CHIMIA 2001, 55, No. 5

Chimia 55 (2001) 429–434

ISSN 0009–4293

Novel Mass Spectrometry Methods in Flavour Analysis

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Abstract: Flavour research is a demanding domain in terms of analytical methodology as key odorants usually occur in trace amounts, often embedded in extracts containing volatile compounds at much higher concentrations. Since its early days, GC-MS has been a key tool in flavour laboratories enabling characterisation of thousands of volatile components in food products. However, as flavour chemists delve deeper into the understanding of flavour generation and delivery, there is a need for more powerful methodologies adapted to their specific needs. This paper will present two techniques that allow flavour separation and characterisation, namely GC-TOFMS and MS/MS. Moreover, APCI-MS, PTR-MS and REMPI-TOFMS will be discussed as they enable direct investigation of volatile compounds without any chromatographic step, thus studying release of flavour compounds during food processing or food consumption.

Keywords: APCI · Flavour · GC-TOFMS · Mass spectrometry · PTR-MS · Real-time monitoring · REMPI-TOFMS

Introduction

Flavour research deals with key odorants that usually occur in trace amounts, often embedded in extracts containing volatile compounds at much higher concentrations. Flavour compounds belong to a wide range of chemical classes, some of which are quite unstable. All this puts a very high demand on analytical techniques. For flavour chemists, accuracy, selectivity, sensitivity, rapidity, and versatility of their instrumental techniques are of utmost importance.

These needs explain the rapid development of mass spectrometry (MS) in flavour laboratories as it offers many of these features. The privileged position of MS for the analytical community comes mainly from the fact that highly instructive information can be obtained about the mass, being directly related to a well-defined property of the compound, without reference to specific apparatus parameters. A range of high-quality instruments is nowadays commercially available, some of which can achieve very high resolution with robust mass calibration. Also the possibility to hyphenate MS with various chromatographic techniques enables the analysis of complex mixtures, which are rather typical in flavour research. Moreover, advanced MS techniques (*e.g.* high-resolution MS or tandem MS) allow the considerable reduction of sample clean up and, thus, the minimisation of losses and distortion of the sample matrix.

In 1955, Gohlke and McLafferty [1] realised the first coupling between a gas chromatograph and a mass spectrometer offering to the analytical chemist one of their most powerful analytical techniques. Gas chromatography/mass spectrometry (GC/MS) is the method of choice for analysis of volatile compounds in complex mixtures, particularly for identification purposes. However, on-line monitoring of known compounds calls for new techniques allowing fast measurements with high selectivity and sensitivity without GC coupling. Several new or re-actualised techniques will be discussed with specific application to flavour research.

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GC-Time of Flight Mass Spectrometry (GC-TOFMS)

In flavour research, MS has been mainly used for the identification of volatile compounds. Indeed, the vast majority of molecules reported in the TNO list was identified on the basis of GC-MS data [2]. Identification by GC-MS is straightforward if its mass spectrum is known and available in a database. However, structure elucidation of unknown aroma-impact molecules is still a challenge in flavour research. Of particular interest is the determination of the elemental composition of the unknown compound. That can be achieved by high-resolution techniques where high sensitivity for such measurements is a prerequisite as many key odorants occur in trace amounts. Highly sensitive high-resolution mass spectrometers are available on the market but such double focusing instruments remain extremely expensive. For the flavour chemist, GC-TOFMS can be a valuable alternative.

GC-TOFMS has been made possible by the development of orthogonal acceleration ion sampling and high data acquisition rates. Thus, the hyphenation between a GC and a TOF instrument has led to the appearance of one of the most powerful tools for volatile compound analysis. GC-TOFMS enables high-through-

put analysis when fast GC is used, allows exact mass measurements and exhibits high sensitivity. For the analysis of complex mixtures, GC-TOFMS offers clear advantages over GC/quadrupole MS because selectivity can be dramatically improved by increasing the mass resolution power. Even if the resolution power of commercially available instruments does not compete with that of double focusing mass spectrometers, exact mass measurements at 7000 resolution can be performed for confirmation of elemental composition of GC eluted molecules. Newton *et al.* showed an average error of 4.6 ppm after exact mass measurement of compounds having molecular weights in the range 140–250 Da [3]. Moreover, the possibility to reconstruct exact mass chromatograms enables compounds in complex mixtures to be targeted with a high degree of specificity.

