



Effect of mass resolution and mass spectrometer on trace gas measurements in a boreal forest comparing three nitrate CIMS

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Abstract. Accurate measurements of oxygenated organic molecules (OOMs) are essential to understand their relevance in secondary organic aerosol formation. Online measurements of OOMs are primarily performed with chemical ionization mass spectrometry (CIMS). These measurements often yield crowded mass spectra due to the molecular complexity of atmospheric OOMs, presenting a challenge for peak assignment and molecular identification. To investigate how mass resolution influences the interpretation of the mass spectrum, we compare three nitrate chemical ionization mass spectrometers: two atmospheric pressure interface time-of-flight (APi-ToF) instruments equipped with different ionization inlets (Eisele type and MION) and an Orbitrap with a MION-inlet. Their resolving powers are 2,500, 7,500 and 280,000 at 200 m/z, respectively. The simultaneous measurements in a Finnish boreal forest demonstrate the advantages of high resolving power for peak identification. In the mass range 260–550 m/z, the MION-Orbitrap identified 1333 non-isotopic peaks compared to the 483 non-isotopic peaks identified by the MION-ToF. By using the Orbitrap peak list, the MION-ToF could identify 1327 peaks. When measuring ions at concentrations higher than 5×10^5 molecules cm^{-3} , the instruments correlate very well, where the MION-Orbitrap and MION-ToF have an average correlation of $\rho = 0.77$. At lower concentrations, the correlations are weak ($\rho = 0.42$), likely due to peak overlap in the ToF mass spectra. Peak lists constructed using Orbitrap-derived molecular compositions showed clear improvements in the number of identified peaks over the conventional ToF peak list. These results demonstrate that high-resolution Orbitrap measurements can substantially enhance molecular identification in widely used ToF datasets, leading to more reliable quantification of atmospheric OOMs.



1 Introduction

35 Atmospheric trace vapours have been established to have diverse effects on environmental and climate systems as well as human health. Most of these compounds are organic and are associated with various complex processes that occur in the atmosphere (Aljawhary et al., 2013; Dada et al., 2017; Zhang et al., 2024). Reaction of organic vapours with hydroxyl radicals, nitrate radicals and ozone leads to formation of oxygenated organic molecules (OOMs) (Li et al., 2021). OOMs are important precursors of secondary organic aerosol formation (Lee et al., 2020; Zha et al., 2023). Beyond this, various laboratory and
40 atmospheric observations have shown that NPF events are driven by gas-phase OOMs, especially low volatility OOMs (Riccobono et al., 2012; Dada et al., 2017; Kupc et al., 2020; Zha et al., 2023; Zhang et al., 2024b). The contribution of organic vapours to atmospheric new particle formation and growth remains an active area of research.

Atmospheric trace gases are present as a complex mixture of molecules with enormous variability in concentrations and chemical formulas, functional groups and volatilities (Ehn et al., 2014; Yuan et al., 2026). To accurately measure reactive
45 OOMs that exist in low concentrations, online measurement techniques are beneficial as no sample preparation is required and sample contamination and loss can be avoided (Lee et al., 2020; Häkkinen et al., 2023). Development of measurements method with chemical ionization mass spectrometry (CIMS) has been critical in addressing this challenge (Zuth et al., 2018; Riva et al., 2020; Zhang et al., 2024a). Several reagent ions like nitrate (Ehn et al., 2014), iodine (Lee et al., 2014), ammonium (Zaytsev et al., 2019), urea (Shcherbinin et al., 2025) and bromine (Sanchez et al., 2016) amongst others are employed for chemical
50 ionization. Along with these different ionization methods, new mass analysers (e.g., ToF (Ehn et al., 2014) and Orbitrap (Zuth et al., 2018; Riva et al., 2019)) have expanded the analytical power of CIMS.

CIMS measurements are affected by multiple factors, such as differences in the physical conditions in ion-molecule reactors where the ion-molecule reaction takes place (Shcherbinin et al., 2024; Aggarwal et al., 2025). High temperatures can induce declustering of weakly bound clusters (Robinson et al., 2022) and pressure is associated with the amount of collision occurring
55 between the reagent ions and the analyte (Shcherbinin et al., 2024). Both factors affect the sensitivity of the CIMS instrument in detecting OOMs. Depending on the specific instrumental parameters and reagent ion used the room humidity can have positive or negative impact on the sensitivity of CIMS instruments (Zaytsev et al., 2019; Huang et al., 2021; He et al., 2023). The reagent ion distribution, i.e., the monomer dimer ratio (Garmash et al., 2024) or the relative intensity of oligomers (De Gouw and Warneke, 2007), influences the sensitivity and the selectivity. Along with that difference in voltages in the ion optic
60 region affects the ability of the CIMS instrument to detect OOMs. (Zaytsev et al., 2019; Aggarwal et al., 2025)

Following ionization, the mass resolution of the mass spectrometer is the fundamental power that enables to separate the ions of different mass. Mass resolution of CIMS used for atmospheric measurements ranges from ~2,000 to 14,000 for Time-of-Flight mass spectrometers to beyond 100,000 for Orbitrap mass spectrometers. (Riva et al., 2020; Yuan et al., 2026) The overlap of multiple peaks complicates the interpretation of mass spectra two-fold: First, the fitting of peaks positions and the
65 assignment of elemental compositions is increasingly more difficult as overlap increases (Cubison and Jimenez, 2015). Building peak list has become easier over the last several years thanks to algorithms that fit a plausible number of peaks into



observed spectra(Stark et al., 2015; Mickwitz et al., 2025) but remains a time-consuming task requiring human quality assurance. At high resolution and fully isolated peaks, discerning individual peaks and fitting peak positions no longer involves the deconvolution of signal and becomes trivial (e.g., Orbitool(Cai et al., 2021)). Second, the retrieval of peak intensities of peaks on the shoulder of stronger peaks is affected by the uncertainty in peak shape and noise from the neighbour peak.(Cubison and Jimenez, 2015) While there is general agreement that a higher mass resolution is welcome, exactly how much mass resolution is sufficient for atmospheric measurements is still the subject of debate.

This paper focuses on the influence of mass spectrometer resolution and data analysis on the obtained mass spectra in atmospheric conditions. The other factors influencing the variation in the results are not explored systematically in this comparison. Three instruments, including one MION-Orbitrap, one MION-ToF and one Eisele-ToF mass spectrometers were simultaneously operated at Hyytiälä forest station using nitrate (NO_3^-) as reagent ions. The detected peaks are compared between the instruments and two peak lists. One peak list has been previously compiled for Hyytiälä using a ToF instrument. The second list is compiled from Orbitrap measurement data.

