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Unambiguous Identification of Volatile Organic Compounds by Proton-Transfer Reaction Mass Spectrometry Coupled with GC/MS

Christian Lindinger,[†,‡,§] Philippe Pollien,[†] Santo Ali,[†] Chahan Yeretzian,*[,†] Imre Blank,[†] and Tilmann Märk[‡,§]

Nestlé Research Center, Vers-chez-les-Blanc, 1000 Lausanne 26, Switzerland, Institut für Ionenphysik, Leopold Franzens Universität Innsbruck, 6020 Innsbruck, Austria, and Ionicon Analytik GmbH, Technikerstrasse 21a, 6020 Innsbruck, Austria

Interest in on-line measurements of volatile organic compounds (VOCs) is increasing, as sensitive, compact, and affordable direct inlet mass spectrometers are becoming available. Proton-transfer reaction mass spectrometry (PTR-MS) distinguishes itself by its high sensitivity (low ppt range), high time resolution (200 ms), little ionization-induced fragmentation, and ionization efficiency independent of the compound to be analyzed. Yet, PTR-MS has a shortcoming. It is a one-dimensional technique that characterizes compounds only via their mass, which is not sufficient for positive identification. Here, we introduce a technical and analytical extension of PTR-MS, which removes this shortcoming, while preserving its salient and unique features. Combining separation of VOCs by gas chromatography (GC) with simultaneous and parallel detection of the GC effluent by PTR-MS and electron impact MS, an unambiguous interpretation of complex PTR-MS spectra becomes feasible. This novel development is discussed on the basis of characteristic performance parameters, such as resolution, linear range, and detection limit. The recently developed drift tube with a reduced reaction volume is crucial to exploit the full potential of the setup. We illustrate the performance of the novel setup by analyzing a complex food system.

Over the past decade, interest in release and delivery of volatile organic compounds (VOCs) from food has been steadily growing, with a particular focus on aroma delivery/release during food preparation and consumption.[1−6] Consequently, considerable effort was invested to develop analytical methods capable of capturing dynamic aroma release processes.[7,8] This led to improvements in electronic sensor methods (often termed "electronic noses"),[9] atmospheric pressure chemical ionization,[3,5] and resonant and nonresonant laser ionization methods.[7] One particularly well performing technique is proton-transfer reaction mass spectrometry (PTR-MS).[10−12]

Since its introduction in 1993, on-line trace gas analysis by proton transfer[13] has become a powerful approach, mainly due to the higher sensitivity and lower ionization-induced fragmentation relative to electron impact ionization (EI). EI leads to a strong ionization-induced fragmentation, preventing efficient on-line trace gas analysis of volatile mixtures via direct MS. In contrast, fragmentation by EI-MS is advantageous if used as a detector for gas chromatography (GC) (identification of pure compounds).

The success of PTR-MS triggered interest in further improving its performance. Indeed, PTR-MS is a one-dimensional technique, and ions from a complex headspace (HS)—e.g., coffee—can often only be tentatively assigned. Ions from different compounds (parent and fragment ions) can overlap in PTR-MS and prevent an unambiguous identification of VOCs in a complex mixture.[14] The aim of this work is to address this problem and present an extension of PTR-MS, which allows for an unambiguous identification of HS compounds. This is achieved by coupling GC with simultaneous PTR-MS and EI-MS detection. In this paper, we introduce the features of the new setup, quantify critical performance parameters, and discuss an application to the HS of coffee.

* Corresponding author. Tel.: +49 (7731) 14 1235. E-mail: chahan.yeretzian@rdsi.nestle.com. Present address: Nestlé Product Technology Center, P.O. Box 671, D-78221 Singen, Germany.

† Nestlé Research Center.

‡ Leopold Franzens Universität Innsbruck.

§ Ionicon Analytik GmbH.

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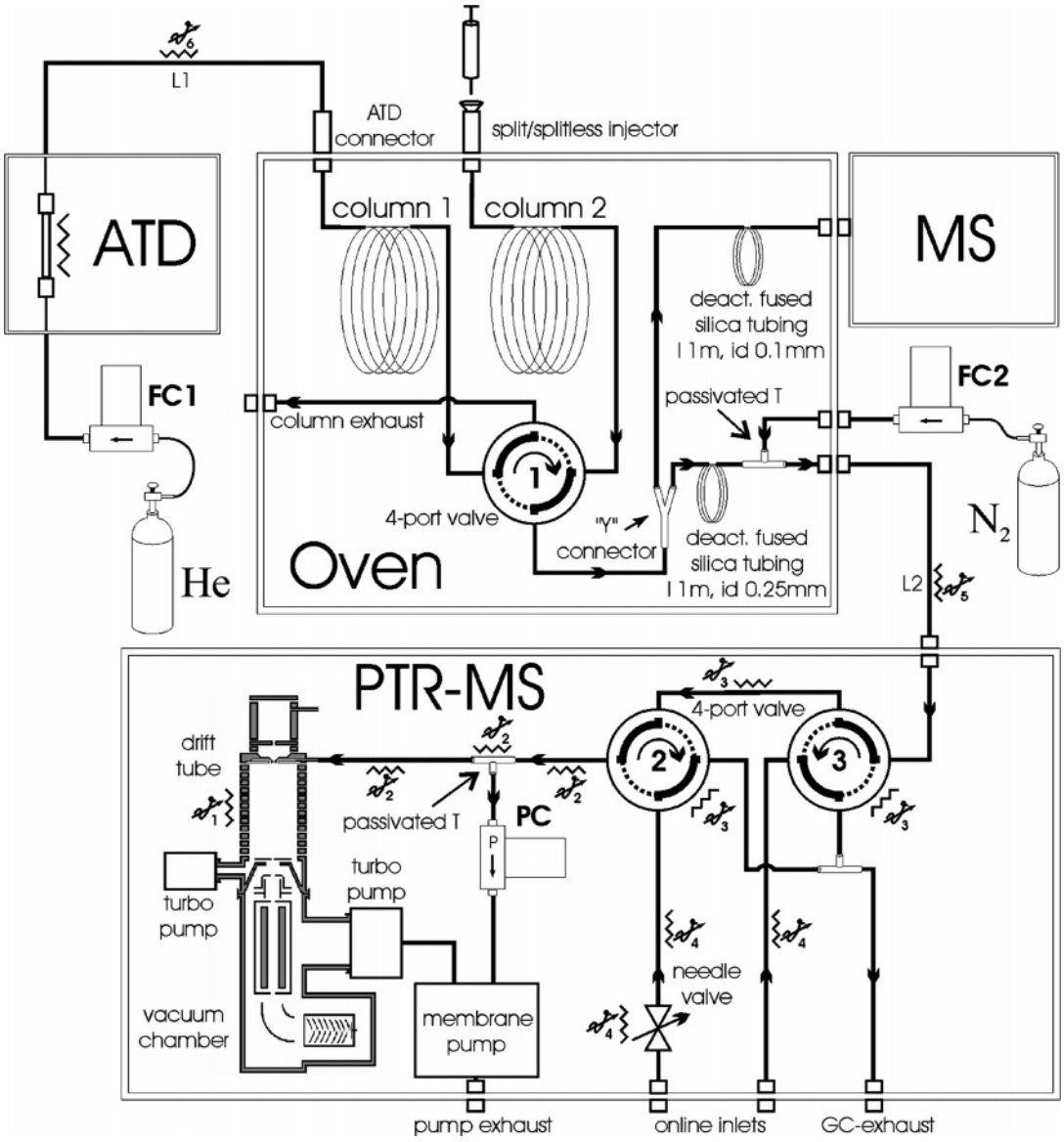

