A non-target approach to identify complexing agents in atmospheric aerosol and rainwater samples

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(1) Introduction

- **Secondary organic aerosol (SOA**) formation and composition remain one of the most intensively investigated but also most poorly understood topic in atmospheric science.
- Up to 100,000 different organic substances can be present in SOA,[1] even by means of non-target screenings an exact structure assignment is challenging due to the scarce availability of standards.
- Organic acids functionalities often form during atmospheric transformation processes therefore their detection is of particular interest.[2]
- Here we developed a method for selective detection of functional groups using a non-target approach in LC-HRMS data sets from environmental samples.

(2) Workflow

Post-column setup

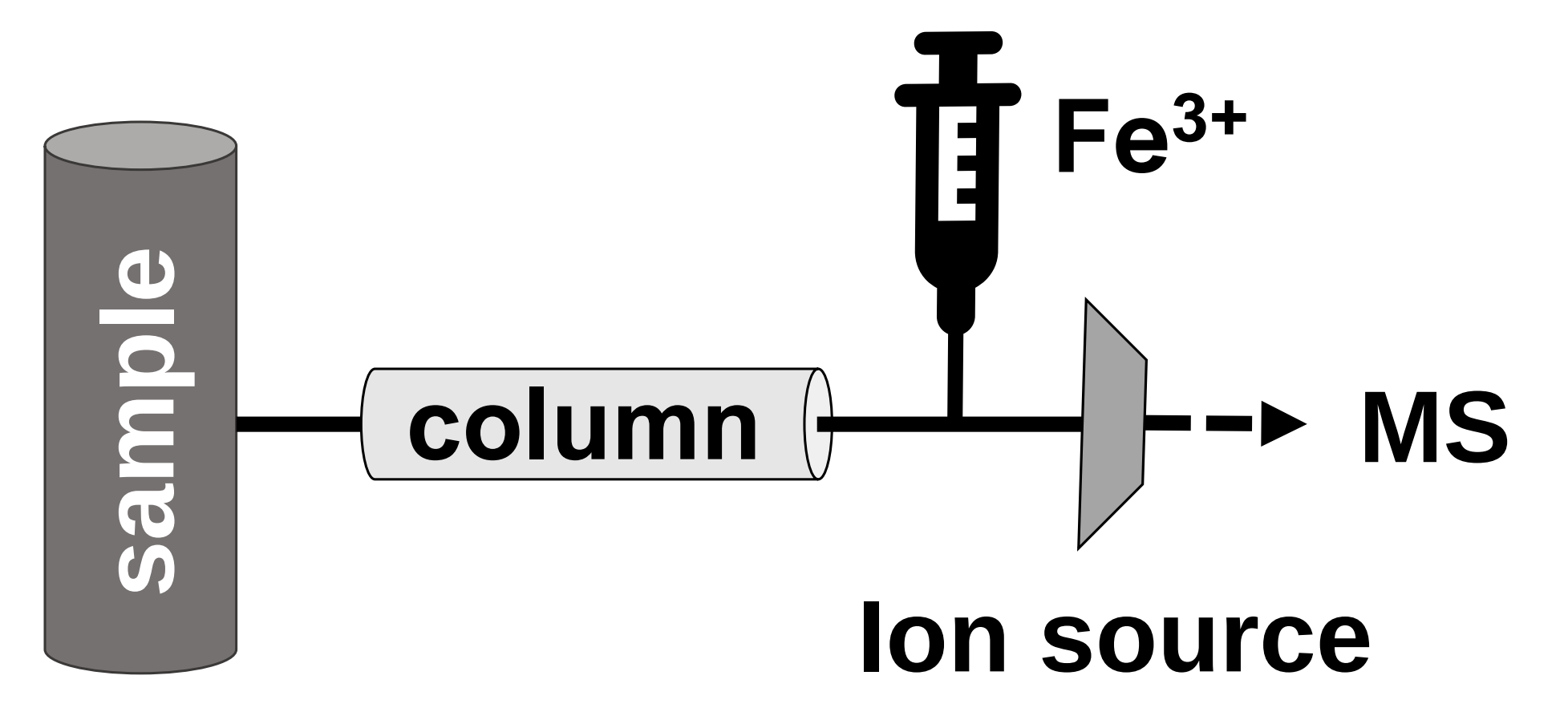

Fig. 1: Scheme of the post-column complexation setup with iron(III) addition.