2 Methods

Measurements were conducted at SMEAR II (Station for Measuring Ecosystem – Atmosphere Relations) at Hyytiälä forest station, located in Juupajoki in Southern Finland. The forest is surrounded and dominated by pine trees and all instruments were operated in a temperature-controlled container(Huang et al., 2021). The instruments deployed were one MION-Orbitrap mass spectrometer (Q Exactive Plus Orbitrap MS, Thermo Fischer Scientific Inc, mass resolution of 280 000 at $m/z=200$) and two atmospheric pressure interference time-of-flight (H-ToF and L-ToF, with mass resolution 2500 and 7500 respectively) mass spectrometers. Orbitrap and L-ToF with resolution 7500 were equipped with a MION inlet(Rissanen et al., 2019) and H-ToF with resolution 2500 was equipped with Eisele inlet(Jokinen et al., 2012).

The MION-Orbitrap and MION-ToF were located on ground level, and the Eisele-ToF at an altitude of 35 m (which is located above the canopy) in the same area. All instruments operated with NO_3^- as the reagent ion, and we assume all of them measured the same sample air due to their close location. Differences that do arise are attributed to the internal parameters of each of the instruments.

The data used here are from 15th of June 2023 to 25th of August 2023. Calibration factors for all the instruments were obtained using gaseous sulfuric acid following the process described in Kürten et al (Kürten et al., 2012).The calibration factors obtained were used to calculate the concentration of all identified compounds by the three instruments. The calibration factors for each of the instruments are listed in Table 1. Mass dependent relative transmission calibration factors for all instruments were obtained for each compound using the process described in Heinritzi et al (Heinritzi et al., 2016). The transmission calibration factor for the Eisele-ToF was deemed unreliable and not applied(Righi et al., 2026).

MION-Orbitrap sampled through a stainless-steel tube (1.2 m length, 22 mm inner diameter, 1 m above ground). The instrument inlet flow rate was 18 L min^{-1} and was connected to the MION inlet. Chemical ionization was employed with



diethylammonium and nitrate. Reagents were in glass vials; through these vials dry clean air was passed and extracted through
100 1/16" stainless steel tubing with a flow of 5 mL min⁻¹ into the MION inlet. The same type of tubing was used for purge flow.
The x-ray flush and exhaust both had 1/16-inch PTFE tubing, and a flow rate 50 mL min⁻¹. The voltage for the ion source was
-2000 V for the accelerator and -300 V for the deflector.

The Orbitrap Q Exactive (Thermo Fisher Scientific) had a mass resolving power 280 000 at 200 m/z. To improve the
sensitivity of the MION-Orbitrap, measurements were conducted in a full mass range mode (50-750 m/z) and an isolated mass
105 range mode (200-750 m/z). In the isolated mass range, the reagent ions were excluded, which improved the sensitivity to organic
species with low concentrations (Yuan et al., 2026). Sampling was performed in cycles of 1 hr which consisted of 12 min full
mass range (50-750 m/z, 6 min with each reagent) and 48 min isolated mass range (200-750 m/z), where the reagent was
switched every 8 minutes. Only NO₃⁻ chemical ionization mode data was used in this study.

Both API12 (MION-ToF) and API3 (Eisele-ToF) instruments were running continuously on site as part of the ACTRIS CiGas
110 measurements of condensable vapours. The MION-ToF instrument consisted of MION1 with NO₃⁻ and Br⁻ reagent ions and
an L-ToF mass spectrometer (ToFwerk). The resolution of the instrument was around 7500. The MION1 inlet was upgraded
so that it also had a purge flow like in MION2 inlet. The reagent feed flow rates for HNO₃ are 5.0 mlpm. The sample flow rate
was ~23.0 lpm with a stainless-steel inlet tube (length 90 cm, ID 22 mm).

The MION-ToF was deployed with 1-hour measurement cycle, which consists of 12 minutes of measurements of both chemical
115 ionization modes, 30 minutes of ambient ions measurements and 6 minutes of ion-filter zero calibration. In this study, only
NO₃⁻ chemical ionization mode data were used. MION-ToF measured in a temperature-controlled container at ground level
(inlet altitude ~1.5 m).

The Eisele-ToF consisted of a custom-build Eisele-type inlet and a H-ToF mass spectrometer (ToFwerk) with an inlet flow rate
of 10 lpm and HNO₃ flow rate of 5 mlpm. Chemical ionization is performed with NO₃⁻ only and 30-minute averages were used
120 for further analysis. The instrument dates to 2010 and has resolution of about 2500. The inlet tube is a stainless-steel tube
(length 70 cm, ID 19 mm). Eisele-ToF measurements took place in a temperature-controlled container at the same site but at
a higher altitude of 35 m, above the canopy level.

Orbitool software (Cai et al., 2021) and Igor Pro were used to analyse the MION-Orbitrap data. Data was exported using the
Orbitool software. Mass calibration of the data was performed externally on the Igor Pro platform. Because of a change in
125 calibration in the instrument data between 10.8.2023-13.8.2023 and 14.8.2023-19.8.2023 were handled and calibrated
separately. Additionally, the bias in intensities introduced from averaging Orbitrap data of non-continuously detected
compounds were corrected for. The correction factor was determined from the ratio of the measured abundance and theoretical
abundance of isotopic peaks. (Cai et al., 2022) This calculated ratio was plotted as a function of the normalized signal of isotopic
peaks (Figure S1). As measurements were done in an isolated mass range, where reagent signals had been excluded, the
130 intensities in the isolated mode were scaled down to the full mass range intensities during data analysis for accurate
concentration calculations (Yuan et al., 2026).