Figure 1. Scheme of the GC/MS coupled to a PTR-MS detector. Controlled temperatures: ϑ_1, ϑ_2, ϑ_3, ϑ_4 = 80 °C, ϑ_5 = 130 °C, ϑ_6 = 180 °C. L1 = 1.5 m, L2 = 2 m. See text for more details.

TECHNICAL SECTION

For the sake of clarity, we divide the experimental setup into three modules: the PTR-MS, the GC/MS, and the automatic thermal desorption (ATD). The basic PTR-MS technique has been repeatedly reviewed in other publications.[10−17] Here we focus on the novel technical features of the setup.

Drift Tube of the Proton-Transfer Reaction Mass Spectrometer. Compared with previous versions of PTR-MS the inner volume of the drift tube (reaction chamber) is decreased by a factor of 10. This allows reaching a purging time of the gas in the reaction chamber of better than 200 ms, which in turn determines the time resolution of PTR-MS. Furthermore, to keep the background signal as low as possible, the Viton rings, previously used in the drift tube, were replaced by Teflon cylinders. This leads to a substantial reduction of the background signal. Both the higher time resolution and better signal-to-noise ratio are critical to the performance of the new setup.

GC/MS and Injection Systems. A detailed schematic of the setup is shown in Figure 1. The GC/MS is composed of Trace 2000 series GC and Automass Multi MS (Thermo Quest Ltd.). The GC is equipped for two different types of sample injection systems. A split/splitless injector is supplied by a PAL autosampler (CTC Analytics AG, Switzerland), which allows for either liquid sampling at a controlled temperature or HS solid-phase microextraction (SPME) sampling. Finally, an ATD (ATD 400, Perkin-Elmer, Boston, MA) unit is used for HS sampling on Tenax traps.

A standard GC oven was modified to hold two independent columns (Figure 1, column 1 and column 2). One is for samples injected through the ATD and the other for samples introduced via the split/splitless injector. Valve 1 (4-port valve, Valco 4N4WT; Vici AG, Schenkon) connected to the glass "Y"-connector (Agilent,

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GlasSeal capillary column connector, deactivated) is installed inside the oven and switches between the two different columns. The valve and all connectors have minimum dead volumes and are Silcosteel coated to prevent interactions with the inner surfaces. One exit port of valve 1 is connected to a "Y"-connector while the second connects to an exhaust port. The "Y"-connector supplies the two different detector systems simultaneously.

GC Column. Since a scan of the (PTR-)MS over 200 amu at a dwell time of 5 ms/amu takes 1 s, the GC column has to be chosen accordingly. Column 2 is a 30-m DB-Wax (J&W Scientific, Folsom, CA) connected to the split/splitless injector, while column 1 is a 60-m DB-Wax connected to the ATD. Both of them are wide-bore (i.d. 0.53 mm) and thick-film (1 μm) capillaries, resulting in a half-height peak width of at least 4 s in isothermal run and a good resolution. Choosing a carrier gas flow in the range 2−4 standard cubic centimeters per minutes (sccm), the linear gas velocity is 0.15−0.30 m/s. The use of a wide-bore capillary column with high film thickness results in a good compromise between obtaining large peak widths (necessary because of the limited time resolution when measuring with PTR-MS) and achieving a good separation.

Injector Types. To increase the versatility of this tool, three different injection modes are possible, realized via two injector ports: (i) a split/splitless injector port for either direct liquid injection or via SPME into the GC column 2, and (ii) an ATD unit using Tenax traps and connected to column 1.

The split/splitless injector port serves to directly analyze the PTR-MS fragmentation pattern of a variety of liquid compounds (pure and dissolved) and is supplied by an autosampler that manages up to 120 vials. The vials can be held in temperature-controlled (−20 to +60 °C) trays and shaken by an automatic agitator.

A second mode to inject trapped HS samples is through the ATD, equipped with a built-in autosampler (50 traps). Well-known problems with trapping efficiency of highly volatile compounds and water vapor will be discussed later. The standard ATD was originally designed for pressure control of carrier gas flow. Yet, for the sake of consistency and stability of the complete setup, it was decided to operate all components under flow-controlled conditions. Therefore, the pressure-controlled circuit was modified to a flow-controlled (FC1) system. The ATD is connected to the GC column via a temperature-controlled (180 °C) capillary line (L1).