As an example, Fig. 1 presents the detection of butylhydroxy toluene in orange oil. The two chromatograms were reconstructed with two different mass windows (± 10 mDa and ± 250 mDa) showing the reduction of nominally isobaric interference when ions are searched in a narrower mass window. GC-TOFMS has been used to identify flavour volatiles in apple, tomato and strawberry fruits [4] [5]. The authors showed impressive results obtained after solid-phase-microextraction GC-TOFMS. A 5 min chromatography on a short capillary column (5 m x 0.1 mm i.d.) allows separation of 29 volatile compounds extracted from apple fruits. A total analysis time of 10 min was required to perform flavour extraction (6 min for fibre cleaning, sample collection and desorption) and GC-TOFMS identification (220 s for the separation of 30 tomato compounds). However, today GC-TOFMS has only a limited linear range rendering quantitation difficult.

Tandem Mass Spectrometry (MS/MS)

The high selectivity of MS was utilised to study mechanistic aspects of flavour formation, *i.e.* to elucidate formation pathways of volatile compounds using specifically labelled precursors. Such labelling experiments allow the better understanding of the reaction pathways leading to key odorants, *e.g.* the formation of γ- and δ-lactones by different biochemical pathways [6][7] and formation of volatile Maillard reaction products [8]. The use of more advanced MS techniques, such as tandem MS, offers new opportunities, especially to study the formation mechanisms of trace components [9]. Tandem mass spectrometry provides a third dimension to GC/MS by adding the electronically based selectivity of collision-induced dissociation (CID) to the chemically-based selectivity of chromatographic separation. However, despite its high analytical potential, tandem mass spectrometry is not frequently used in flavour research. This can be explained by the longer commercial availability of GC/MS instruments as opposed to MS/MS instruments, but also by the high cost of the MS/MS apparatus. Nevertheless, because of its sensitivity and selectivity, MS/MS offers the flavour chemist powerful features allowing structural identification as well as quantitative determination [10].

The MS/MS configurations available can be divided into two categories. The first of these is tandem-in-space mass spectrometers [11] in which two mass spectrometers are assembled in tandem. This group of instruments is dominated by triple quadrupole mass spectrometers. The second group contains tandem-in-time mass spectrometers in which the analysers are able to store ions. The ion trap mass spectrometer is a typical representative of this category [12]. Using tandem-in-space mass spectrometers, three main scan modes are available: daughter ion, parent ion and neutral loss scans. Tandem-in-time mass spectrometers can only give product ion scans but the process can be repeated yielding a MS^n product ion spectrum [13].

Because three main scan modes (daughter ion, parent ion and neutral loss scans) are available with triple quadrupole instruments, they have been preferably chosen for structural identification. Neutral loss and parent scanning experiments were used to confirm minor sesquiterpenes (α-cedrene, acoradiene and khusimene) in Chinese vetiver oil [14]. In our laboratory we have used such instrumentation to identify 3(2*H*)-furanones and pyrazines formed through the Maillard reaction based on pentose sugars and to understand the mechanism of their formation using isotopically labelled precursors [15][16]. During the study of the formation of 3(2*H*)-furanones, daughter experiments were carried out on molecular ions generated by electron impact