The initial Orbitrap peak list is built with a program written in Igor Pro, where several possible formulas are generated for each peak based on the mass. The formulas are then filtered based on the double bond equivalence (DBE), intensities of isotopic peaks and tolerance. Ions with negative and fractional DBEs are excluded as they are chemically unfavourable. If there are several formula suggestions for a certain peak, the isotopic distributions can also be used for filtering. If one formula has better agreement with isotopic distribution and abundance, it will be chosen as the formula for the peak in question. The generated peak list was further enhanced by manually adding formulas based on patterns in the mass defect plot. The peak list for Eisele-ToF was built with Tofware (Stark et al., 2015)(version 3.3.0) developed by Tofwerk on Igor Pro platform. The built-in ‘add peaks by threshold’ option in Tofware was used (Figure S3). The maximum number of peaks per nominal mass m/Q was set to 8 (Figure S8). A significant user bias arises when building the peak list from using the inbuilt composition finder in Tofware (Figure S2). Multiple suggestions are given for each m/z , and the user must check the isotopes, plot and timeseries at each m/z to determine the identification of the peak (Fig S4, S6 and S7). If the time series was not continuous for the compound, it was interpreted that that peak was not detected and was removed. The composition finder gives multiple suggestions for each peak determining the correct identification becomes challenging and careful verification is required. These steps can cause multiple biases and hence this automated list of ToF was not used for the comparison. Instead, the Orbitrap peak list is transferred to Tofware to generate a peak list for both the ToFs. To evaluate its comparability, the Orbitrap list was compared to an established list in Hyytiälä (Huang et al., 2021). The established list was based on measurements conducted with MION-ToF in Hyytiälä.

Table 1: Summary of the specifics of the three instruments

	MION-Orbitrap	MION-ToF	Eisele-ToF
Mass Resolution	280 000*	7 500	2 500
Inlet	MION 2	MION 1	Eisele
Reagent	NO ₃ ⁻ / DEA	NO ₃ ⁻ / Br ⁻	NO ₃ ⁻
Duty cycle (min h⁻¹)[†]	24	12	60
Sampling tube	stainless-steel tube (length 1.2 m, ID 22 mm)	stainless-steel tube (length 90 cm, ID 22mm)	stainless-steel tube (length 70 cm, ID 19mm)
Flow	18 L min ⁻¹	23 L min ⁻¹	10 L min ⁻¹
Data Analysis (Software)	Orbitool 2.5.3	Tofware 3.3.0	Tofware 3.3.0
Calibration coefficient (molecules cm⁻³)[‡]	3.0×10 ¹⁰	7.4×10 ⁹	5.7×10 ⁹

*At $m/z=200$

[†] Total duration of acquisition mode used for comparison within one hour

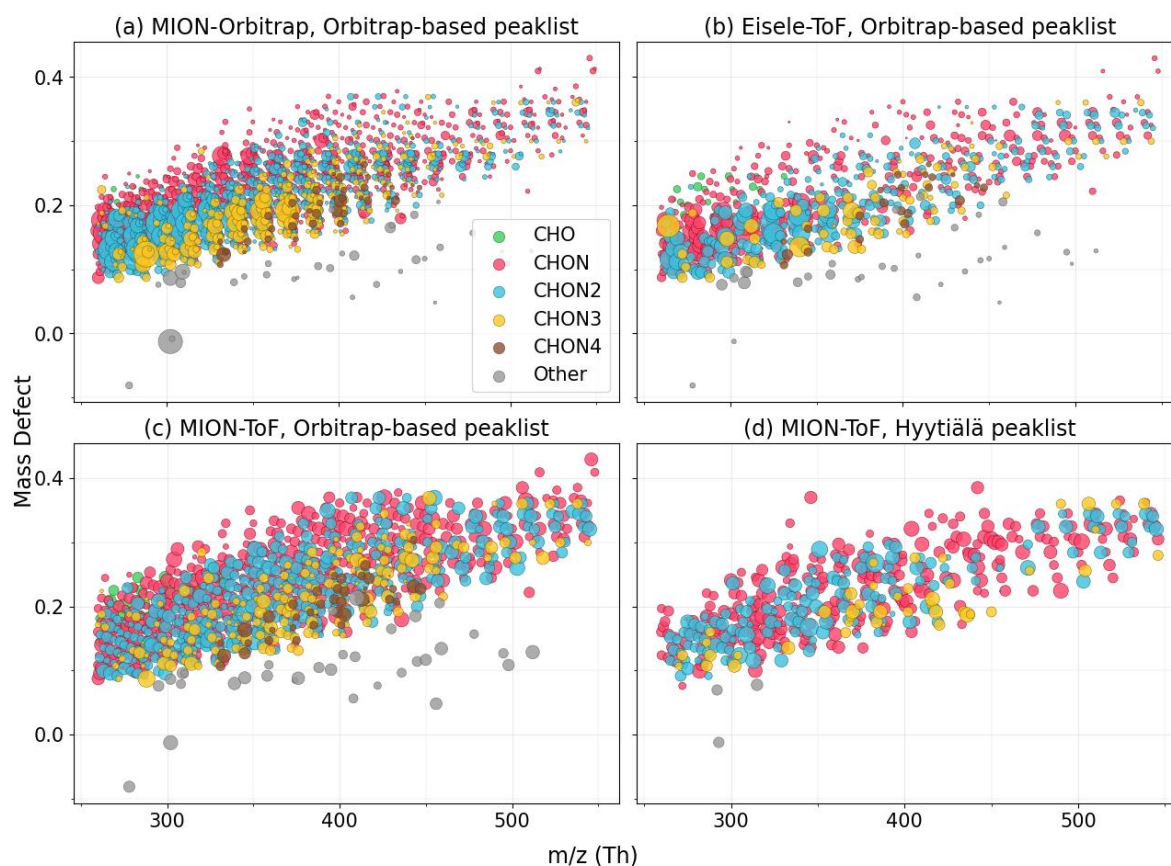
[‡] concentration = $\frac{I_{Analyte}}{I_{Reagent} + I_{Reagent\ dimer}} * calibration\ coefficient$



3 Results and Discussions

3.1 Peak List

155 From 24h averaged data 10.08.2023 13:30 - 11.08.2023 13:30 the MION-Orbitrap identified 1839 peaks in the 260-550 m/z mass range, of which 1333 were non-isotopic. This peak list was used as a basis for the MION-ToF and Eisele-ToF peak lists. For comparison, a previously established Hyytiälä peak list was used for the MION-ToF (Huang et al., 2021), with 483 peaks. The established Hyytiälä peak list is not as extensive as the Orbitrap peak list because of the limited mass resolution. The Eisele-ToF has primarily been used to monitor known species and therefore does not have an established peak list. Therefore, 160 Eisele-ToF data is only analysed using the Orbitrap peak list while the MION-ToF data has been analysed with both lists.