Coupling GC Simultaneously to PTR-MS and EI-MS. Coupling of the GC via a "Y"-connector simultaneously to two MS, each of them operating under very different conditions, creates a series of issues that need to be resolved. The GC/MS works with helium carrier gas, at 1×10^{-4}−1×10^{-5} mbar, while the drift tube of the PTR-MS works under air or nitrogen as buffer gas at an operation pressure of ~2 mbar. Furthermore, the inlet systems of the PTR-MS had to be modified, so that it can be operated alternatively either as a GC detector (as discussed above) or as an independent on-line trace gas analyzer.

Carrier Gas. In a standard GC, the carrier flow is calculated from the carrier gas flow resistance value and pressure difference between the inlet and outlet of the column. Usually, the pressure on the detector side is either atmospheric (e.g., FID) or vacuum (e.g., MS). In our GC/PTR-MS/EI-MS interface, the pressure at the end of the column is between 0.7 and 1.5 bar, and hence, the internal calculation (automatic column adaptation program) of the flow is not valid. The flow needed to be determined according to the optimum of the van Deemter curves[18] by setting the linear velocity of injected methane to 20 cm/s. Based on that, the helium carrier gas flow was calculated to be 2.29 sccm using the Flow Calc v2.0 program (Hewlett-Packard).

To allow a proper coupling of GC/MS with PTR-MS, the effluent gas from the GC column (helium) is mixed with a 10-fold volume of nitrogen (Figure 1, at "passivated T" oven). This dilution ensures that the ion mobility in the drift tube is not significantly affected by the residual helium content of the buffer gas. A flow controller (FC2) controls the admixture of the helium carrier gas with nitrogen. To avoid back-diffusion of nitrogen to the MS (through the "Y"-connector), a 1-m capillary line is introduced between the "Y"-connector and the nitrogen admixture (deactivated fused silica, i.d. 0.25 mm). The dimensions of the capillary were chosen to maintain a stable flow of 1.5 sccm at the "Y"-connector to the PTR-MS, which amount to a GC column carrier gas flows of 2.29 sccm. This specific setup guarantees defined flow conditions in the mixing region (admixture of N_2).

Pressure. The EI-MS operates with helium at 1×10^{-4} to 1×10^{-5} mbar. Due to the connection of the PTR-MS to the GC column, the pressure at the "Y"-connector is between 0.7 and 1.5 bar, depending on the admixture flow rate of N_2 or air (ranging between 30 and 200 sccm at passivated T oven). This problem is resolved by introducing a 0.3-m-long capillary (deactivated fused silica, i.d. 0.1 mm) between the "Y"-connector and the EI-MS. The dimensions of the capillary were chosen to maintain the pressure of 1×10^{-4} and 1×10^{-5} mbar at the EI-MS ionization chamber.

The T connector (Swagelok silica coated T 1/16 in., in Figure 1, passivated T oven) and the capillaries for pressure adaptation are installed inside the GC oven, to guarantee optimal temperature stability.

PTR-MS Inlet Systems. The PTR-MS is equipped with three distinct inlets, switched by valves. One inlet is for coupling to the GC and the two others for direct on-line analysis (Figure 1, "on-line inlets"). The PTR-MS is coupled to the GC through a 2-m gas line, heated to 130 °C, while the two direct on-line inlets are heated to 80 °C. To achieve high time-resolution, dead volumes in all connections and valves are minimized, and all lines are coated to prevent interactions with the inner surfaces. Internally silica-coated tubes (Silcosteel, Restek Corp.) with an inner diameter (i.d.) of 0.53 mm and external diameter (e.d.) of 1.6 mm are tightly inserted into a copper tube (i.d. 1.6 mm, e.d. 3.2 mm) heated by a temperature-controlled heating wire (Isopad Tyco Thermal Controls, Pembroke HM 08). The copper tube increases the heating efficiency, maintains stable and homogeneous temperature conditions throughout the complete gas line, and avoids cold spots. To switch between the three inlets to the PTR-MS, two heated valves are installed (Valco 4N4WT; Vici AG, Schenkon; four-port valves 2 and 3 in Figure 1).

At the PTR-MS side of the valves, the flow rate may vary from 50 to 200 sccm, resulting in strong variations of the pressure in the drift tube of the PTR-MS. For stable operations of the PTR-MS, a pressure-controlled bypass system maintains a defined

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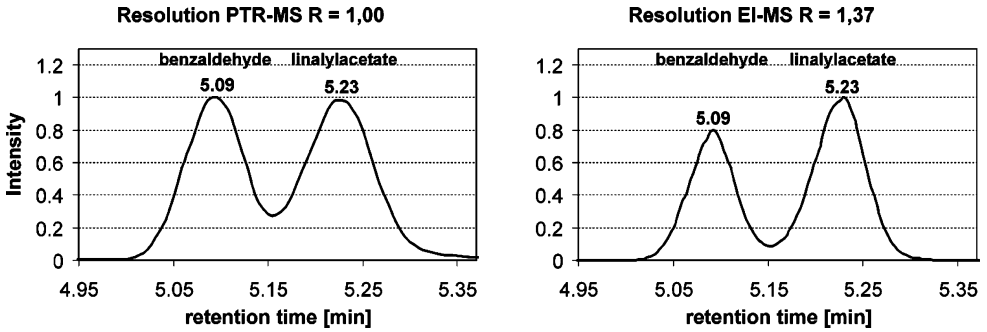

Figure 2. Resolution (R) of both MS detectors coupled to the GC column run isothermally (130 °C).[18] The test solution (1 μL) composed of benzaldehyde and linalyl acetate (each 1% diluted in ethanol) was split injected (split ratio 1:50). For graphical reasons (number of pixels in plot per time unit), this resolution is not reflected in the overview spectra shown in Figures 6−8. $R = 2[t_{R(x+1)} - t_{R(x)}]/1.699[W_{h(x+1)} + W_{h(x)}]$. $t_{R(x+1)}$, retention time of second peak; $t_{R(x)}$, retention time of first peak; W_h, half-height peak width.