- Addition of 155 µM **$FeCl_3$** via syringe pump into T-junction between LC outlet and ion source
- **Complexation after LC separation**[3]
- Measurements with UPLC/Orbitrap-MS
- Negative mode, MS^1, R=70k, $\Delta m/z \leq 3$ ppm

Complex formation types

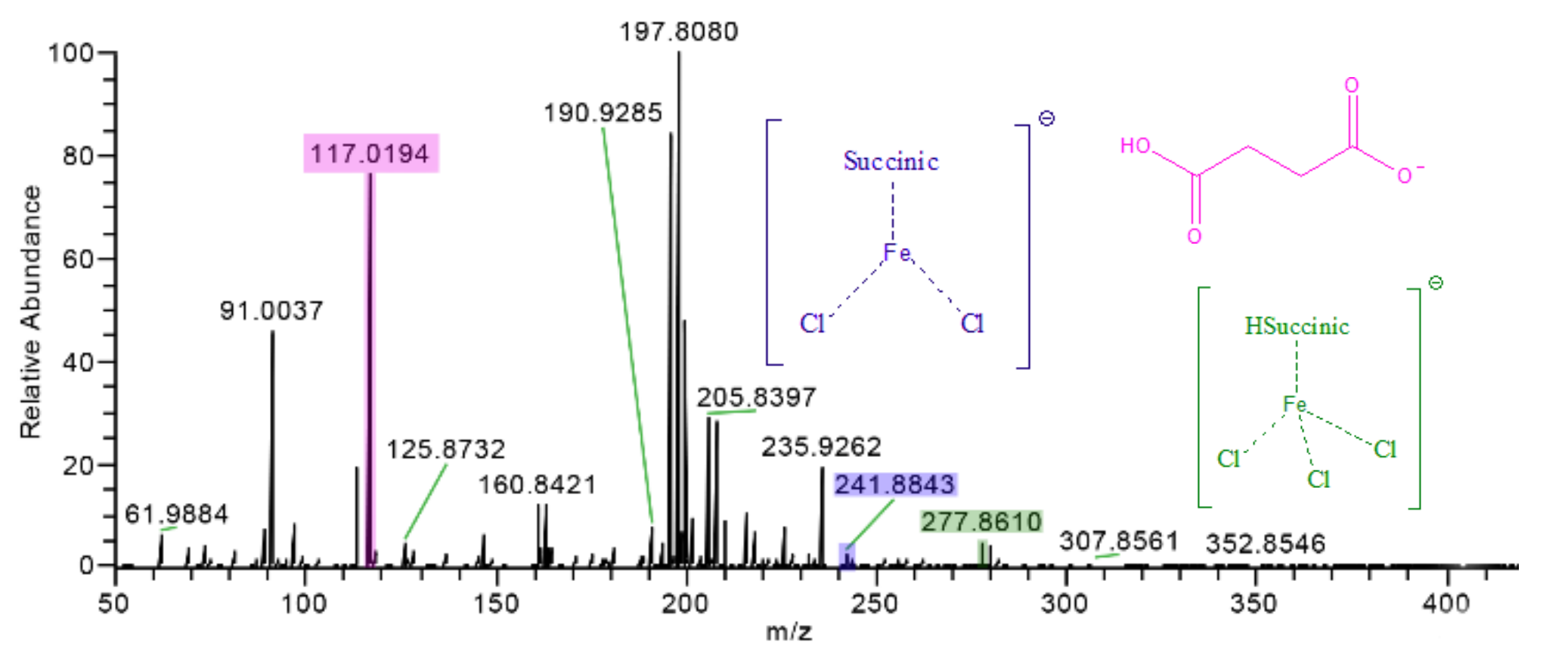

Fig. 2: Detection of iron(III) complex species using the example of succinic acid.

- Test with eleven organic **di- and tricarboxylic acids**
- Signal *m/z* 197.8080 belongs to $[FeCl_4]^-$
- Investigation on most intensive iron complex signals

