KARSA

Application Note: Rapid, Ultra sensitive Detection of Atmospheric Organonitrates

Harnessing Karsa's MION2 Orbitrap CIMS for real-time insights into oxidation chemistry

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Why Organonitrates Matter

Organonitrates regulate the NO_x budget, drive secondary organic aerosol formation, and act as reservoirs for long-range nitrogen transport. They influence climate-relevant particle growth and the oxidative capacity of the atmosphere. Measuring organonitrates at parts-per-quadrillion (ppq) to parts-per-trillion (ppt) levels is demanding because their presence in humid, complex air requires instruments with exceptional sensitivity, selectivity, and mass resolution. The Karsa MION2 Orbitrap system meets these demands with its ability to perform real-time, in-situ measurements, offering ultra-low detection limits and stable performance across a wide range of humidity.

Challenge: Detecting ppq–ppt levels of organonitrates in humid, complex air masses demands exceptional sensitivity, selectivity, and resolution.

Solution: Karsa MION2 Orbitrap enabling real-time, in situ detection with ultra-low limits and stable performance in any humidity.

Instrument Capabilities for Organonitrates

The MION2 system couples chemical ionization source with a high-resolution Orbitrap MS (Exploris, 120,000 Th/Th). The combination measures organonitrates in both positive and negative ion modes and can automatically switch chemical ionization methods in seconds. Atmospheric chemistry involves highly complex mixtures of volatile and semi-volatile organic compounds, many of which differ by just a few milli-Daltons. Traditional chemical ionization mass spectrometry (CIMS) methods, typically with 10,000–20,000 resolution, often fail to resolve isobaric or isotopically substituted compounds. This limitation severely hampers identification, quantification, and mechanistic interpretation of atmospheric oxidation processes.