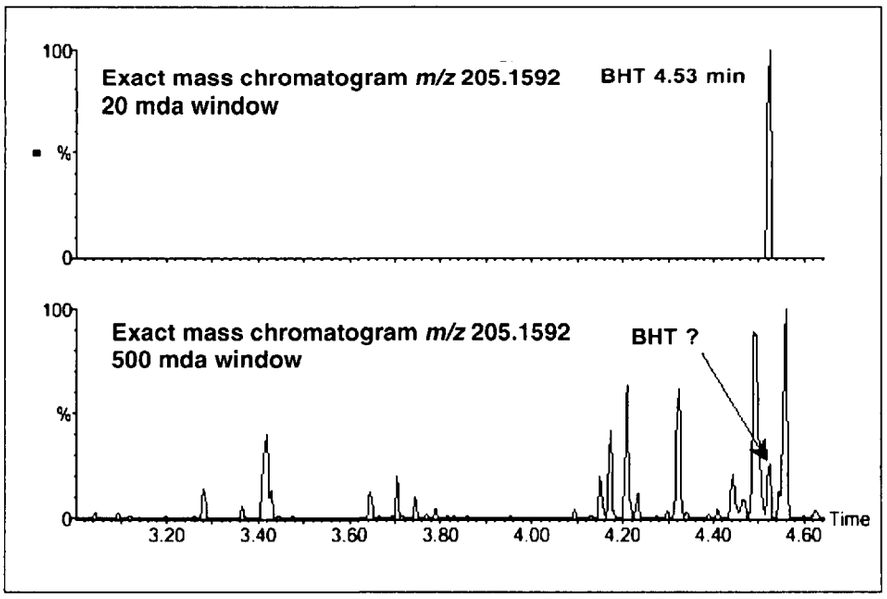

Fig. 1. Detection of butylhydroxy toluene (BHT) in orange oil. Two mass chromatograms were reconstructed with two different mass windows (± 10 mDa and ± 250 mDa). A narrower mass window enables reduction of nominally isobaric interferences. Reproduced from A. Newton, P. Hancock, M. Green, R.H. Bateman, S. White, *Proceedings of the 48th ASMS Conference on Mass Spectrometry and Allied Topics*, **2000**, Long Beach, CA, with permission of the authors.

(Fig. 2). The fragmentation pathways of the compounds were established based on the isotopic shift in the mass spectra [17]. This knowledge enabled structure elucidation of the reaction products between xylose and alanine or glycine, and formulation of the formation mechanisms.

Ion trap mass spectrometers are known to be extremely sensitive and were found to be very powerful to detect off-flavours in food products [18]. However, sensitivity in flavour research is an issue and even if tandem mass spectrometers can detect compounds present in the ppt range, they still cannot compete with the human nose capabilities. As an example, 1-octen-3-one can be detected by GC-olfactometry in coffee samples 500 times less concentrated than those required for the detection of this compound by GC/MS/MS working in selected reaction monitoring after negative chemical ionisation [19].

Another challenging problem in the use of MS/MS to identify compounds is the lack of MS/MS spectral libraries. In-house libraries can be built-up. Nevertheless, there are several instrumental parameters that can cause significant differences in the observed MS/MS spectra for a given molecule. Even if a protocol has been recently proposed to overcome this problem [20], no commercial library is currently available.

On-line Measuring Techniques

On-line measurement of volatiles has become important in order to obtain insight into the kinetics of flavour formation in complex mixtures and their dependence on process parameters. To achieve the time resolution needed for on-line measurement of fast processes, GC can be replaced by MS as a means to separate volatile compounds within a fraction of a second. Yet, the prerequisite for separation in a mass filter is ionisation. This introduces complications due to potential ionisation-induced fragmentation. It was, therefore, only when soft and sensitive ionisation techniques became available that direct injection into a mass spectrometer developed into a valuable approach for flavour analysis. Currently, two soft ionisation modes have been implemented in actual instruments – chemical ionisation and laser ionisation. **A**tmospheric-**P**ressure **C**hemical **I**onisation-MS (APCI-MS) and **P**roton-**T**ransfer-**R**eaction MS (PTR-MS) are based on chemical ionisation. APCI-MS utilises a conventional CI cell combined with a newly developed inlet system for breath-by-breath analysis, while the strength of PTR-MS is its unique design of the chemical ionisation cell. Both approaches are unselective in their ionisation process, detecting essentially all volatile organic compounds in the headspace. They are hence one-dimensional techniques and an unambiguous assignment of compounds requires additional sources of information. In contrast, resonance-enhanced multiphoton ionisation (REMPI) introduces selectivity in the ionisation step. In combination with the mass filter, REMPI TOFMS represents a two-dimensional technique that can serve to identify volatile compounds. Common to all three techniques (APCI-MS, PTR-MS and REMPI TOFMS) is speed, enabling direct introduction of the volatile compounds into the instruments without any pre-separation process. Therefore, these various instrumentations can be applied to study flavour release and *in situ* flavour formation.