165 **Figure 1: Oxygen based Kendrick mass defect plots 260-550 m/z for a) MION-Orbitrap b) for Eisele-ToF, where the Orbitrap peak list is used for peak identification, c) for MION-ToF, where the Orbitrap peak list is used for peak identification and d) MION-ToF, where the established Hyytiälä list is used for peak identification. The diameter of the marker represents the intensity of the peak. Only peaks with identified composition are shown.**

Figure 1 shows the identified compounds by all three instruments. Figures 1a, 1b and 1c use the Orbitrap peak list while 1d uses the established Hyytiälä peak list. The number of non-isotopic compounds identified, referring to compounds to which a



molecular formula was assigned, in the 260-550 m/z mass range was 1333 for the Orbitrap. The MION-ToF identified 1327 peaks with the Orbitrap list and 483 peaks with the established Hyytiälä list. The Eisele-ToF identified 748 peaks with the Orbitrap list.

The most significant differences in the two peak lists (Figure 1c and 1d) are the number of peaks and the type of ions. Note that unidentified peaks are not shown in Figure 1. In Figure S4 and S5, compounds that were detected but not identified with composition are shown for each ToF instruments. At low masses, the MION-Orbitrap detects more peaks than the MION-ToF.

For both the ToFs, low concentration compounds are difficult to identify as they are close to the noise or hidden beneath higher intensity peaks. A notable difference in the Orbitrap and established Hyytiälä peak list is the number of species with $N \geq 2$, as can be seen in Table 2. The Orbitrap peak list can be used for building a comprehensive peak list to avoid user biases in species identification that arise from peak fitting. The amount of time spent on building the peak list can also be reduced when building a peak list for a certain environment. The limitation is that even after transferring Orbitrap peak list to Tofware, each peak should be checked individually to avoid errors.

Table 2: Number of compounds detected by each instrument according to molecular group.

Molecular Group	MION-Orbitrap	MION-ToF (Orbitrap list)	MION-ToF (Established list)	Eisele-ToF (Orbitrap list)
$C_xH_yO_z^-$	38	38	-	22
$C_xH_yO_zN^-$	616	613	286	345
$C_xH_yO_zN_2^-$	404	402	151	254
$C_xH_yO_zN_3^-$	201	200	43	75
$C_xH_yO_zN_4^-$	41	41	-	19
Other	33	33	3	33
Total	1333	1327	483	748

The MION-Orbitrap detected a large band of compounds that none of the other instruments detected (Figure S2). After closer inspection, the compounds were determined to be contaminants and excluded from the comparison. Some contaminant peaks were identified to be PVCs, PFAs and siloxanes.

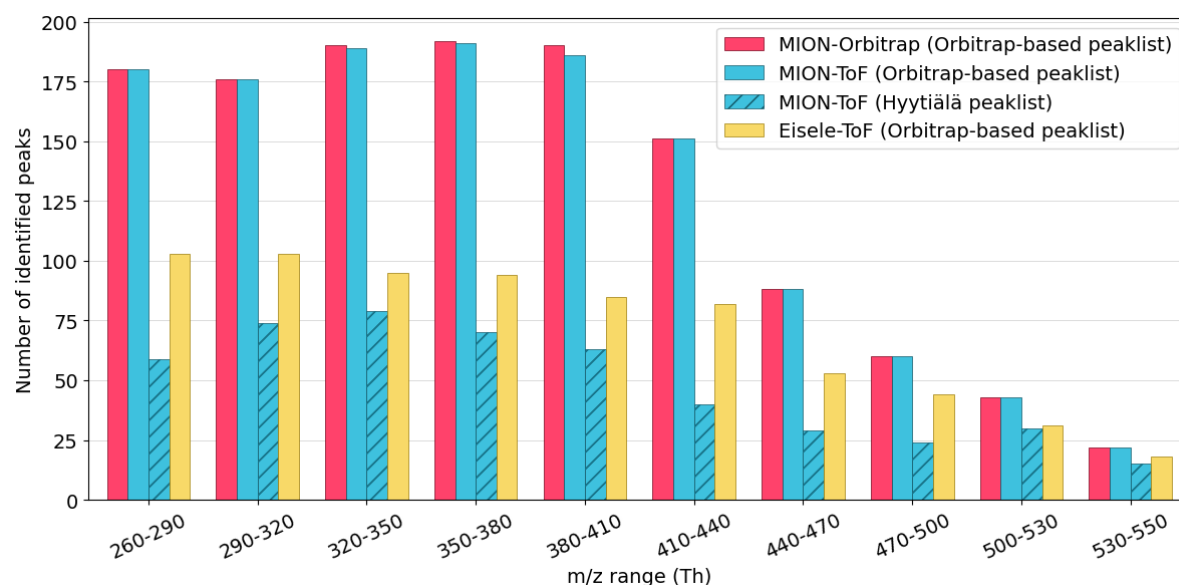


Figure 2: Peaks identified for MION-Orbitrap and ToF instruments per 30 m/z in the range 260-550 m/z during 10.08.2023 13:30 - 11.08.2023 13:30.

Figure 3 shows the number of identified and detected peaks in all three instruments at different mass ranges. When using the established Hyytiälä peak list with MION-ToF, the number of identified peaks is lower compared to MION-Orbitrap in all mass ranges. This is especially notable at lower masses, where there are many ions at a certain unit mass. The MION-ToF identifies essentially as many peaks as the MION-Orbitrap at all mass ranges when using the Orbitrap peak list. The Eisele-ToF detects a notably lower number of peaks even when using the Orbitrap peak list. The reason for this is the low resolution of the Eisele-ToF, which causes difficulties in clearly resolving peaks (Figure 2).