→ Find **recurring complex formation patterns**

Identification in non-target analyses

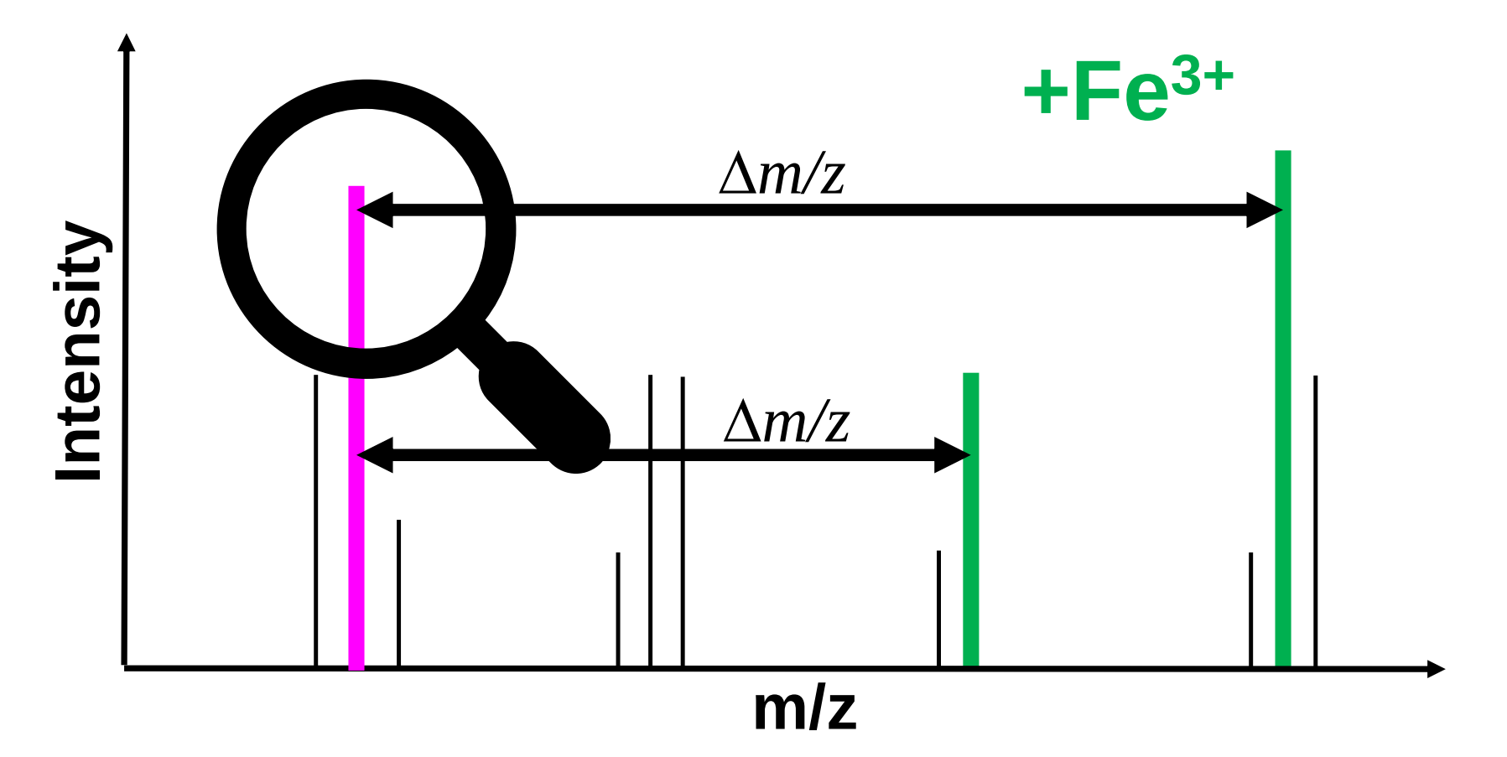

Fig. 3: Scheme on the identification of new complexing agents during a non target analysis.

- Screening of mass spectra for characteristic Δ*m/z* between iron complex and complexing agent*:*

  $[M\text{-}H+FeCl_3]^-$ ($\Delta m/z$ 160.8416)
  $[M\text{-}2H+FeCl_2]^-$ ($\Delta m/z$ 124.8648)
  $[M\text{-}3H+FeCl]^-$ ($\Delta m/z$ 89.8959)