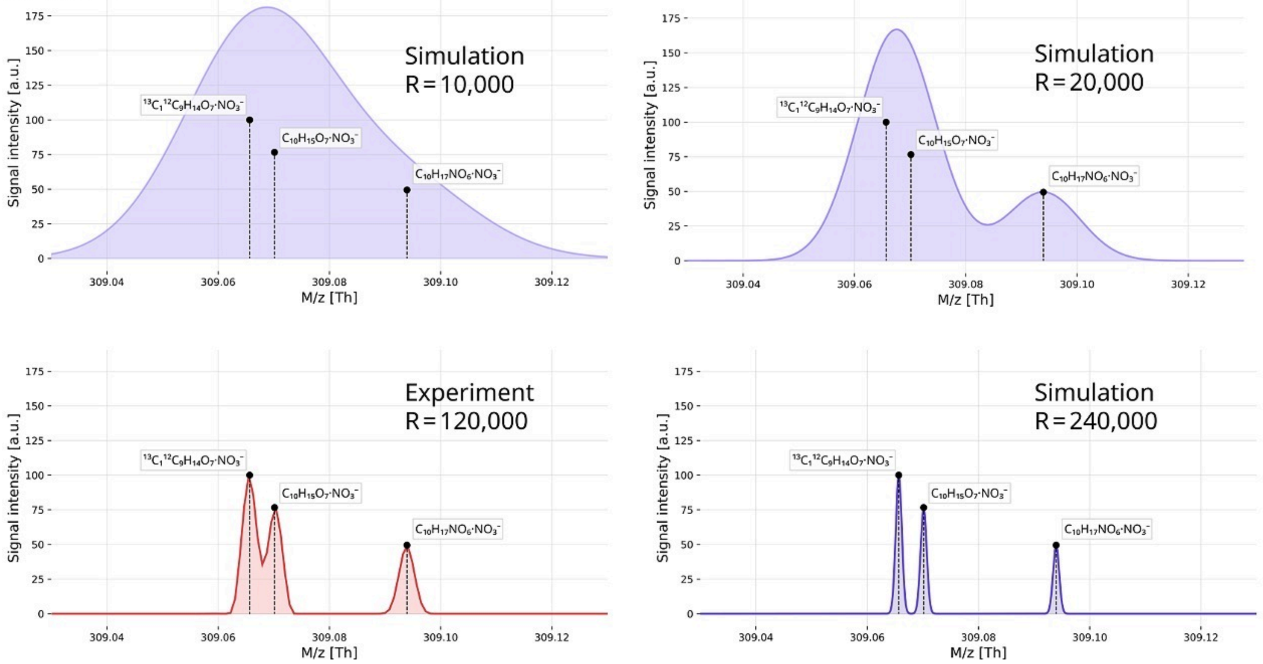


Figure 1. Simulated mass spectrum with resolutions of 10'000 (top left), 20'000 (top right) and the absolute positions of the identified molecules (black solid lines). With 10'000 resolution, deconvolution involves making assumptions on the strength and composition of molecules potentially contributing to the measured spectrum. The measured spectrum with a mass resolution of 120 000 (bottom left, red) and simulated for 240'000 (bottom right) both enable to clearly separate the molecules with one additional hydrogen atom ($C_{10}H_{15}O_7NO_3$) from the one with isotopic substitution ($^{13}C_1C_9H_{14}O_7NO_3$).

Reagent Ions and Ionization Modes

The MION2 Orbitrap system offers switching between multiple options for quasi-continuous real-time measurements, enabling targeted and un-targeted analysis of oxidation events. Some of the options are listed in the Table 1:

Mode	Reagent	Targets
Negative mode, ambient pressure	Nitrate (NO_3^-) bromide (Br^-)	high sensitivity for acidic species, halogenated species and oxygenated organic compounds
Positive mode, ambient pressure	Uronium ($CH_4N_2OH^+$)	moderately polar and alkaline species
Positive mode, low pressure	Fluoranthenium ($C_{16}H_{10}^+$)	weakly polar compounds

Table 1: Ionization modes, recommended reagent ions, and target molecules

Experimental setup: α-Pinene Nitration

In a flow tube experiment at Professor Matti Rissanen's laboratory at the University of Helsinki, we studied organonitrate products. These products were formed from the oxidation of α-pinene by ozone and nitration by NO_2.

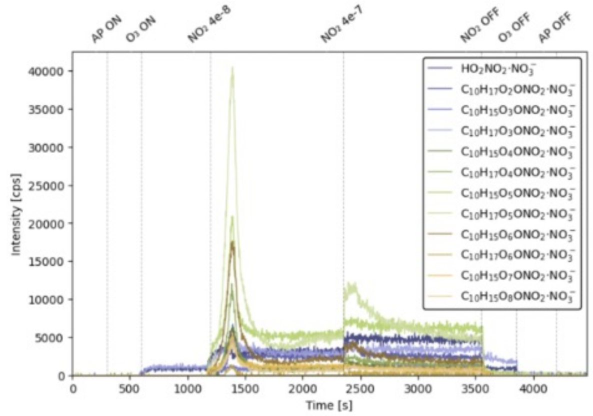
The experiment lasted for 1:15 hour as shown in Figure 2. The flow tube was configured for 9 seconds residence time with a 12 L/min flow of nitrogen N_2. After 250s, α-pinene vapors were introduced by bubbling nitrogen through a liquid reservoir. After 600s, Ozone was generated from synthetic air using UV light irradiation and introduce. After 1200s, the

NO_2 volume mixing ratio was set to $4x10^{-8}$, and after 2400 s, increased to $4x10^{-7}$, before being turned off at 3600s, followed by ozone off at 3800s and α-pinene off at 4200s. During these experiments, both nitrate and uronium chemical ionizations were employed.

Results

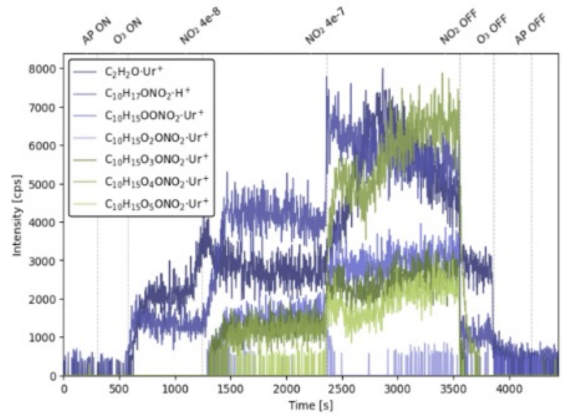
In Figure 2, we present the time series of the nitrate cluster of $C_{10_{10}}H_{15\text{-}17}O_{2\text{-}8}\,ONO_2{\cdot}NO_3^-$ and $C_{10_{10}}H_{15}O_{1\text{-}4}ONO_2{\cdot}Ur^+$ species. A clear correlation between $C_{10}H_{14}O_3$ concentration and NO_2 levels was observed.