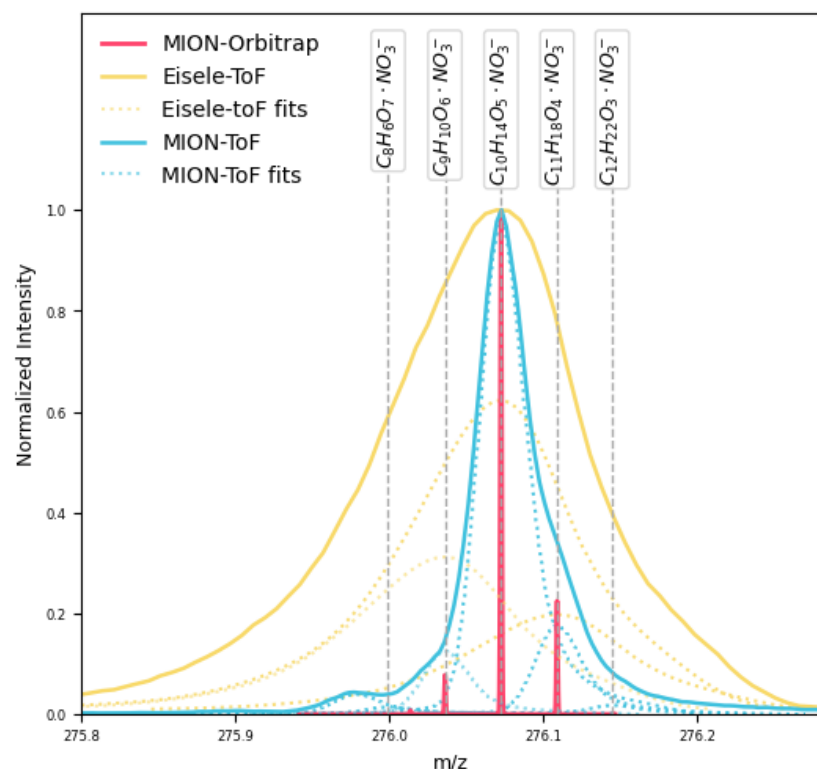


Figure 3: Comparison of fitted peaks at m/z 276 for all three instruments via the MION-Orbitrap automated list. The solid lines represent the measured intensity at m/z 276 and the dashed lines represents fitted isobaric peaks.

Figure 2 shows the assignments of compounds to fitted peaks and the difference in the peaks from different instruments using an example at m/z 276. It illustrates the practical benefit of a high resolution when identifying peaks. MION-Orbitrap can separate all the detected compounds $C_9H_{10}O_6 \cdot NO_3^-$, $C_{10}H_{14}O_5 \cdot NO_3^-$, $C_{11}H_{18}O_4 \cdot NO_3^-$, $C_{12}H_{22}O_3 \cdot NO_3^-$. A peak was detected at 276.01 m/z , but a formula could not be assigned; likely it is a contaminant. The intensity of a $C_{12}H_{22}O_3 \cdot NO_3^-$ is quite low for the Orbitrap yet the composition could be assigned. MION-ToF (blue) and Eisele-ToF (yellow) show an overlap between all peaks. Eisele-ToF has a greater overlap and can detect only three out of the five compounds, $C_9H_{10}O_6 \cdot NO_3^-$, $C_{10}H_{14}O_5 \cdot NO_3^-$, $C_{11}H_{18}O_4 \cdot NO_3^-$, detected by the other instrument. Similarly, MION-ToF can detect $C_8H_6O_7 \cdot NO_3^-$, which is present in the Orbitrap but below the LOD. Therefore, it is not accounted for in the peak list. The peak is not detected by Eisele-ToF. Another small possible peak is observed at around 275.98 m/z in the MION-ToF which is not detected by the other two instruments this peak was not identified by the peak lists used. This peak list mostly focused on compounds containing nitrate groups hence neglecting compounds beyond the composition listed in Table 2.

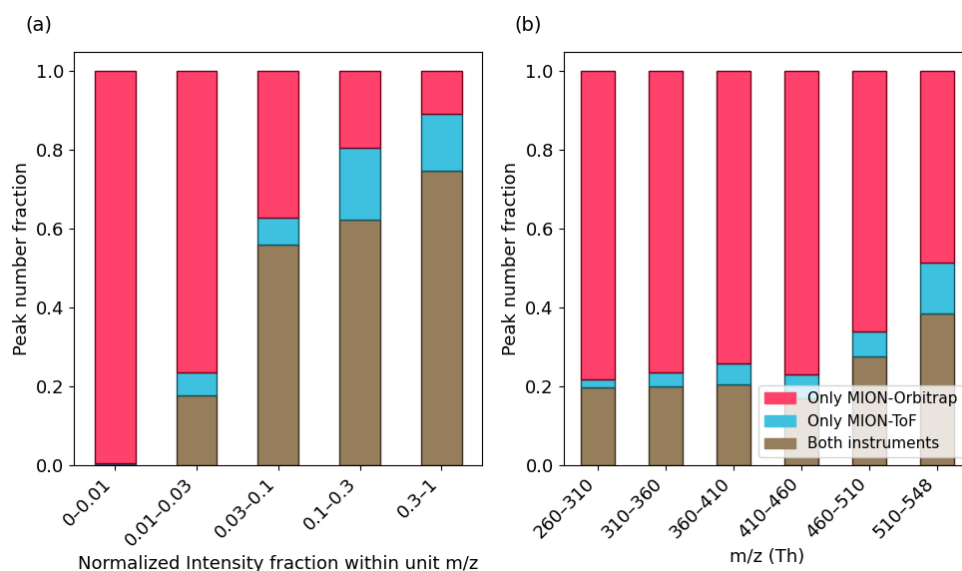


Figure 4: Fraction of peaks detected by either MION-Orbitrap, MION-ToF (Established Hyytiälä peak list) or both instruments as function of normalized signal intensity (a) and m/z (b).

The fraction of signal detected by two instruments is compared in Figure 4. The Orbitrap signals are based on the MION-Orbitrap list, and the MION-ToF signals are based on the established Hyytiälä list. The peak number fraction increases clearly for peaks that contribute more strongly to the total intensity within a unit mass range (Figure 4a). This suggests that mass resolution of ~ 7500 is generally sufficient to detect the dominant, high-intensity peaks, whereas peaks with low intensities are easily missed or obscured by peak overlap. The higher mass resolution of the Orbitrap allows it to separate and resolve shoulder peaks that would not be possible to observe with ToF. With ToFs, the shoulder peaks with low intensity appear in the tails of the adjects and are overlapped (Figure 2). Peaks with low intensity may not appear as a distinct peak in ToF especially with low resolution like the Eisele ToF (Figure 2, yellow peaks).

Comparing across m/z (Figure 4b), Orbitrap detects unique factors of peaks. MION-ToF with the established peak list identified 74 ions (Table S1) that were not present in the MION-Orbitrap peak list. The Orbitrap did not measure any ions at the same masses. The reason for this could be that the intensities are below the Orbitrap detection limit or that the established Hyytiälä list has been generated during a different time-period than the Orbitrap list. This means that the MION-ToF was able to fit ions which were not present according to the MION-Orbitrap.