- Formula assignment for complexing agents

(3) Method optimization

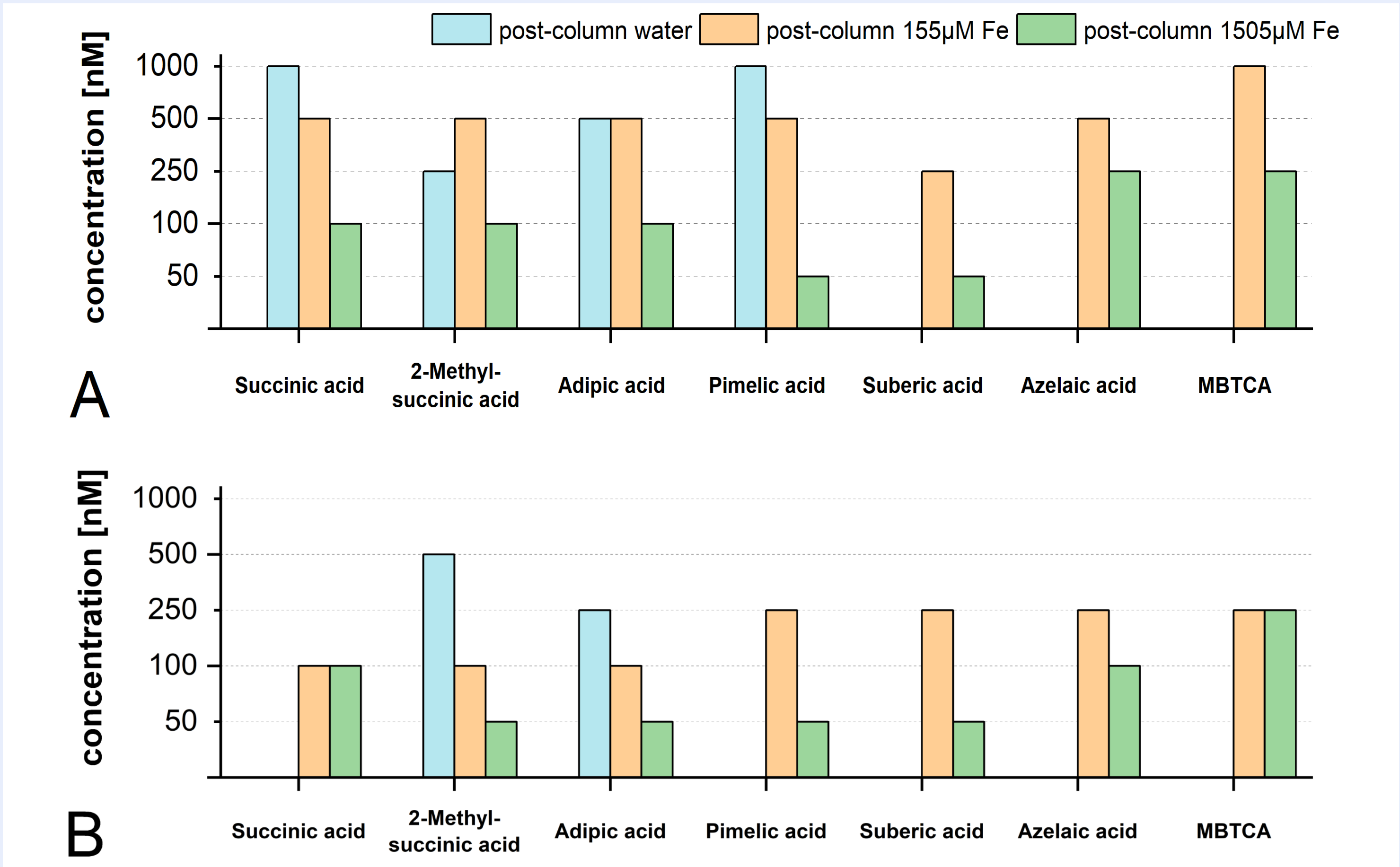

Fig. 4: Lowest concentration of respective organic acid at which the iron complexes $[M\text{-}2H+FeCl_2]^-$ (A) and $[M\text{-}H+FeCl_3]^-$ (B) could be detected for each series. Different colors indicate the experimental conditions.

- $[M\text{-}H+FeCl_3]^-$ complex is more sensitive
- Improved limit of detection with higher iron(III) addition
- Compromise between cleaning effort and increased sensitivity is addition of 155 µM Fe^{3+}
- **Detection without external iron addition possible!**