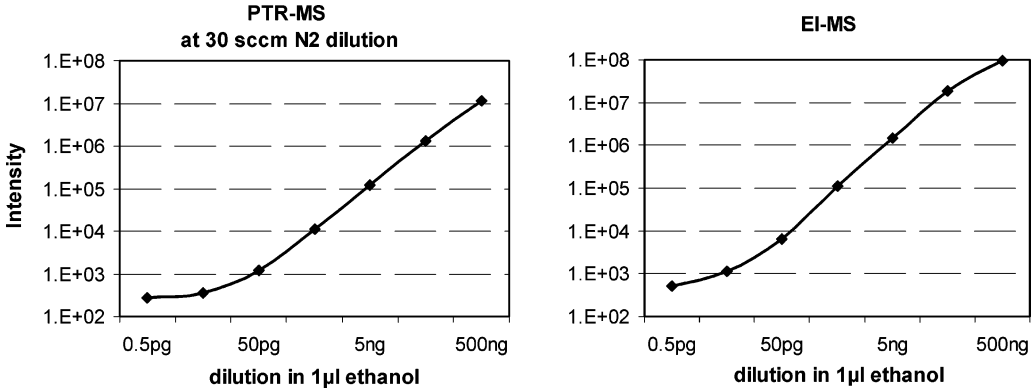

Figure 3. Linearity and detection limits of both MS detectors coupled to the GC column run isothermally (130 °C). The test solution (1 μL) composed of benzaldehyde (1% diluted in ethanol) was split injected (split ratio 1:50).

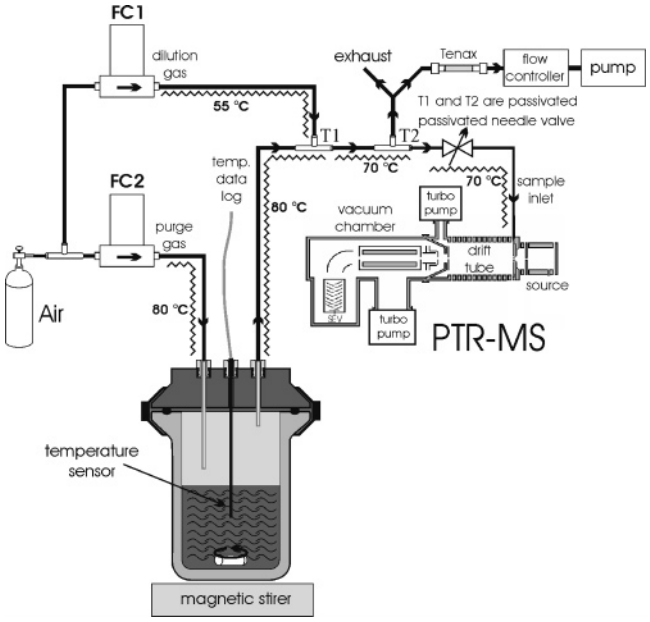

Figure 4. On-line HS measurement of coffee HS with simultaneous Tenax trapping. See text for more details.

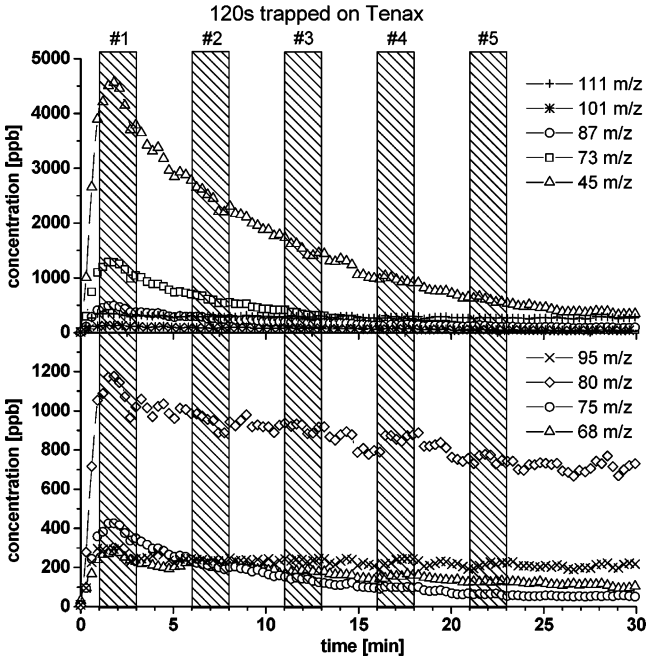

Figure 5. On-line HS time intensity profile of selected ions signal by PTR-MS, from the HS of a freshly prepared espresso coffee. A total of 28 mL of liquid coffee was extracted in ~20 s from 5 g of roast and ground coffee, and HS analysis was started immediate thereafter. The time periods during which subsequent Tenax samples were collected are indicated with #1−#5. The trapping time was 120 s for each trap period.

pressure of 2 mbar in the drift tube, introducing 14 sccm of sample gas (see Figure 1, PC and membrane pump).

Performance Characterization. Prior to demonstrating a typical application, a few characteristic performance measures of the setup will be discussed using a simple model system composed of two compounds. This includes resolution (compound separation efficiency), range of linear response, and detection limits.[19,20]