3.2 Concentrations

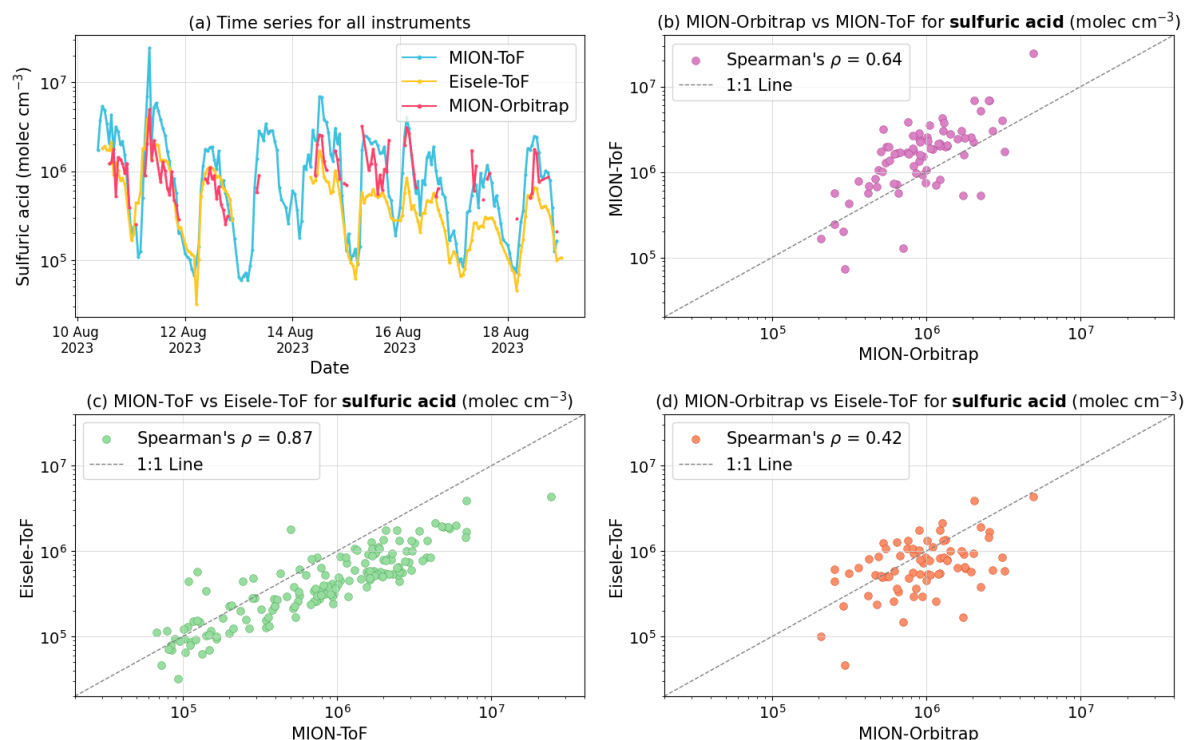


Figure 5: Spearman rank correlations and timeseries for H_2SO_4 (detected as HSO_4^- and $\text{H}_2\text{SO}_4\text{NO}_3^-$) from all three instruments for 10.08.2023-19.08.2023

230 Since all three instruments were calibrated using sulfuric acid, the measured sulfuric acid concentrations should be similar. This is confirmed in Figure 5, where the time series of sulfuric acid measured by these three instruments agree with each other for 1h averaged data for 10.08.2023-19.08.2023. We further quantify this agreement using the Spearman rank correlation. The ToFs correlate well with each other ($\rho=0.87$) but concentrations of the MION-ToF are on average 2.1 times those measured by the Eisele-ToF. The Orbitrap correlates well with the MION-ToF ($\rho=0.64$) but poorer with the Eisele-ToF ($\rho=0.42$). The

235 concentrations of the MION-Orbitrap are on average 1.4 times the Eisele-ToF and 0.56 times that of MION-ToF. The Eisele-ToF also sees lower concentrations of sulfuric acid during daytime. This is likely explained by the altitude difference of the instruments, where the Eisele-ToF is located above the canopy.(Zha et al., 2018) There are some gaps in the Orbitrap nighttime data due to instrument malfunctions that could not be addressed until the following mornings. The partial lack of nighttime data together with higher detection limit results in smaller variability in observed concentrations and explains the slightly lower

240 correlations. The uncertainty of the HSO_4^- calibration is 33 %(Kürten et al., 2012), which can further explain differences in



concentrations.