(4) Application to field samples

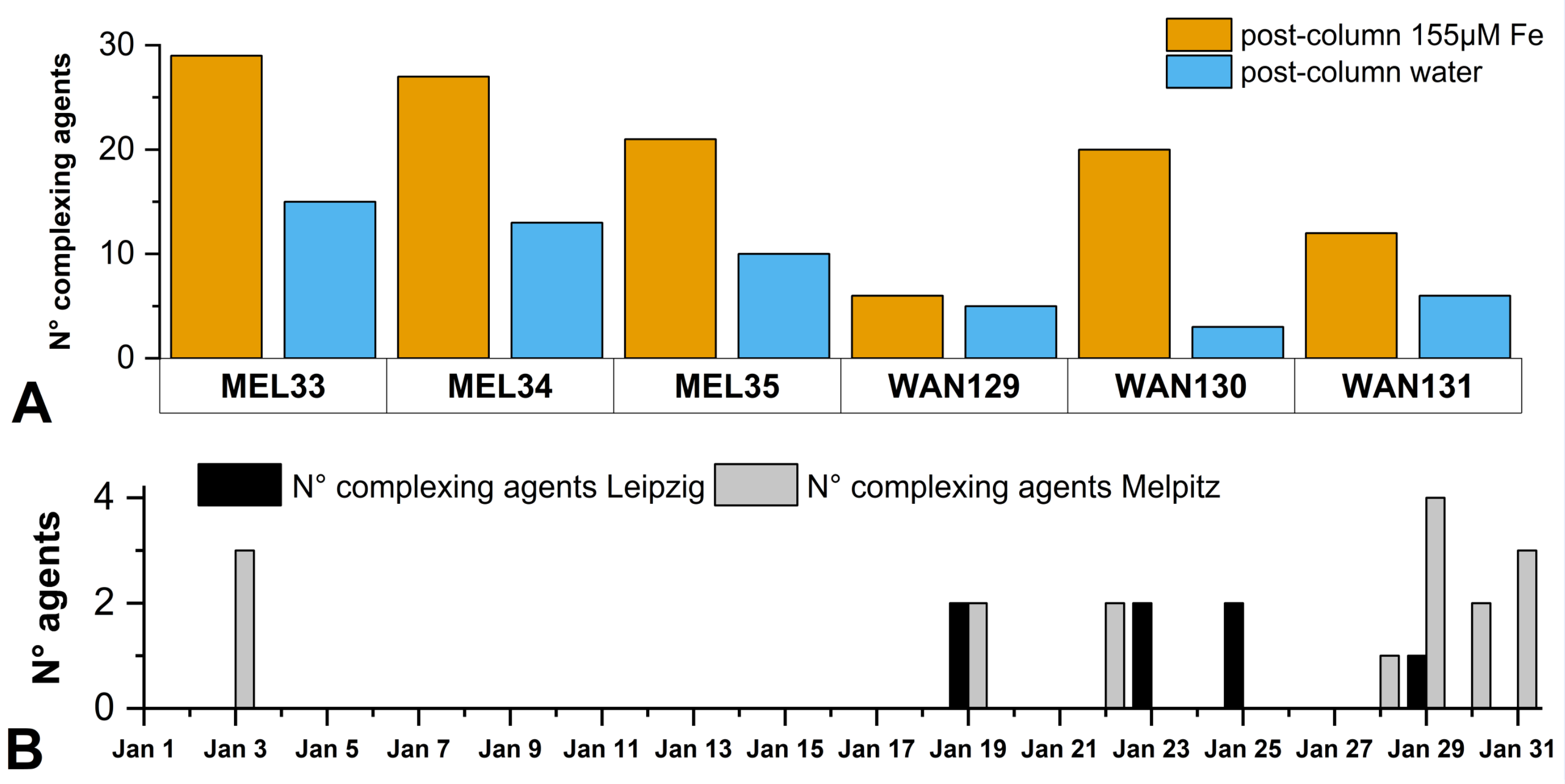

Fig. 5: Number of identified complexing agents for the aerosol particle samples (A) from Melpitz (MEL) and Wangdu (WAN) and for the rainwater samples without iron addition (B) in Leipzig and Melpitz.

- Measurement of particle samples from two sites (Melpitz, Germany, and Wangdu, China) reveal more complexing agents in Melpitz.
- Formation of **carboxylic acids** was suppressed in China.[4]
- Collected rainwater from winter time 2021 in Germany revealed a few complexing agents without iron addition.
- **4-Nitrophenol** and **4-Nitrocatechol** could be identified as new complexing agents in samples from China and in the rainwater.

(5) Summary and Outlook

Summary

- Developed method can be applied to field samples, to improve LOD iron(III) concentration can be raised.
- Iron traces of the separation system are sufficient to obtain complexation of most dominant complexing agents.
- NTS approach is only sensitive to strong complexing agents → high selectivity

Outlook

- Increased understanding of different atmospheric reaction regimes leading to different sample composition.
- Method is a promising tool to clarify functional groups without standards or MS^n experiments.

(6) References

[1] Spranger et al. (2019), *Environ. Sci. Technol.* 53 (19), 11353–11363. **[2] Herrmann et al. (2015),** *Chem. Rev.* 115 (10), 4259–4334. **[3] Aron et al. (2022),** *Nat. Chem.* 14 (1), 100–109.
[4] Brüggemann et al. (2019), *Environ. Chem.* 16 (5), 333.