



Selective-Reagent-Ionization Mass Spectrometry: New Prospects for Atmospheric Research

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Proton-Transfer-Reaction Mass Spectrometry (PTR-MS), which was introduced to the scientific community in the 1990's, has quickly evolved into a well-established technology for atmospheric research and environmental chemistry [1]. Advantages of PTR-MS are i) high sensitivities of several hundred cps/ppbv, ii) detection limits at or below the pptv level, iii) direct injection sampling (i.e. no sample preparation), iv) response times in the 100 ms regime and v) online quantification. However, one drawback is a somehow limited selectivity, as in case of quadrupole mass filter based instruments only information about nominal m/z are available. In Time-Of-Flight (TOF) mass analyzer based instruments selectivity is drastically increased by a high mass resolution of up to 8000 $m/\Delta m$, but e.g. isomers still cannot be separated.

In 2009 we introduced an advanced version of PTR-MS, which permits switching the reagent ions from H_3O^+ to NO^+ and O_2^+ , respectively [2]. This novel type of instrumentation was called Selective-Reagent-Ionization Mass Spectrometry (SRI-MS) and has been successfully used to separate isomers, e.g. the biogenic compounds isoprene and 2-methyl-3-buten-2-ol as shown by Karl *et al.* [3]. Switching the reagent ions dramatically increases selectivity and thus applicability of SRI-MS in atmospheric research.

Here we report on the latest results utilizing an even more advanced embodiment of SRI-MS enabling the use of the additional reagent ions Kr^+ and Xe^+ [4]. With this technology important atmospheric compounds, such as CO_2 , CO , CH_4 , O_2 , etc. can be quantified and selectivity is increased even further. We present comparison data between diesel and gasoline car exhaust gases and quantitative data on indoor air for these compounds, which are not detectable with classical PTR-MS. Additionally, we show very recent examples of isomers which cannot be separated with PTR-MS but can clearly be distinguished with SRI-MS.

Finally, we give an overview of ongoing SRI-MS developments, which include TOF based instruments with increased sensitivity of one order of magnitude (i.e. in the 10^3 cps/ppbv regime) by means of using a quadrupole ion guide between the drift tube and the TOF analyzer. It is expected that these developments will have a serious impact in atmospheric research, because increased sensitivity implies reduced measurement times and thus, e.g. even more accurate flux measurements.

References

- [1] J. de Gouw, C. Warneke, T. Karl, G. Eerdeken, C. van der Veen, R. Fall, *Mass Spectrometry Reviews*, 26 (2007), 223-257.
- [2] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, J. Herbig, L. Märk, R. Schottkowsky, H. Seehauser, P. Sulzer, T.D. Märk, *International Journal of Mass Spectrometry*, 286 (2009), 32 - 38.
- [3] T. Karl, A. Hansel, L. Cappellin, L. Kaser, I. Herdinger-Blatt, W. Jud, *Atmospheric Chemistry and Physics*, 12/24 (2012), 11877-11884.
- [4] P. Sulzer, A. Edtbauer, E. Hartungen, S. Juerschik, A. Jordan, G. Hanel, S. Feil, S. Jaksch, L. Märk, T.D. Märk, *International Journal of Mass Spectrometry*, 321 (2012), 66-70.

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