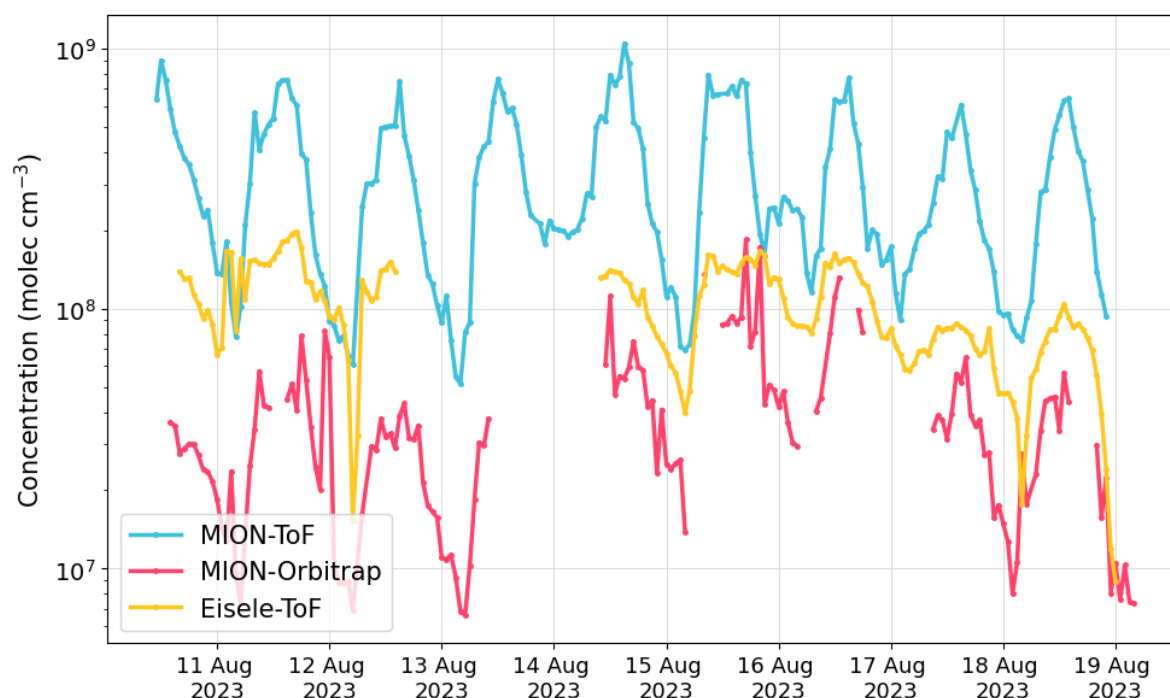


Figure 6: The total concentration of identified compounds in the 260-550 m/z mass range for all three instruments from 10.08.2023-19.08.2023. MION-ToF and Eisele-ToF use the Orbitrap peak list.

245 Figure 6 shows the total concentration of identified organic compounds determined by all three instruments, using the common Orbitrap-based peak list. The concentrations determined by MION-Orbitrap and MION-ToF were corrected for the mass-dependent transmission within the mass spectrometer and for inlet losses. For the Eisele-ToF, the calibration of mass-dependent transmission predicts extremely low transmission even in the monomer range (240-390 m/z), in contradiction to empirical intensities in this range, and in stark contrast to other ToF instruments (Righi et al., 2026). Therefore, the

250 characterization was deemed unreliable and not applied.

The concentration estimate by MION-ToF exceeds those of the other instruments by almost one order of magnitude and is high compared to previous measurements at Hyytiälä (Jokinen et al., 2022). While some of the differences might be expected, especially when comparing below- and above-canopy measurements (Zha et al., 2018) the proximity of the measurement sites for MION-ToF and MION-Orbitrap suggests a better agreement. The Eisele-ToF located in a tower above the canopy; this

255 difference can lead to an analysis bias as measurements concentration may not be comparable when boundary layer mixing is unstable. During daytime, the boundary layer is well mixed vertically and the concentrations above and below the canopy should be the similar (Zha et al., 2018).



260 The inter-instrument spread exceeds what can be explained from conventional calibration uncertainties alone. Previous studies that applied the sulfuric acid calibration factor to OOMs have similarly found Orbitrap CIMS to retrieve lower concentrations than ToF CIMS, albeit by a factor of just 1.9 (Liu et al., 2026).

265 The dependency of ion transmission on m/z is substantial for both ToF and Orbitrap. The transmission determined for MION-Orbitrap is comparable to that in Yuan et al 2025 (Figure S8). Monomers are transmitted about 5 times more efficiently than the reagent ion, both in MION-ToF (Righi et al., 2026) and MION-Orbitrap. When the ratio of abundances between instruments is compared as a function of m/z (Fig. S9), a near constant ratio of about 10 is present across the entire 250–450 m/z range. The ratio approaches unity at 550 m/z and at 159 m/z (sulfuric acid). It is not clear whether this distinctive m/z trend is due to limitations inherent to the current transmission calibration or stems from other processes.

270 Fragmentation has previously been suggested to explain lower retrieved abundances. If nitrate—analyte clusters de-cluster during ion transfer (into predominately nitrate and neutral analyte), the relative abundance of deprotonated analyte should be higher. The data are not strong evidence supporting this idea (Fig. S9, (Liu et al., 2026)). We consider fragmentation within the spectrometer to not be a conclusive explanation.

275 The reagent ion distribution is different between instruments. The ionization via $\text{HNO}_3\text{NO}_3^-$ is energetically different than via NO_3^- (Garmash et al., 2024); $\text{HNO}_3\text{NO}_3^-$ should be more selective. The ratios of reagent ion monomers to dimers were 0.53 for the Eisele-ToF, 0.58 for the MION-Orbitrap and 2.2 the MION-ToF. Newer generations of Orbitrap mass spectrometers appear to be less fragmenting, especially when the mild-trapping mode is enabled. (Wang et al., 2024; Makarov, 2026). While applying the sulfuric acid calibration factor to the whole compound matrix has its inherent limitations, it is also likely to lead to different biases in different ion-molecule-reactors.

280 Overall, while we are convinced that the mismatch is likely not rooted in the mass resolution of the systems, we cannot pinpoint the instrument parameters that cause the concentration disagreement, and we cannot positively identify the “true” concentrations. The discrepancy underlines the challenge of quantification and showcases the need for better and field-deployable calibration procedures.

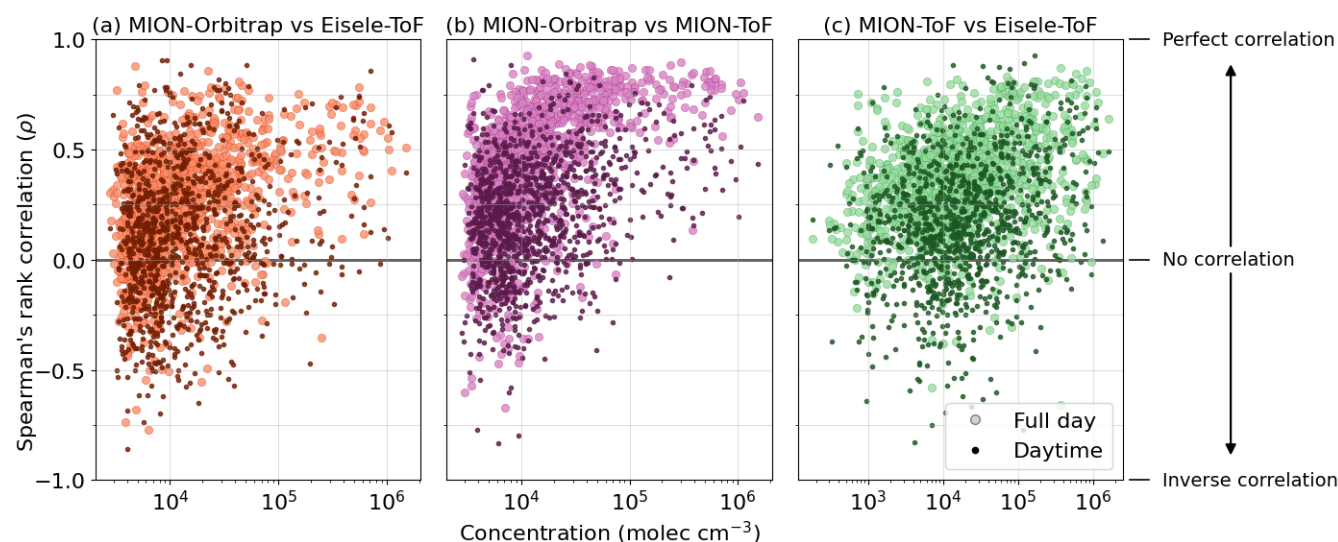


Figure 7: The Spearman's rank correlation coefficient as a function of the mean concentration of the identified organic species in all three instruments using the Orbitrap based peak lists. The data is separated in full day and daytime (10:00-16:00). In a) and b) the concentrations are from the MION-Orbitrap, in c) the concentrations are from the Eisele-ToF.

