

# Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) with Real-Time Nosespace Air Sampling - Air Sampling - an Essential Tool for Food and Flavor Analysis



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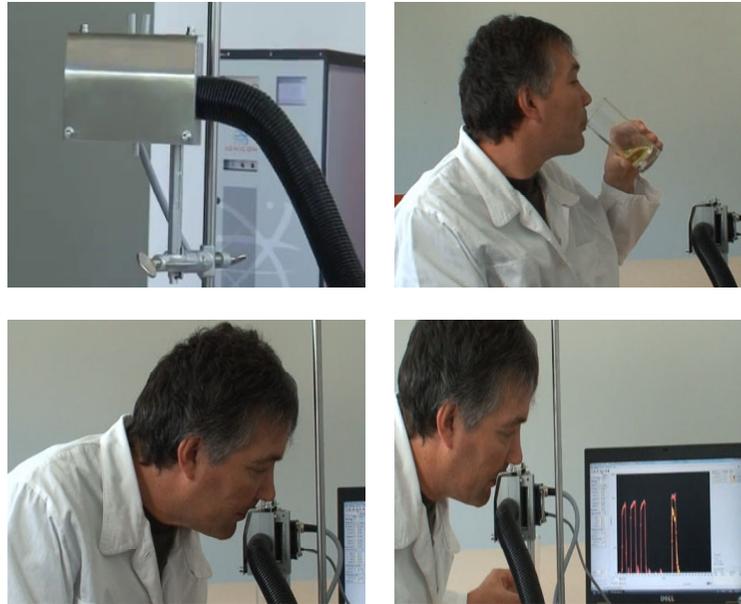
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## Abstract

Since many years **Proton-Transfer-Reaction - Mass Spectrometry (PTR-MS)** is a well established technology for real-time trace gas analysis (see [1] and recently [2]). In short, in a hollow cathode ion source reagent ions are produced at very high purity levels (up to 99.5%). Without the need of a mass filter the  $H_3O^+$  is introduced into the adjacent drift tube where the proton transfer to all molecules which possess a higher proton affinity than water takes place. Finally either a quadrupole or a time-of-flight mass spectrometer analyzes the product ions according to their masses and yields. This ionization process produces low fragmentation and is very efficient, permitting real-time quantification and extremely low detection limits.

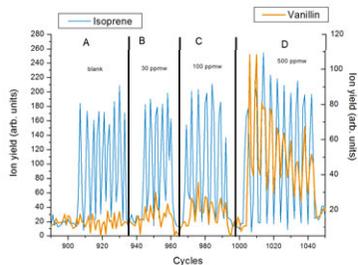
Here we report on the latest application of PTR-MS in food and flavor science. Several improvements during many years offer the capability of on-line monitoring of sticky aroma compounds namely i) the improvement of the detection limit that now allows measuring trace gas compounds down to concentrations in the ppqv (parts-per-quadrillion) region with a typical response time well below 100 ms and ii) the coupling of our sophisticated PTR source to two different types of time-of-flight (TOF) mass analyzers, iii) the possibility to switch between  $H_3O^+$ ,  $NO^+$  and  $O_2^+$  as reagent ions [3] and iv) our novel heated Nosespace Air Sampling Extension (N.A.S.E.).



**N. A. S. E.**  
NOSESPLACE AIR SAMPLING EXTENSION

"Sticky" compounds are very common in flavor and food science but challenging for analysis since they tend to condensate in the inlet lines of trace gas analyzers which reduces the sensitivity, extends the response time and leads to memory effects. Our recently developed **Nosespace Air Sampling Extension (N.A.S.E.)** overcomes these difficulties, since the whole line to the drift tube can be heated to 120 °C without any cold spots. So sticky compounds enter the drift tube without any condensation in the inlet line.

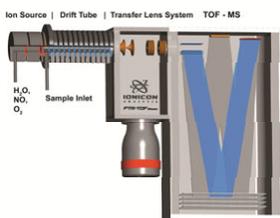
The photo sequence on the left shows a typical application of this new device. The first picture shows that the N.A.S.E. is well designed for measurements with different panelists since the parts where the person has to breath into are removable. In the second picture the panelist takes a sip of a vanillin-water mixture and after swallowing starts breathing into the N.A.S.E. In the fourth picture the immediate (within a ms time scale) response of the instrument is visible (vanillin signal in yellow).