Atmospheric Pressure Chemical Ionisation-MS (APCI-MS)

APCI is a method designed for the analysis of moderately polar and volatile compounds present in aqueous solvents. To analyse flavour molecules present in the gaseous phase, Lindforth and Taylor modified an APCI source to enable introduction of gas phase samples [21][22]. As APCI is a soft ionisation technique which protonates the analytes (in positive mode) almost without fragmentation, protonated molecular ions are observed for each flavour compound present in the gas phase. This technology avoids extraction of the flavour compounds from the food matrix. Therefore, real-time flavour monitoring can be performed for analysis of breath air during eating. For example, experiments carried out with flavoured yoghurts differing in fat content showed that low-fat yoghurts (0.2%) released volatiles more quickly than yoghurts containing 3.5 and 10% fat [23]. Similar analyses were carried out monitoring for example menthol and menthone during eating mint-flavoured sweets or 2-isobutylthiazole and (*Z*)-3-hexenal from tomatoes. This enables the study of the effect of flavour encapsulation, food formulation or food texture on the aroma perceived by the consumer and will support flavour reformulation of low-fat products [24]. Additional improvement of sensitivity would allow minor volatile

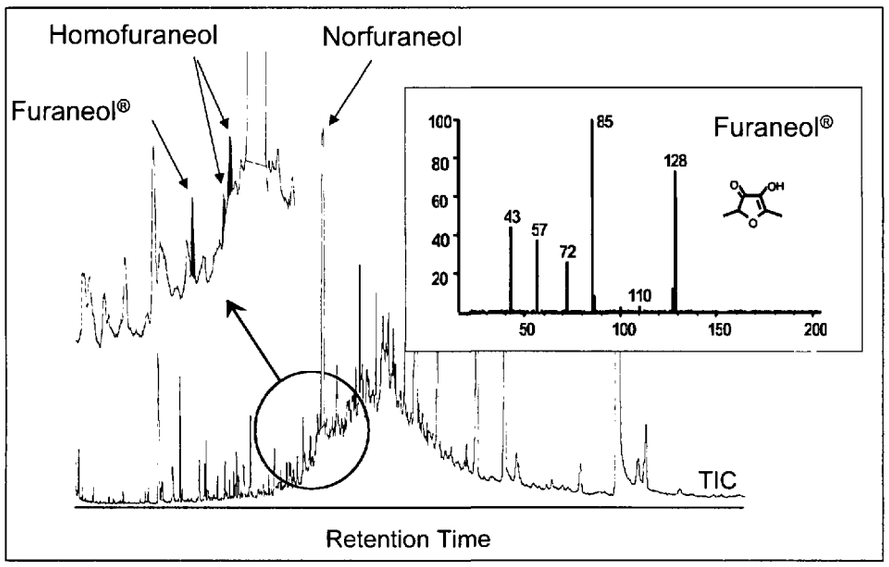

Fig. 2. GC/MS/MS identification of 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (furaneol®) formed by the Maillard reaction of xylose and alanine. Because of the complexity of the sample, GC/MS/MS is ideally suited to identify the 3(2*H*)-furanones such as 4-hydroxy-5-methyl-3(2*H*)-furanone (norfuraneol), 4-hydroxy-2(or 5)-ethyl-5(or 2)-methyl-3(2*H*)-furanone (homofuraneol) and furaneol®, particularly those which occur in low concentrations. The interference-free daughter mass spectrum of furaneol® was obtained after collision-induced dissociation of the ion at *m/z* 128 (molecular ion of the compound after electron impact ionisation at 70 eV).

constituents to be monitored, which very often belong to key odorants of food products.

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS)

PTR-MS [25][26] is based on a novel design for the chemical ionisation cell [27], which had developed out of the swarm technique of flow-drift-tube type [28]. The gas to be analysed is continuously introduced through a ventury-type inlet system into the chemical ionisation cell (drift tube), which, besides buffer-gas (air), contains a controlled ion density of H_3O^+. Volatiles that have proton affinities larger than water (proton affinity of H_2O: 166.5 kcal/mol) are ionised by proton transfer from H_3O^+, and the protonated compounds are mass analysed in a quadrupole MS.

Since its introduction in 1993, PTR-MS has been steadily improved and applied to a variety of fields. Medical and nutritional applications of breath analysis allow monitoring of metabolic processes in the human body [29][30]. Environmental applications include investigations of volatile emissions from decaying bio-matter [31][32], or diurnal variations of organic compounds in the troposphere. Monitoring of food processing was investigated on the example of coffee roasting [33]. Finally, PTR-MS has been shown to be an ideal tool to measure Henry's law constants and their dependence on temperature and matrix [34].

