# REAL-TIME PTR/MS AND ELECTRONIC NOSE SIMULTANEOUS MEASUREMENTS ON SAME SAMPLES

Luigi Quercia[1,2], Rosamaria Capuano[1], Iuliia Khomenko[3], Alexandro Catini[1], Eugenio Martinelli[1], Roberto Paolesse[4], Franco Biasioli[3], Corrado Di Natale[1]

[1] *Department of Electronic Engineering, Università di Roma Tor Vergata, Italy*
[2] *ENEA, Casaccia Research Centre, S. Maria di Galeria, Roma, Italy*
[3] *Department of Food Quality and Nutrition, Fondazione E. Mach, S. Michele all'Adige (TN), Italy*
[1] *Department of Chemical Science and Technology, Università di Roma Tor Vergata, Italy*

The analysis of volatile organic compounds (VOCs) is of paramount importance for the characterization of diverse kinds of samples. The applications range from those more traditional such as food quality and environmental control to emerging fields such as metabolomics.

The unparalleled properties of gas chromatrography coupled with mass spectrometer (GC-MS) still makes this technique the gold standard for VOCs analysis. However, GC-MS is a time consuming technique that requires long sample collection and analysis time.

In applications aimed at screening large sets of samples and at following the time evolution of processes there is the necessity to replace GC-MS with more rapid and simpler methods.

Arrays of partially selective gas sensors, also known as electronics noses, have been proposed for this scope. However, in spite of several positive achieved results in many different fields [1], their intrinsic lack of selectivity makes the interpretation of the results rather difficult. For this reason, electronic noses are usually complemented by GC-MS in order to identify the relevant VOCs for each application. However, being the two instruments based on different methodologies their results are hardly comparable.

Direct iniection mass specrtometers are good candidates for the real time analysis of VOC mixtures. Among these techniques, Proton Transfer Reaction - Mass Spectrometer (PTR-MS) is one of the most promising in terms of rapidity and sensitivity. Furthermore the moderate molecular fragmentation results in a simplified interpretation of the results [2].

In this paper, we show that PTR-MS and electronic nose can be connected in series to measure the same samples at the same time.

For this scope, an electronic nose made of 12 porphyrinoids coated Quartz Microbalances [3] has been connected in series to a PTR-TOF-MS, This is an improved version of the PTR-MS instrument where the usual quadrupole detector is replaced with a time of flight mass analyzer.

The hyphenated instruments have been tested in an experiment aimed at the identification of tomato pastes after different storage procedures. Three sets of 10 replicas have been measured to evaluate the tomato sauce headspace: a) after one week storage at 8°C once inoculated with Penicilium spp. Fungi; b) after one week storage at 8°C and treated with a natural antifungine once inoculated with Penicilium spp.; c) fresh tomato sauce.

Samples have been placed in an automated sampler, in order to condition the samples to a standard temperature and perform the measurement with the same carrier flow.

Results show that the two instruments can operate simultaneously on the same sample. This feature allows to measure the exact composition of the sample analyzed by the electronic nose. This preliminary result removes the serendipitous character of electronic nose applications providing an optimum tool for a more accurate and effective design and test of sensors for selected applications.

**References**

1. F. Röck et al. Chem. Rev. 108 (2008) 705
2. F. Biasioli et al. Trends in Analytical Chemistry 30 (2011), 968
3. R. Paolesse et al. Chem. Rev. 117 (2017) 2517

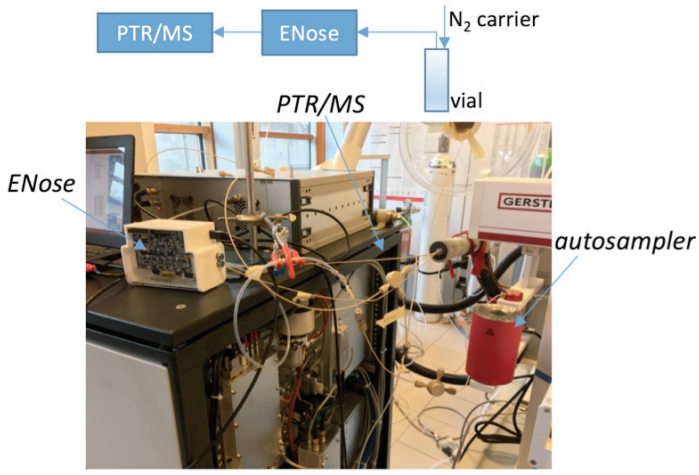


*Figure 1. Sketch of the experimental setup and picture of the instruments arrangement.*

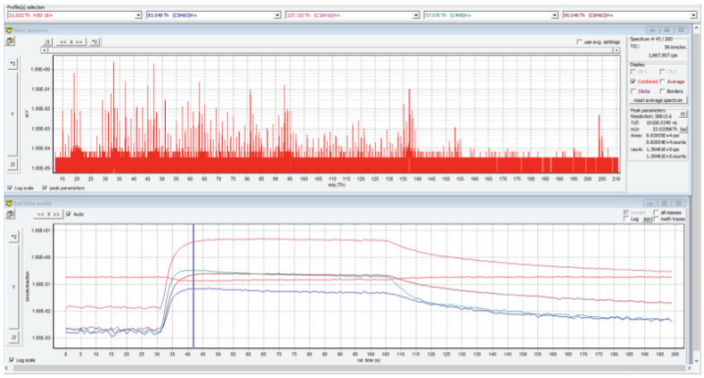

*Figure. 2. Example of a measurement of a tomato paste with a natural antifungine by PTR-ToF-MS: PTR-ToF-MS spectrum (upper panel) and time evoution during the measurment of 5 selected peaks (lower panel). Both graphs are with log y-axis.*

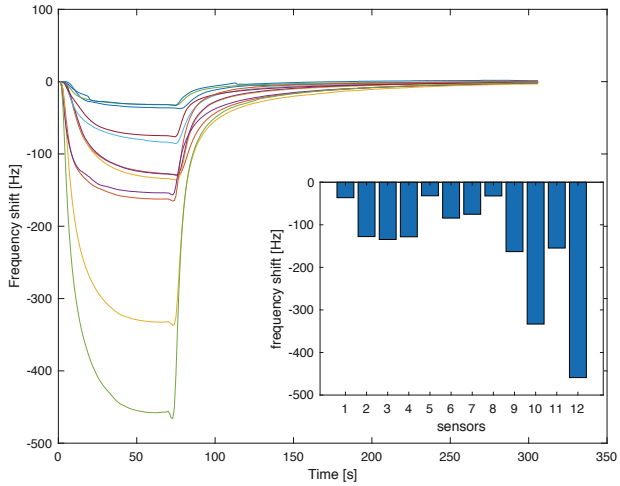


*Figure 3. Example of the signals of the sensors of the electronic nose to same sample shown in figure 2. In the inset the pattern of responses of the sensors is shown.*