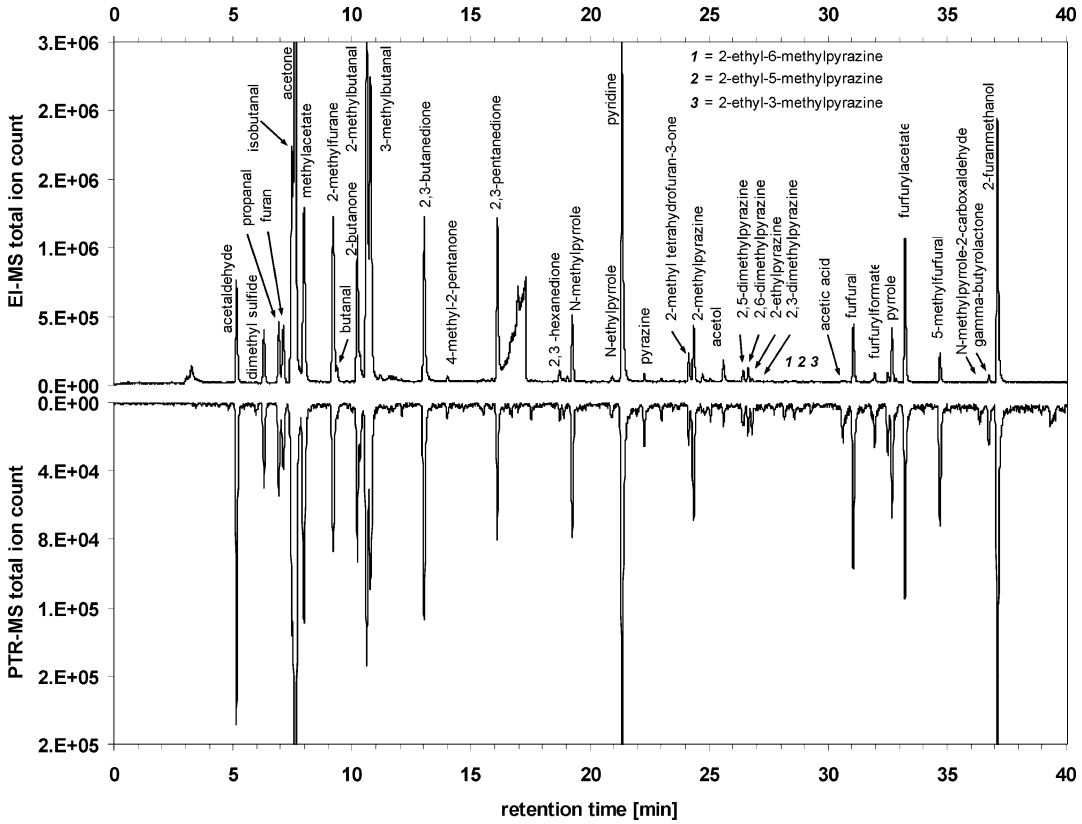

Figure 6. Simultaneous EI-MS (top trace) and PTR-MS (bottom trace) total ion count analysis of coffee HS. Identification was based on MS spectra obtained at 70 eV and retention index of the reference compounds.

Resolution. The objective was to achieve a resolution for the PTR-MS suitable as GC detector. This was accomplished by comparing the peak resolution of the PTR-MS with that of standard EI-MS. A test mixture containing 1% linalyl acetate and 1% benzaldehyde diluted in ethanol was injected into the column. The liquid injector was used in split mode, diluting the injected sample by a factor of 50, while the oven was kept at 130 °C. The measurements were performed in the single ion monitoring (SIM) method by recording the following fragment ions: for EI-MS, linalyl acetate and benzaldehyde were recorded at m/z 93 and 77, respectively, both at 50-ms dwell time; for PTR-MS, linalyl acetate was recorded as the sum of the ion intensities at m/z 137 and 81 and benzaldehyde as the sum of at m/z 107 and 79, at 50-ms dwell time. As shown in Figure 2, the resolution is very similar for both detectors (1.37 for EI-MS and 1.00 for PTR-MS) although the inlet systems are completely different. The slightly weaker resolution in the case of PTR-MS can be explained by the influence of the 2-m-long transfer line (L2 in Figure 1), before the effluent reaches the reaction chamber. In the case of EI-MS, this transfer line is much shorter (0.2 m) and is directly connected to the ionization chamber. The difference in peak height and area between the different detectors and injected molecules can be explained by the fact that measured concentrations with the PTR-MS are correlated to molar ratios of dilutions (number of moles of benzaldehyde injected), while the integrated peak areas measured with EI-MS correspond rather to the total mass of injected substances.

Linearity and Detection Limit. The linearity range and detection limits of both detectors were determined using a dilution series of a model system based on benzaldehyde diluted in 1 μL of ethanol in the range of 0.5 pg up to 500 ng (dilutions in steps of one decade). The SIM method was used with a 50-ms dwell time, i.e., EI-MS, fragment at m/z 77; PTR-MS, molecular ion at m/z 107. Figure 3 shows that the detection limit of both detectors is around 5 pg with an signal-to-noise ratio higher than 3. Saturation effects are observed above 50 ng for EI-MS and 500 ng for PTR-MS. A linear behavior between the injected quantity of benzaldehyde and detected peak area is observed over 4 orders of magnitude in the case of PTR-MS and over 3 orders of magnitude for the EI-MS as detector. Overall, the linearity range is better with PTR-MS while the resolution is slightly weaker compared to EI-MS. In conclusion, the performance of the PTR-MS is almost the same as of standard EI-MS, with respect to resolution, linearity and detection limit.

ANALYSIS OF COFFEE HEADSPACE

To demonstrate the performance of the PTR-MS coupling with GC/MS, we analyzed the HS of a freshly prepared espresso coffee (28 mL of liquid coffee extracted from 5 g of roast and ground coffee). In the first few minutes after preparation, an espresso HS typically shows hundreds of different VOCs, whose HS concentrations strongly evolve with time.[21] While we analyzed and assigned the completed HS spectrum of coffee, the performance of the setup is discussed here based on a series of nine representative PTR-MS ion signals.

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(21) Lee, K.-G.; Shibamoto, T. *Flavour Fragrance J.* **2002**, *17*, 349−51.

Sampling of the Coffee Headspace. Figure 4 shows a detailed scheme of the setup to measure on-line and under controlled conditions the dynamic release of VOCs into the HS of an espresso coffee. Freshly prepared espresso is placed into a 350-mL glass vessel and the HS swept with a continuous flow of air through the top cover containing a gas inlet and a gas outlet for purging the HS. The gas flow is controlled with two flow controllers, i.e., FC1 and FC2 (mass flow controller, Brooks Instruments B.V.), and the lines are heated with heating wires (active control of all temperatures with thermocouples). FC2 maintains the purging gas flow (zero air) at 200 sccm. The air is preheated to 80 °C and introduced through a 0.25-in. Teflon tubing into the glass vial. The 200-mL flow of purge gas ensures that the gas volume inside the 350-mL sample glass vial (350 − 28 = 322 mL) is renewed every ~2 min. This is to simulate an open system similar to the situation of a free-standing cup of coffee.