PTR-MS experiments provide information that can be roughly divided into two classes, as shown in Fig. 3. On one hand, one can record direct-sampling mass spectra of a given headspace (HS) profile, and average these data over a time window (static data). Such spectra closely match genuine HS distributions and can be used to assess authenticity, monitor deviations in production from a reference or classify products and raw materials. Provided mass peaks can be assigned to compounds, absolute HS concentrations can be determined from HS profiles. On the other hand, one can record the temporal evolution of a series of mass intensities over a given time window (dynamic data).

PTR-MS is an one-dimensional method that characterises compounds by their mass. The ionisation process in PTR-MS is unselective in the sense that all compounds having proton affinities exceeding 166.5 kcal/mol are protonated; a condition fulfilled for essentially all volatile organic compounds. The only dimension along which compounds are separated is their mass, which in general is not sufficient for an unambiguous assignment. In many cases unselective ionisation is an advantage since one obtains mass spectra that closely reflect the genuine headspace distribution. Yet in the case of isobaric compounds or for trace compound analysis this poses some problems, and PTR-MS data have to be complemented with additional information to achieve assignment. High-resolution MS would eliminate the problem related to the overlap of isobaric compounds, but at the expense of versatility, robustness and price. Furthermore, PTR-MS still suffers from some residual fragmentation, which can complicate the interpretation of mass spectra. While it is important to keep these potential limitations in mind, a series of specific PTR-MS experiments have been developed to circumvent many of these shortcomings [26]. If used in combination with GC, the speed, sensitivity and soft-ionisation realised in PTR-MS largely overshadow these limitations, and add real value to the work of a flavour scientist. This is particularly true when it comes to investigating fast temporal changes and flavour release in real time. PTR-MS clearly holds the promise to become a powerful tool for flavour analysis and will complement the information obtained by the more traditional GC-based techniques.

Among the many dynamic studies performed by PTR-MS, one interesting application examined the emission of volatiles emitted from leaves that had been wounded [32]. Particular attention was given to compounds of the hexenal family, which are otherwise difficult to analyse due to their intrinsic chemical instability and transient formation after leaf wounding. Within 1–2 seconds of wound-