a)



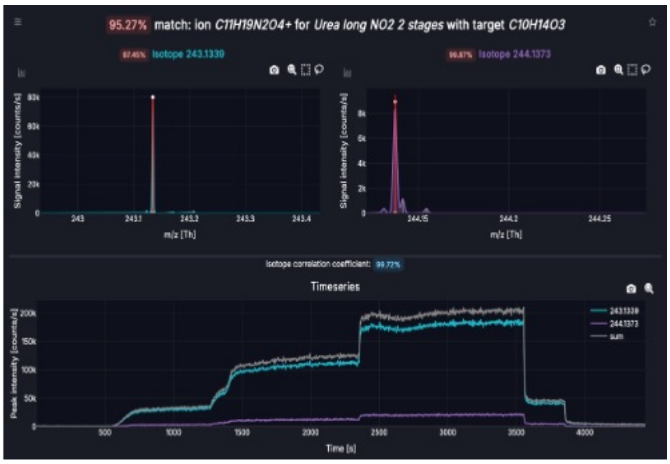
Time-series of nitrate-cluster ions with the general formula $C_{10}H_{15\text{–}17}O_{2\text{–}8}\,ONO_2{\cdot}NO_3^-$.
The individual traces are color-coded by the total number of oxygen atoms, fewer oxygens in cooler colors, more oxygens in warmer ones.

b)



Same compound class as panel a) measured during a different run in positive-ion mode with uronium reagent (Ur^+). These appear as either protonated or uronium-adduct ions and have the composition $C_{10}H_{17}\,ONO_2{\cdot}H_+$ and $C_{10}H_{15}O_{1\text{–}4}\,ONO_2{\cdot}Ur_+$.

c)



Concentration of $C_{10}H_{14}O_3$ tracks closely with the sequential NO_2 stages throughout the experiment, demonstrating a strong correlation.

Figure 2. Real-time detection of α-pinene–derived organic nitrates during flow-tube oxidation (residence time ≈ 9 s, 12 L min^{-1} total N_2 flow).

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We monitored ambient air in Helsinki for five days using MION2 Orbitrap multi-pressure CIMS configured to automatically switch between high-pressure ionizations (uronium in positive mode / nitrate in negative mode) and low-pressure ionization (fluoranthene in positive mode) without interrupting sampling. As shown in Figure 3, we detect the organonitrate $C_{10}H_{16}O_6N$ (i.e., $C_{10}H_{16}O_3NO_3$) at very low concentrations with a clear diurnal cycle.