The exit-side 0.25-in. stainless steel tubing is heated to 80 °C to avoid condensations. The temperature and humidity of the sample gas is reduced by admixture of dry air of 55 °C at T1 (passivated T) to maintain simple reaction kinetics between the primary ions and the reactant gas in the reaction chamber (drift tube) of the PTR-MS, thus ensuring a proper functioning of the drift tube. FC1 controls the flow of dilution gas and maintains it at 3000 sccm. At T2 (passivated T), the sample gas is split into two flows. A flow of 14 sccm is continuously introduced into the PTR-MS. Figure 5 shows the time−concentration evolution for a series of PTR-MS ion traces. The espresso coffee is introduced into the HS sampling vial at time zero. While some volatile compounds show a strong release in the first few minutes with a rapid decrease of HS concentrations with time (e.g., m/z 45), others remain at a nearly constant HS concentration over 30 min (e.g., m/z 95).

During consecutive periods of 120 s (corresponding to the time windows shown in Figure 5), 50 sccm HS is actively drawn through a Tenax tube. The flow through the trap (50 sccm) is adjusted via a flow controller and a membrane pump in series, on the exit side of the Tenax trap. The superimposed dashed bars, labeled 1−5, correspond to time windows over which the HS was traps on consecutive Tenax traps. The remaining gas flow at T2 (200 + 3000 − 14 = 3186 sccm) is mostly discarded through the exhaust.

Identification of the On-Line Trace Ions. As shown in Figure 1, the VOCs adsorbed on the Tenax trap are thermally desorbed (250 °C, 10 min) on the ATD, entrained with a helium flow of 20 sccm, cryofocused at −30 °C, and injected from the cold trapped (250 °C, 3 min) into the GC column 1. The column is kept at 20 °C for 20 min, increased at 4 °C/min to 220 °C, and maintained for 10 min at 220 °C.

The column outlet of the GC-separated compounds is split into two at the gas "Y"-connector for simultaneous analysis by EI-MS and PTR-MS. Figure 6 shows the simultaneously recorded total ion counts of the EI-MS (top frame) and PTR-MS (bottom frame) for VOCs trapped on the Tenax 1. The GC-separated pure compounds are identified by comparison of their EI-MS fragmentation patterns with the Wiley database (Wiley 7th edition) as well as their retention indices obtained with reference compounds. The PTR-MS spectrum allows identifying the PTR-MS fragmentation pattern of the GC-separated pure compounds.

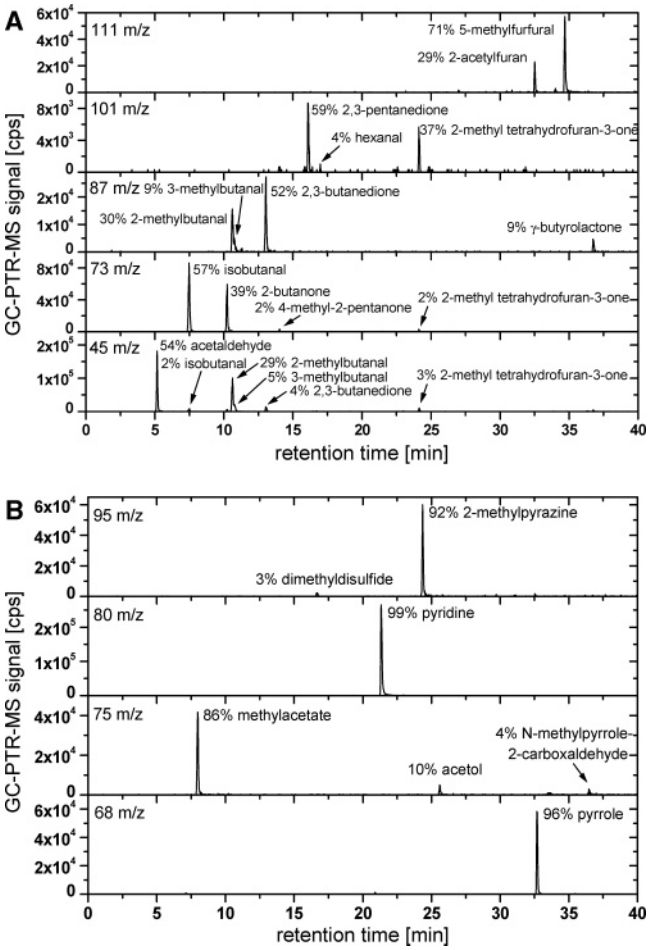

Figure 7. (A) Unambiguous identification of the molecules assigned to the trace ions shown in the upper frame of Figure 5. This identification is only valid for the first 120-s period of Tenax trapping indicated in Figure 5 as 1. Due to the limited pixel/time resolution of the plot, the small size of the figure, and the width of the line, the spectra shown here do not exhibit the full analytical resolution of the setup. For example, the two isomers 2-and 3-methylbutanal are indeed analytically well resolved (see Figure 6), although this does not show at the resolution shown here. (B) Unambiguous identification of the molecules assigned to trace ions shown in the lower frame of Figure 5. This identification is only valid for the first 120-s period of Tenax trapping indicated in Figure 5 as #1.

