

## Metal Ionization in Gas Phase Mass Spectrometry (MIG MS): A New Tool for Analysis of Volatile Organic Compounds

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### Summary

In the current work, we proposed the ions of coinage metals belonging to 11 group – Cu<sup>+</sup>, Ag<sup>+</sup> and Au<sup>+</sup> as chemical ionization agents for mass spectrometry (MS) analysis of volatile organic compounds (VOCs). Among these ions, especially Au<sup>+</sup> attracts considerable interest due to its rather high reactivity associated with relativistic effects and ability to activate C-H and C-C bonds.

The metal ions were generated by laser ablation of a metal nanolayer with the UV laser (355 nm) in a commercial dual sub-atmospheric pressure MALDI/ESI interface attached on ultra-high resolving power mass spectrometer with orbital trap. VOCs belonging to different chemical classes (alkenes, alcohols, aldehydes, ketones, aromatic compounds, carboxylic acids, ethers, and organosulfur compounds) were infused via the ESI capillary and quickly formed ion-molecular complexes in the ion source with general formula [M+VOC+H<sub>2</sub>O]<sup>+</sup> and [M+2VOC]<sup>+</sup> [1]. Utilization of Ag<sup>+</sup> ions yielded also intense signal of [M+VOC]<sup>+</sup>. Au<sup>+</sup> ions being the most reactive among the studied metal ions interacted with VOCs in a way that was more intricate and often resulted in formation of side products through hydride abstraction, loss of water or cleavage of carbon chain. These side reactions complicated the spectra, but on the other hand, they also allowed detecting saturated hydrocarbons, which did not produce any signals with Ag<sup>+</sup> and Cu<sup>+</sup>. The detection limits of the selected compounds in the gas were in the range of 0.1 – 1.4 nmol/L [2].

The developed technique brings novel utilization of the dual MALDI/ESI interface for studying gas-phase chemistry of metals and expands the portfolio of currently available methods for the analysis of VOCs.

### Acknowledgement

We gratefully acknowledge the financial support of the Czech Science Foundation (projects 19-20927Y, 21-12262S and 24-10924S).

### References

- [1] A. Bednařík, V. Prysiachnyi, J. Preisler, Metal Ionization in Sub-atmospheric Pressure MALDI Interface: A New Tool for Mass Spectrometry of Volatile Organic Compounds, *Anal. Chem.* 93 (2021) 9445–9453.
- [2] M. Koktavá, V. Prysiachnyi, J. Preisler, A. Bednařík, Comparison of Cu<sup>+</sup>, Ag<sup>+</sup>, and Au<sup>+</sup> Ions as Ionization Agents of Volatile Organic Compounds at Subatmospheric Pressure, *J. Am. Soc. Mass Spectrom.* 35 (2024) 307–316.