Direct-injection mass spectrometry adds the time dimension to (B)VOC analysis

Franco Biasioli, Chahan Yeretzian, Tilmann D. Märk, J. Dewulf,
H. Van Langenhove

In the past decade, we have witnessed rapid development of direct-injection mass spectrometric (DIMS) technologies that combine ever-improving mass and time resolution with high sensitivity and robustness. Here, we review some of the most significant DIMS technologies, which have been applied to rapid monitoring and quantification of volatile organic compounds (VOCs) and biogenic VOCS (BVOCs). They include MS-e-noses, atmospheric-pressure chemical ionization (APCI), proton-transfer-reaction mass spectrometry (PTR-MS), and selected ion-flow-tube mass spectrometry (SIFT-MS). DIMS-based MS-e-noses provide the possibility to screen large sample sets and may yield rich analytical information. APCI is a widespread ionization method and pioneered DIMS in environmental and flavor-release applications. SIFT-MS and PTR-MS allow better control of precursor-ion generation and hence of the ionization process. SIFT-MS puts the focus on control of the ionization process, while PTR-MS does so on sensitivity. Most (B)VOCs of interest can be efficiently detected and often identified by DIMS, thanks also to the possibility of switching between different precursor ions and the recent realization of time-of-flight-based equipments. Finally, we give selected examples of applications for each of the key technologies, including research in food-quality control (MS-e-nose), flavor release (APCI), environmental sciences (PTR-MS) and health sciences (SIFT-MS).

Keywords: APCI; BVOC; Chemometrics; CIR-MS; DIMS; Direct-injection mass spectrometry; MS-e-nose; PTR-MS; SIFT-MS; VOC

Franco Biasioli*
IASMA Research and Innovation Centre,
Fondazione Edmund Mach, Food Quality and Nutrition Area,
Via E. Mach, 1, 38010, S. Michele a/A, Italy

Chahan Yeretzian
Zurich University of Applied Sciences,
Department of Life Sciences and Facility Management, Institute of
Chemistry and Biological Chemistry, Campus Reidbach,
Einsiedlerstrasse 31, CH - 8820, Wädenswil, Switzerland

Tilmann D. Märk
Institut für Ionenphysik und Angewandte Physik,
Leopold Franzens Universität Innsbruck, Technikerstr. 25,
A-6020, Innsbruck, Austria

J. Dewulf, H. Van Langenhove
Research Group ENVOC, Ghent University,
Coupure Links 653, 9000 Ghent, Belgium

1. Introduction and fields of applications

The rapid, non-invasive and direct on-line measurement of volatile organic compounds (VOCs) and biogenic VOCs (BVOCs), in particular, plays an increasingly relevant role in various fundamental and applied research fields. Indeed, numerous (biological) processes and products constantly release (B)VOCs. While such compounds generally appear at trace concentrations in the gas phase, they are often linked to important characteristics and properties of processes and products and can be of great economic relevance, as they provide relevant, transparent information on biological, legal, safety, quality and value aspects (e.g., of our environment or food). Here, we discuss novel analytical technologies that allow non-invasive, non-destructive and selective monitoring of (B)VOCs in complex mixtures at trace concentrations. These

---

*Corresponding author.
Tel.: +39 0461 615 187;
E-mail: franco.biasioli@iasma.it

0165-9936/$ - see front matter © 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.trac.2011.04.005

technologies are opening new avenues and approaches to rapid process monitoring and control, fast characterization of products, and timely assessment of environmental, medical and nutritional conditions that open a new window on fast, fundamental processes and permit immediate corrective re-actions in applications, some of the most important of which are:

- atmospheric and environmental chemistry
- medical sciences
- biotechnology
- metabolomics
- biological research
- food and flavor science and technology
- homeland security
- waste incineration and waste-disposal monitoring
- industrial process monitoring
- outdoor and indoor air quality monitoring

Analytical technologies for rapid (B)VOC monitoring in all the above-mentioned areas will bring new research perspectives and are of clear benefit to their advancement. For example, metabolomics and food technology, in particular quality control in food production, face the need for rapid, high-throughput measurement of large sample sets, preferably without affecting the sample and without interfering with the production process. Environmental chemistry and plant studies exploit fast response times to follow rapidly varying processes, while the analysis of exhaled breath, called ''breath analysis'' in medicine and ''nose-space'' analysis in food science, takes advantage of the non-invasive sampling that allows work with human volunteers without excessive stress and minimally affects their normal behavior during respiration or food consumption.