Referring to the series of PTR-MS ion traces shown in Figure 5 (dynamic HS time intensity profile), GC traces over the entire 40 min of the GC run are shown in Figure 7A and Figure 7B, for the compounds desorbed from Tenax cartridge 1 (trapping time window between 1 and 3 min). The data reveal, for example, that the PTR-MS ion signal at m/z 111 is a superposition of ions originating from two different compounds, i.e., 2-acetylfuran and 5-methylfurfural, contributing with 29 and 71%, respectively.[22] Similarly, the PTR-MS ion signal at m/z 73 is a superposition of 57% isobutanal and 39% 2-butanone, with traces from 4-methyl-2-pentanone and 2-methyltetrahydrofuran-3-one (2% each). While the single PTR-MS traces shown in Figure 7A represent a superposition of several compounds, a series of PTR-MS ion traces are shown in Figure 7B that are nearly pure (more than 86%),

(22) Hansel, A.; Jordan, A.; Holzinger, R.; Prazeller, P.; Vogel, W.; Lindinger, W. *Int. J. Mass Spectrom.* **1995**, *149*−*150*, 609−19.

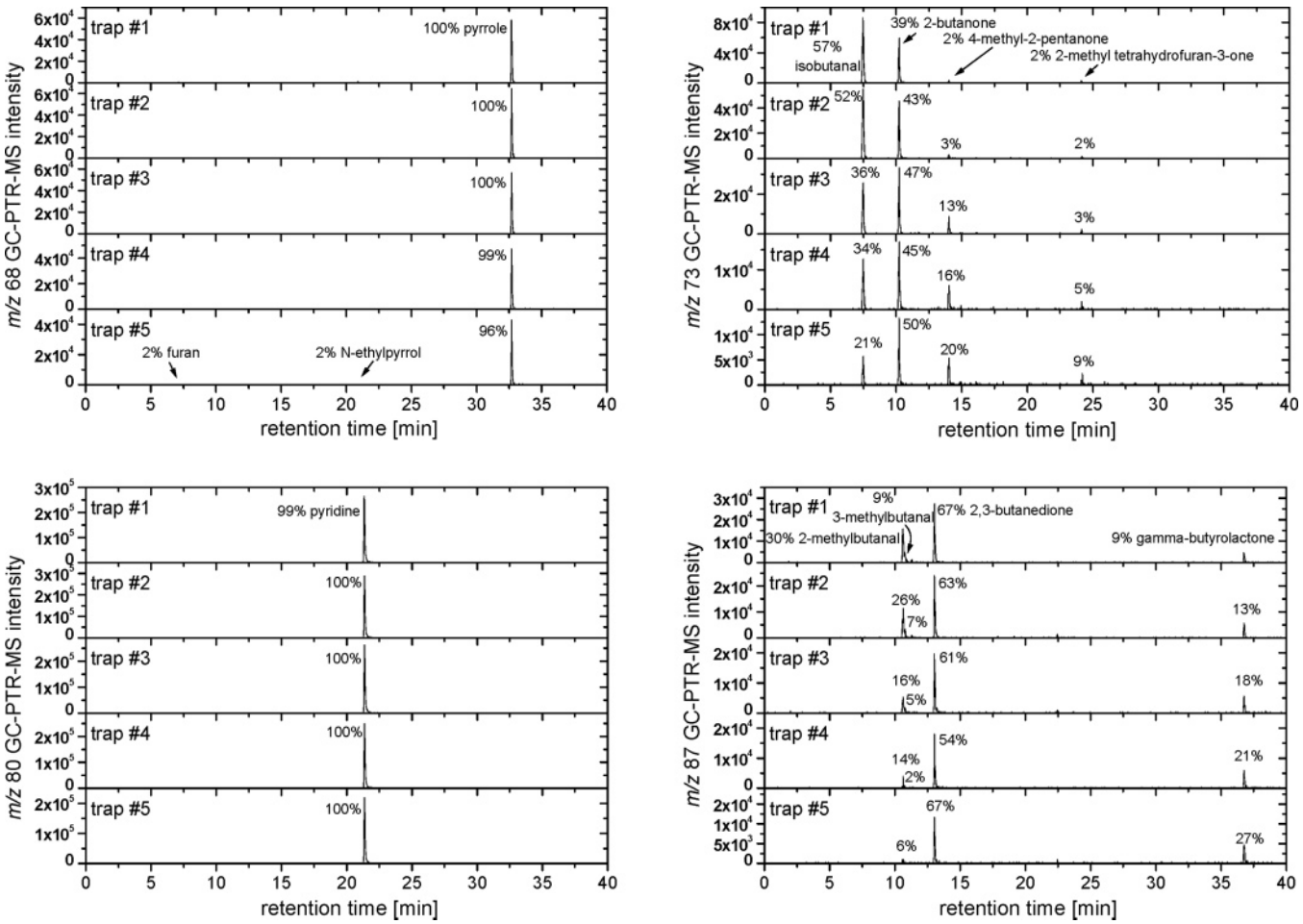

Figure 8. Unambiguous identification at different time frames (traps 1−5) of the molecules assigned to ion mass *m*/*z* 68, 73, 80, and 87 shown in Figure 5.

indicating that essentially only one single compound contributes to the ion signal (with only traces from other VOCs). Hence, in an on-line PTR-MS measurement of coffee HS, the ion masses at m/z 68, 75, 80, and 95 can be assigned to pyrrole, methylacetate, pyridine, and 2-methylpyrazine, respectively. The coupling of PTR-MS with GC/MS, as introduced here, allows identifying and quantifying the VOCs that contribute to a single PTR-MS ion signal.