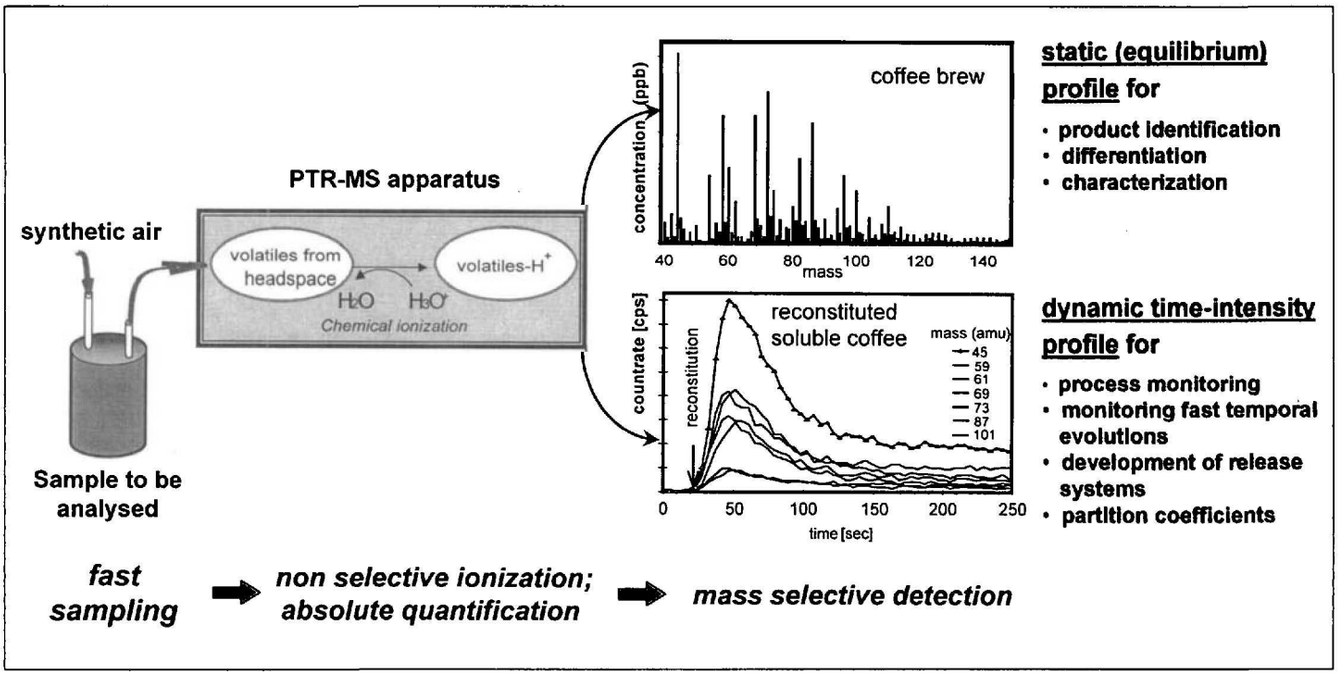

Fig. 3. Two qualitatively distinct types of information can be obtained by PTR-MS. Headspace profiles can either be averaged over a given time to yield concentration *vs.* mass spectra (static data), or temporal changes are analysed *via* time-intensity plots (dynamic data). The above static data represent an equilibrium headspace profile above a coffee brew. The dynamic time-intensity traces below represent the temporal evolution of a series of selected mass while reconstituting soluble coffee.

ing in air, (Z)-3-hexenal appears in the headspace of the leaf before it starts again to decrease after a few minutes. At this point metabolites of (Z)-3-hexenal – (E)-2-hexenal, hexenols and hexenyl acetates – are gradually generated and their release is monitored on-line by PTR-MS. These experiments allow monitoring of the time-intensity release curves and quantifying volatiles generated by the oxidative cleavage of membrane fatty acids, linoleic and α-linolenic acid, in the presence of oxygen.

Resonant MultiPhoton Ionisation Time-of-Flight MS (REMPI-TOFMS)

APCI-MS and PTR-MS both rely on soft chemical ionisation. **R**esonant **M**ulti **P**hoton **I**onisation (REMPI) with pulsed lasers is another soft ionisation mode that has been shown to have a high potential for fast on-line analysis of complex gas-mixtures [35][36]. In contrast to APCI- and PTR-MS, laser ionisation is based on a pulsed ionisation scheme. This makes a time-of-flight (TOF) mass filter highly suited for mass analysis.

REMPI-TOFMS is a two-dimensional analytical technique. The first selection step is *via* the UV absorption spectrum of the volatile compounds. Exploiting the fact that each molecule has a characteristic UV spectrum, a resonant multiphoton ionisation scheme allows the selective ionisation of compounds from of a complex mixture, by tuning the laser in resonance to a UV transition of a target molecule. Hence, REMPI can be extremely sensitive (*e.g.* single atom detection [37], detection limits in the low ppt range are reported [38][39]), and selective (isomer selectivity [40]). This high selectivity in the ionisation step distinguishes REMPI-TOFMS sharply from PTR-MS and APCI-MS. Following selective ionisation, the charged compounds are separated by mass.

REMPI-TOFMS is particularly suited to monitor target compounds present at trace concentrations in complex mixtures. In contrast, it is less suited for obtaining an overview of a genuine headspace profile. Furthermore, knowledge of the UV spectra of the target compound is a prerequisite, in order to be able to ionise it. Finally, several substance classes have small cross sections for fragmentation-free resonant laser ionisation and can hardly be detected by this technique. Hence, sensitivity can vary over many orders of magnitude among different chemical classes. For instance, REMPI-TOFMS has a very limited sensitivity for diketones or thiols, compounds of significant importance for food flavours. An additional consequence of the large differences in ionisation cross section among different compounds is that relative ion-intensities can not be directly related to relative concentrations in the headspace.

Coffee roasting is the food process most intensely studied by REMPI-TOFMS [41]. From the green beans all the way to dark roasted beans, the volatile compounds were analysed on-line in the off-gas of a roaster. Fig. 4 schematically demonstrates the typical experimental set-up. The two examples shown on the right are taken from coffee roasting studies and exemplify on the one hand a profile over the full mass range early on during the roasting process (266 nm), and on the other hand a time-intensity profile of one selected mass over the entire roasting process.

Considering the prospect of being able to selectively and sensitively probe individual trace volatiles compounds in complex mixtures, REMPI-TOFMS may become a unique research tool for on-line monitoring of volatile key or marker compounds of food products and processes. This is the case particularly when these trace compounds are at very low concentrations, embedded within many other odourless volatiles of much higher intensity. Tuning the laser to a UV transition of a particular compound will allow the compound of interest to be selectively ionised, while being transparent to the remaining strong background of the other volatiles present in the headspace.