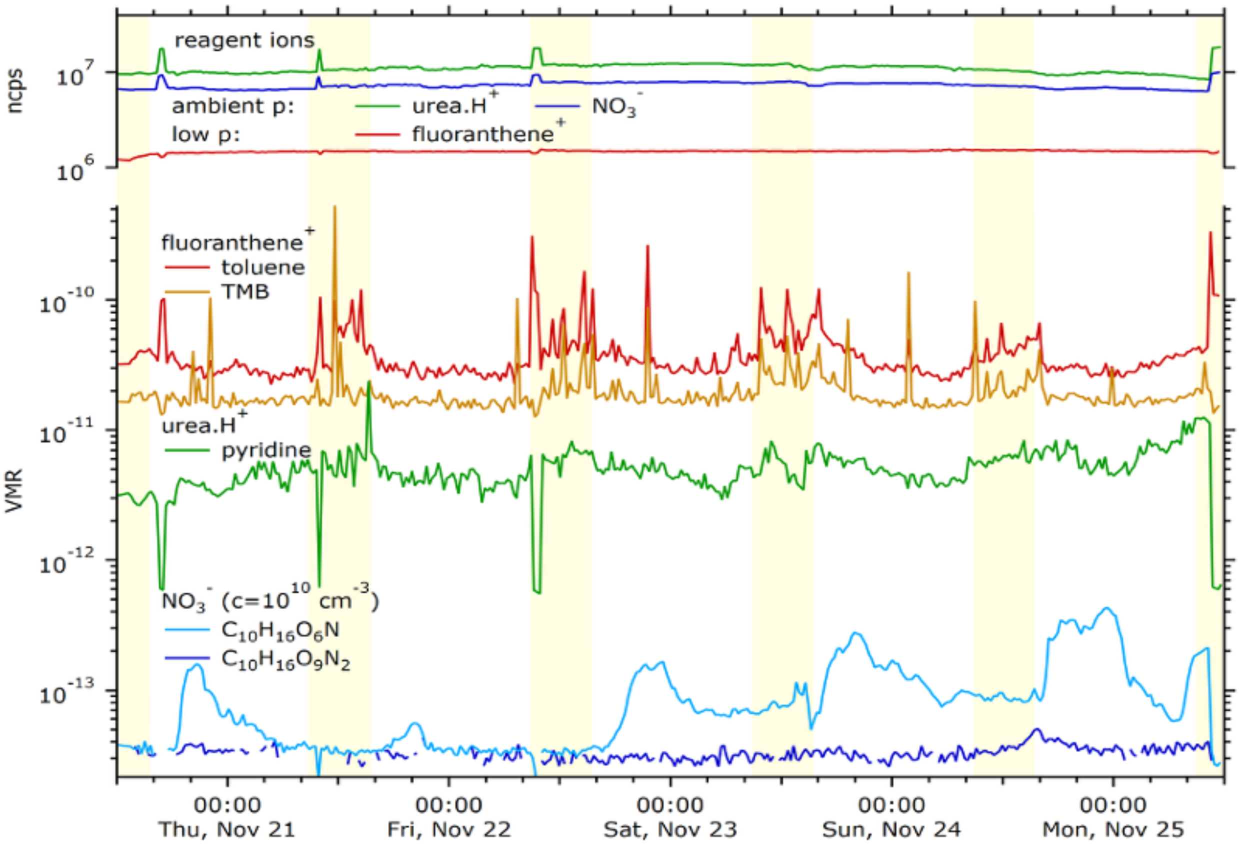

Figure 3. Five-day ambient measurements in Helsinki with the MION2 Orbitrap multi-pressure CIMS. The instrument auto-switches between high-pressure ionization (uronium/nitrate) and low-pressure ionization (fluoranthene) without interrupting sampling. VMR (Volume Mixing Ratio), 10^{-13}= 100 ppqv. Weather conditions in Helsinki were cold and humid, yet the signal remained robust.

Sensitivity and Detection Limits

- Sub-pptv detection for various oxygenated organics using uronium and nitrate ionization.
- Verbenone (m/z ≈150), an α-pinene oxidation product, showed detection limits in the single-digit ppqv range with a sensitivity of 2×10^4 cps/ppt
- Comparable performance observed for pyridine, dimethyl sulfoxide, dimethylformamide and many other functionalized molecules.

Humidity Independence

Humidity-independent detection is essential for ambient measurements. MION2 system maintains:

- ≤30% signal variation at 20-80% RH for key analytes and reagents.
- Automated sample dilution (1:10) to minimize humidity impact on Br^- reagent performance.
- Calibration factor variations remain <10–30% across typical environmental humidity ranges.

Conclusion

This study shows that the MION2 Orbitrap multi-pressure CIMS delivers successful organonitrate detection where it matters: ppq–ppt levels, real air, real time. Automatic switching between uronium$^+$/nitrate$^-$ (high-pressure) and fluoranthene$^+$ (low-pressure) maintains continuous coverage and high selectivity. We resolve organonitrate signals in both controlled α-pinene experiments and under cold Helsinki ambient conditions. The system demonstrated robust performance across a range of humidity and a clear diurnal pattern. The results show that MION2 Orbitrap CIMS is a reliable platform for both lab and field studies of atmospheric oxidation chemistry.

Acknowledgments

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