The assignment and the related contributions are valid only for the 120-s time window trapped on the Tenax trap 1, as the relative concentrations of the identified molecules may change over time. To assess and quantify these changes, a series of Tenax traps (traps 1−5 in Figure 5), trapped at consecutive time windows, were analyzed. Figure 8 shows how the related percentage contributions for the ion traces at m/z 68, 73, 80, and 87 change over time. One can observe that in the case of m/z 68 and 80 the relative contribution to the molecules pyrrole and pyridine stays nearly 100% all over the HS measurement time (Figure 5). In the case of m/z 73 and 87, the composition changes with time. This is most likely due to the fact that compounds that are more volatile will be released more efficiently than relatively less volatile ones. As an example, 2-methylbutanal (partition coefficient $K_{37°C} = C_{air}/C_{liq} = 2.7 \times 10^{-2}$ measured according to Karl et al.[23]) has a decreasing contribution to the PTR-MS ion trace m/z 87 while compounds such as 2,3-butanedione ($K_{37°C} = 2.2 \times 10^{-3}$) and γ-butyrolactone ($K_{37°C} = 4.4 \times 10^{-6}$) show an increasing contribution with time.[24]

Tenax Trapping Efficiency. The use of Tenax traps is a good compromise for analyzing complex food systems such as coffee where a large number of compounds with very different volatilities need to be trapped and subsequently thermally desorbed while ensuring low background contamination after heating and limiting degradation or irreversible adsorption.[25] Yet, a well-known problem of any trap is the variable trapping efficiencies depending on the molecule's physical properties. The trapping is less efficient for small polar compounds such as methanol and acetaldehyde. Depending on the sample trapped on the Tenax cartridge, this may cause problems for relative (and eventually absolute) quantification. In contrast, the Tenax trap has the advantage that water adsorption is very inefficient, allowing the trapping of VOCs from vapor-saturated HS samples, such as the HS of hot coffee beverages. To confirm the different trapping efficiencies, the VOC concentration of coffee HS was measured before and after the Tenax trap.

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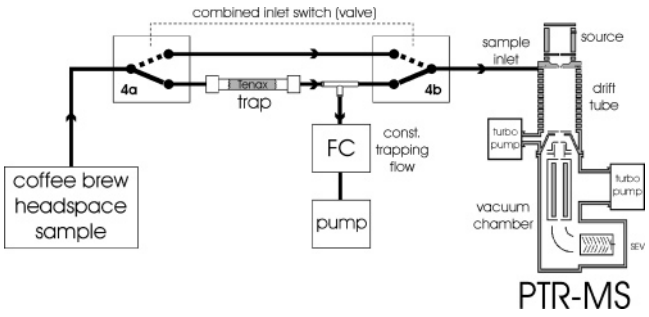

Figure 9. Setup to measure the trapping efficiency of Tenax traps. See text for more details.

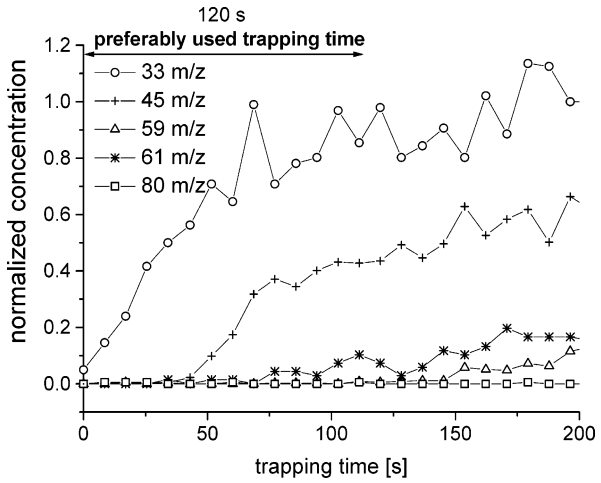

Figure 10. Normalized trapping efficiency for some volatile compounds in a coffee sample. See text for more details.

Figure 9 shows the experimental setup for carrying out the measurement by switching the valves 4a and 4b simultaneously, thus obtaining the corresponding concentrations. Figure 10 shows the results of the measurement where the concentration before the Tenax trap had been used for normalization. The trap contained 100 mg of absorbent, and the trapping flow rate was kept constant at 50 sccm (FC). One can see that during the chosen trapping time methanol (m/z 33) is only partially trapped already from the very beginning, whereas acetaldehyde (m/z 45) starts to get insufficiently trapped after 40 s. This corresponds to a breakthrough of 330 mL/g of Tenax under our specific conditions. In conclusion, only ~30% of the methanol and 50% of acetaldehyde are trapped using a trapping time window of 2 min. The other VOCs shown in Figure 10 are trapped close to quantitative. This measurement can be used to correct for the differences in trapping efficiency and hence allows for a more proper quantification of coffee HS compounds.

Another well-known problem of using Tenax traps is the degradation of thermolabile molecules. Methylmercaptan and, in general, thiols are important flavor compounds in coffee that are likely to degrade under thermal stress. However, it is possible, indeed, to monitor this odorant as a trace compound in coffee because its relative contribution to PTR-MS ion trace at m/z 49 is 100% (data not shown). The measured trapping efficiency using the above-mentioned method is 70%. Furthermore, a degradation of 70% was observed when injecting a well-defined amount of methlymercaptan into the GC column. In conclusion, considering the whole setup from sampling to GC detection, only ~21% of the HS concentration reaches the PTR-MS detector at the end of the GC column. The quantification of differences in trapping efficiencies and eventual degradations are needed, to determine the contribution of various compounds to the actual HS concentrations (see Figures 7 and 8).

CONCLUSION

The performance of the PTR-MS setup, including the various novel features introduced here, was first described in detail and characterized based on three parameters, using a model system: resolution (compound separation efficiency), range of linear response, and detection limits. It was concluded that the performance of the PTR-MS detector is comparable with that of a standard EI-MS while preserving the salient and unique features of PTR-MS.

The performance was then demonstrated on a practical application, using coffee as an example. The dynamic PTR-MS HS spectrum of a freshly prepared espresso was analyzed, and nine selected ion signals were fully assigned in order to demonstrate the approach on a complex food system. It should be stressed that several known impact compounds of coffee[26,27] could be identified, such as 2,3-butandione, 2,3-pentanedione, isobutanal, and 2-/3-methylbutanal. However, there are still several key odorants occurring in very low concentrations that cannot be monitored by PTR-MS. This requires further improvement of the sensitivity.

These technical and analytical developments open new avenues to a precise and quantitative application of PTR-MS to on-line VOC analysis. It is expected that it will accelerate our understanding of dynamic volatile release phenomena in fields such as food processing (e.g., process monitoring/control, aroma formation) and food consumption (nose-space analysis) and become a standard analytical tool for dynamic VOC analysis.

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