VOC monitoring for the above-mentioned applications not only relies on high time resolution, better than 1 Hz [1], but also takes advantage of the high sensitivity provided by most direct-injection mass spectrometry (DIMS) technologies. Rapid monitoring does not allow for pre-concentration and the compounds of interest may well be present in the gas phase in the sub-ppt range, for both environmental and medical applications. Moreover, the low olfactory threshold of several compounds makes it necessary to measure in the ppt or sub-ppt range in both air-quality monitoring and nose-space analysis in food science. In such situations, the very high sensitivity achieved by state-of-the-art DIMS technologies, allows direct monitoring of (B)VOCs in the gas phase.

An additional qualifying feature of on-line DIMS technologies is the large dynamic range that is required for certain applications. An exemplary case is the measurement of BVOCs released from food matrixes, where simultaneously compounds in the ranges ppm (e.g., alcohols), ppb (e.g., esters) and ppt or below (e.g., sulfur compounds) are present [2]. Similar situations occur in process monitoring, where a large number of compounds over a large range of concentrations need to be monitored simultaneously.

The analysis of VOCs is thus challenging from various perspectives:

(1) first, they are often embedded in complex volatile mixtures;
(2) second, their concentrations may evolve rapidly with time; and,
(3) third, they may be present on a wide range of concentration and often also in trace amounts.

Traditional MS-based analytical technologies are hardly suited to address these analytical challenges. Samples have to be introduced via a gas-handling system; and, the atmospheric pressure sample has to be diluted to vacuum conditions necessary for operating a mass spectrometer (indirect gas injection).

In classical analytical chemistry, the mass spectrometer is usually preceded, in VOC detection, by a gas chromatographic (GC) separation step, and GC-based methods [3] are the benchmark analytical methods for (B)VOC identification and quantification. Although very valuable and, in many cases, indispensible, they are not designed to examine the temporal changes of VOCs in fast processes (i.e. for time resolutions of a few seconds to sub-second time scales). Even when using high-speed GC [4], the time resolution of GC-based methods is at best in the minute range, and, often, a necessary sampling and pre-treatment phase [3] introduces time averages of the concentration of the measured mixture. Because of these drawbacks, other methods have been developed over the years to complement GC-based methods with simplified, high sensitivity, fast and direct on-line monitoring of (B)VOCs, with a high (even sub-second) time resolution.

Among the various options to address these needs, from spectroscopic methods [5] to solid-state gas sensors arrays [6], advanced DIMS has proved to be a high-performance technology and a valuable complement to existing methods. Besides its technological performances (e.g., sensitivity and selectivity), advanced DIMS is also increasingly being used because of its stability (not prone to drifts) and because MS measures a well-characterized, intrinsic physical property of the compounds – the mass/charge ratio – that is not convoluted and does not vary with the experimental conditions. A number of methods have been developed, aiming to exploit the potential of MS (high sensitivity, fast monitoring), not restricted to VOCs, while avoiding the drawbacks inherent in chromatographic separation and sample pre-treatment methods. These have been given different names (e.g., DIMS, infusion MS or inlet MS), mostly in metabolomic studies [7,8] and, not necessarily for VOCs, direct sampling MS [9] or finger/footprint MS for rapid classification of samples [10]. The greatest difficulties arising in DIMS are the needs to interface directly atmospheric pressure samples to the vacuum usually needed for a proper functioning of a mass spectrometer and to