## Vanillin

**left**  
For these measurements a PTR-TOF 8000 (for a schematic view of the instrument see picture below) was coupled to the N.A.S.E. device described above. Isoprene (a product of human metabolism and therefore a good marker for breath cycles) and **vanillin** (example for a sticky compound in food science) were measured as a function of time. In section A human breath without vanillin was measured (only the breath cycles indicated by isoprene are visible), whereas in section B the test person had taken a sip of a drink containing 30 ppmw vanillin dissolved in water. Section C shows the signal response after taking a sip of a 100 ppmw solution, whereas in section D the panelist had drunk a 500 ppmw vanillin mixture before.

In conclusion this experiment shows an immediate signal response. Moreover the different concentrations can be distinguished nicely. Consequently the N.A.S.E. enables real-time monitoring also for very sticky compounds

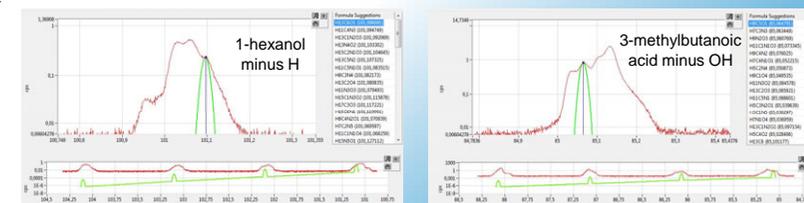
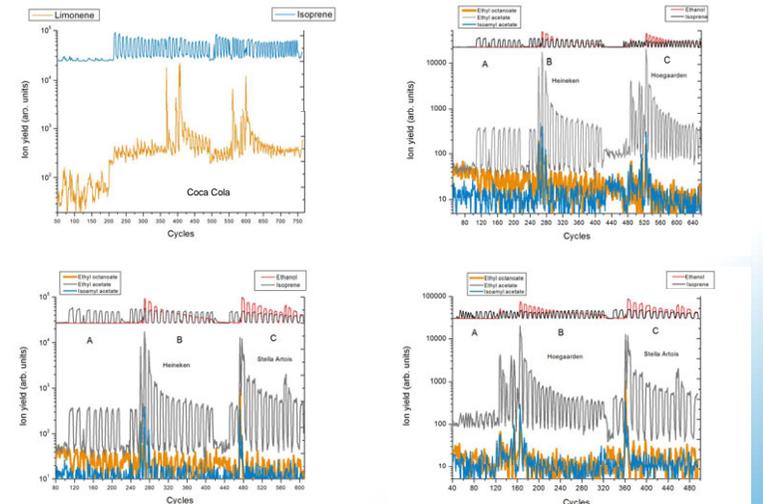


## Beverages

**right**  
Another application of the N.A.S.E. is the analysis of three different kinds of **beer** regarding their aromatic compounds as well as the aromatic characterization of **Coca Cola**<sup>®</sup>. The measurement setup was like in the photo sequence illustrated above. In all the figures on the right section A is showing the plain breath of the panelist which is indicated through the lack of ethanol at the top of each figure. Section B and C are showing the ion yields for different beer brands after the panelist had swallowed and started breathing. With the help of PTR-MS combined with the N.A.S.E. it is possible to see differences between the beers, e.g. Stella Artois<sup>®</sup> seems to have the highest ethyl octanoate content of all three types. Moreover the results show that the dominant aroma compound of Coca Cola<sup>®</sup> is limonene.

### bottom right

The two figures on the right (please note the logarithmic scale) were obtained from measurements utilizing the SRI functionality (i.e.  $NO^+$  as a reagent ion). Due to the high mass resolution of the PTR-TOF 8000 used the chemical composition of each of the multitude of peaks (that is present at nearly every nominal mass due to the high number of aroma compounds in beer) can be approximated and the compounds be quantified individually.



### References

- [1] W. Lindinger, A. Hansel, A. Jordan; Int. J. of Mass Spectrom. and Ion Processes, 173/3 (1998) 191-241
- [2] F. Biasioli, Ch. Yeretizian, T.D. Märk, J. Dewulf, H. van Langenhove, Trends Anal. Chem., 30 (7) (2011), 1003-1017.
- [3] A. Jordan, S. Haidacher, G. Hanel, E. Hartungen, L. Märk, H. Seehauser, R. Schottkowsky, P. Sulzer and T.D. Märk, Int.J. Mass Spectrom., 286 (2009) 32-38.