285 3.3 Correlation of time series

Figure 7 shows the inter-instrument correlation of compounds – a measure that is independent of calibration factors. Given that below-canopy (MION-Orbitrap, MION-ToF) and above-canopy (Eisele-ToF) level chemistry proceeds differently, the correlational analysis for both full-day and daytime-only data is presented. Compounds with higher concentrations ($>5 \times 10^5$ molecules cm^{-3}) correlate strongly between MION-Orbitrap and MION-ToF (average Spearman rank correlation $\rho = 0.74$), meaning that the measured species are likely the same and the peaks are detected well. Correlations in figures 7a and 7c are lower than in 7b. At the lower concentrations ($>5 \times 10^5$ molecules cm^{-3}) the correlations are lower and more dispersed. The Spearman rank correlation coefficients between the common compounds identified can be found in Table S1. MION-Orbitrap and MION-ToF were found to have on average the highest correlations (mean 0.43, median 0.46), while MION-Orbitrap and the Eisele-ToF had the lowest correlations (mean 0.23, median 0.25).

A somewhat worsening correlation of compound abundances measured in MION-Orbitrap and MION-ToF at low abundances can be expected: Generally, the comparison of signals with lower signal-to-noise ratio yields lower correlation coefficients. Close to the single-scan detection limit of MION-Orbitrap ($<1 \times 10^5$ molecules cm^{-3}) the correlation worsens, as ion intensities below a certain threshold are truncated and can only be partially recovered after averaging. Spatial variability likely only accounts for little of the dispersity, considering the proximity of the instruments. Overall, the correlation of MION-Orbitrap and MION-ToF at non-miniscule concentrations $> \sim 3 \times 10^4$ molecules cm^{-3} is what can be expected from two mass spectrometers of same ionization scheme but different implementation.



The resolution of the Eisele-ToF is lower than the other two instruments, hence, there is more influence of peak overlap. At the low resolution, weak peaks are not quantitatively resolved among stronger adjacent peaks. Eisele-ToF is located above the canopy compared to the MION instruments below canopy. The correlation between Eisele-ToF against MION-Orbitrap is as poor as to MION-ToF. This weak correlation can be attributed to both the different location and the weaker resolution of the Eisele-ToF. Further measurements at identical locations would help determine which factor is more dominant at influencing the correlation.

4 Conclusions

The aim was to observe similarities and differences in data collected by three mass spectrometers in a similar location with the same reagents but different mass analysers and inlets. For the experiment, an Orbitrap with MION inlet, and two ToFs with Eisele, and MION inlets were deployed at the SMEAR II station with all three instruments using NO_3^- as their reagent ion. Our results show that the high mass resolution of MION-Orbitrap allowed for better determination of the oxidized organic vapours, resulting in an accurate understanding of the composition of the organic vapours. Low resolutions of the atmospheric pressure interference time-of-flight (Api-ToF) hinder the ability to resolve the chemical composition of trace organic vapours. By using the Orbitrap peak list, the number of identified peaks could be significantly improved from the established Hyytiälä peak list. More compounds with $N_N \geq 2$ could be observed with the Orbitrap peak list. It was observed that at low masses, there are large differences in the number of detected peaks between the two peak lists, while at high masses, the peak detection is very similar.

In this comparison, the established peak list for MION-ToF was extended from 438 peaks to 1327 peaks using the Orbitrap list. Similarly, the lacking peak list for Eisele-ToF due to its low resolution was overcome by the Orbitrap list. The re-analysis of the peak list allowed identification of low-resolution peaks corresponding to same m/z as in the Orbitrap (Table S1). Despite this, when comparing overlaid mass spectra at unit masses, at low intensities the peaks are not separated leading to missed peak identification for Eisele ToF, hence it is able to identify less peaks compared to other two. The missed peak identification can lead to biased intensity assignment for compounds in low concentration areas. This indicates that compounds with lower signals can merge with neighbouring peaks. MION-ToF with the resolution of 7 000 can also be subject to this bias at low concentration peaks which compared to Orbitrap (Fig 2). Hence, the correlation when low concentrated organic compounds are examined are poor compared to high concentration organic compounds. This indicates the importance of higher mass resolution when measuring low concentration compounds.

Overall, the results demonstrate that high-resolution measurements provide a notable advantage for a comprehensive characterization of organic vapours, especially for low concentration species, where overlapping peaks make peak identification less reliable. Despite the improvements in peak identification, substantial differences remain in concentrations retrieved from the different instruments. The MION-ToF measured concentrations approximately one order of magnitude higher than the MION-Orbitrap. Our results show that no single instrument-specific process can explain the process. While



improved mass resolution reduced identification bias, achieving accurate concentration requires addressing calibrations
335 differences for each compound class.

Supplement link

https://helsinkifi-my.sharepoint.com/:w:/g/personal/koiralam_ad_helsinki_fi/IQBAn3nxaKNdSodgWpPU49iBAYgSEL0aeLZSfPs874HKCZA?e=6MyfKX

340 The data used in this manuscript are provided in the public data repository at <https://doi.org/10.5281/zenodo.22827596>.

Author contributions

RC, JK, HF and NS participated in conceptualization; AB, MKo, RC, HF, SH, LA, VK, RB, FS-O and YL participated in instrument maintenance during data collection; AB analysed MION-Orbitrap data; MKo analysed Eisele-ToF data; CL analysed MION-ToF data; CR conducted transmission experiments; AB and MKo wrote the original manuscript draft. All
345 authors have contributed to the final draft.

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