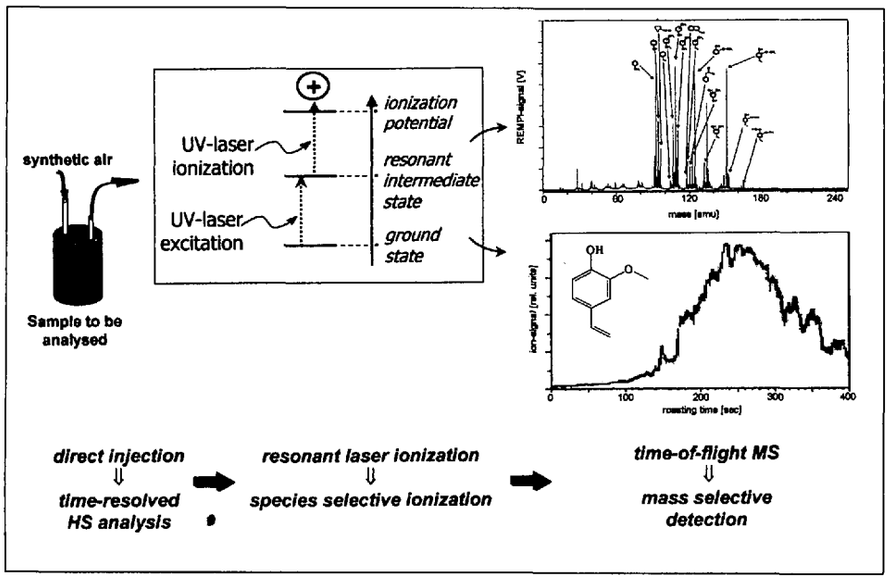

Fig. 4. Schematic representation (energy diagram) of the resonance-enhanced multiphoton ionisation process. Two-photon REMPI ionisation occurs when the laser photon energy is tuned in resonance with an UV-spectroscopic transition of the molecule of interest and if the combined energy of two laser photons exceeds the ionisation potential. The ions formed subsequently are mass-analysed in a time-of-flight mass spectrometer (TOFMS). This adds the mass spectrometric selectivity in the detection to the spectral selectivity in the ionisation process. The examples shown on the right are taken while roasting coffee beans. The top spectrum shows the mass distribution of volatile organic compounds at an early stage of the roasting process, selectively ionised using a laser photon of 266 nm. The bottom spectrum shows the time-intensity profile of a particular compounds, 4-vinyl guaiacol, during the whole roasting process.

Conclusion

Here we have briefly reviewed some recent developments in the area of mass spectrometry from the perspective of analytical flavour scientists. Mass spectrometry hyphenated with other separation techniques and detectors is without doubt a central instrument in flavour laboratories. Progress has taken many different lines. The resolution, mass-range and speed of analysis have steadily improved. Instruments have become increasingly robust and user-friendly. A wide range of powerful software tools now assists the flavour analyst in performing sophisticated experimental schemes and in the data analysis of large multidimensional datasets. MS tools have been developed to increase sample throughput and reduce minimum amount of sample needed, without hampering the quality of results. GC-TOFMS allows high-resolution measurements in a cost-efficient way. MS/MS is an extremely

powerful method for identification and quantification of flavour compounds and allows direct analysis of complex mixtures due to the selectivity of the collision-induced dissociation process.

Analysis time has become one of the key parameters to consider when setting up an analytical methodology in a flavour research laboratory. One development that might represent a breakthrough is the use of fast on-line techniques that are based on direct injection into a mass spectrometer in combination with soft-ionisation. Real-time monitoring of flavour formations and release allows intervention in the process and the real-time analysis of the impact of process parameters on flavour. APCI-MS, PTR-MS and REMPI-TOFMS enable direct investigation of volatile compounds without any chromatographic step, thus studying flavour release during food processing or food consumption. The central role of mass spectrometry for flavour analysis developed over the last four decades, will be strengthened in the near future for real-time studies through the appearance of novel applications such as direct injection coupled with soft ionisation methods.

Acknowledgement

The authors are grateful to Dr. E. Prior for critical proof-reading of the manuscript.

Received: March 14, 2001

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