1st OGTAC-CC community meeting 2024 (online) – Agenda Tuesday April 9	
13:00 - 13:15	Welcome
13:15 - 13:45	Introduction of OGTAC-CC
13:45 - 14:30	Presentation of the Tech
	- Draft list of target co
	- Sampling procedure
	- Sample pre-treatmer
	- Maintenance (Sampl
14:30 - 14:45	Coffee break
14:45 - 15:30	Presentation of the Tech
	- Data resolution, cove
	- Sample handling and
	- Recommended and s
15:30 - 16:00	Outlook on the Measurement Guidelines
16:00 - 16:15	Coffee break
16:15 - 16:45	Introduction ILC autumn 2024
16:45 - 17:00	Time for further discussion

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