Technical Note

Optically Heated Ultra-Fast-Cycling Gas Chromatography Module for Rapid Separation of Direct Sampling and Online Monitoring Applications

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Optically Heated Ultra-Fast-Cycling Gas Chromatography Module for Rapid Separation of Direct Sampling and Online Monitoring Applications

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ABSTRACT: This work describes an ultra-fast-cycling gas chromatography module (fast-GC module) for direct-sampling gas chromatography - mass spectrometry (GC-MS). The sample can be introduced into the fast-GC module using a common GC injector or any GC×GC modulator. The new fast-GC module offers the possibility to conduct a complete temperature cycle within 30 s. Its thermal mass is minimized by using a specially developed home-built fused silica capillary column stack and a halogen lamp for heat generation, both placed inside a gold-coated quartz glass cylinder. A high airflow blower enables rapid cooling. The new device is highly flexible concerning the used separation column, the applied temperature program and the integration into existing systems. An application of the fast-GC module is shown in this work by thermal analysis coupled to gas chromatography - mass spectrometry (TA-GC-MS). The continuously evolving gases of the TA are modulated by a liquid CO_2 modulator. Due to the rapid cycling of the fast-GC module, it is possible to obtain the best separation while maintaining the online character of the TA. Restrictions in separation and retention time shifting, known from isothermal and normal ramped fast-GC systems, are overcome.

INTRODUCTION

In the last decades, there has been a tendency to make conventional gas chromatography (GC) ovens smaller, portable, power efficient and to develop fast-GC systems. Resistive heating technology may be a suitable approach to realize these goals. Resistively heated GC ovens exist in various types with several sample introduction methods according to their purpose. In general, there are two possibilities described in literature for resistive heating: 1) direct heating of a metal compound, or 2) by heating wires in coaxial or collinear arrangement to the analytical column.[1-3] In the first approach, homogeneous temperature distribution of a resistively heated metal column depends on a uniform wall thickness, which is challenging to provide. The second approach with heating wires requires sufficient insulation to ensure a homogeneous temperature, which is disadvantageous regarding the thermal mass and rapid cooling.

Important parameters for fast-GC ovens are the heating and cooling rates. Resistive heating enables very fast heating and is therefore the technique of choice for commercial fast-GC systems. For example, Agilent's Low thermal mass (LTM) module has a maximum heating rate of 30 K/s and a cooling rate of 8 K/s (250–50 °C in 25 s) without cryogenic consumables.[4,5] Recently, Romano et al. reported that their fast-GC technology, which also uses resistive heating, achieves cooling rates higher than 7.5 K/s (200–50 °C in less than 20 s).[6] Fialkov et al. gave 33.3 K/s for heating and 29 K/s (340–50 °C in 10 s) for cooling as performance information for their LTM fast-GC. At these velocities, they are able to conduct complete analysis cycles in less than 1 min.[7]

Harder and Walte presented a GC oven heated by infrared (IR) radiation.[8,9] They place a halogen lamp in the center of a cylindrical 3 m (steel)-capillary. In contrast to resistive heating, IR heating performs without any wires, fibers or insulation around the column. They use a closed furnace design with a movable lid. The reported separation (heating) and cooling times were approximately 5 and 2 min, respectively.

However, the aim of this work was to achieve a complete temperature sequence within 30 s, including heating and cooling. Short and repetitive cycles are necessary to fit the requirements of online measurements. Extreme heating rates are usually not necessary or beneficial, because the separation power of the column is not used efficiently in this case. On the contrary, rapid cooling remains the major issue. The separa-

tion of analytes in GC takes place during heating. Therefore, the heating duration should be maximized in order to obtain the best separation performance. Consequently, the cooling time should be minimized within one sequence.

The intension was to increase the cooling rates and therefore the duty cycle of the fast-GC module. Employing IR radiation for heating similarly to Harder and Walte and minimizing the thermal mass of the separation column, faster cooling rates were realized. Of course, heating rates of lamp-based GCs are not competitive with those using resistive heating, but they are still sufficient. Details of the construction will be described in the experimental section.

As mentioned above, many sample injection methods are known. A fast-GC sample can be introduced, for example, with a common GC injector (liquid), or it can be coupled to any kind of online gas source with a GC×GC (gaseous) modulator. Various techniques examine online continuous processes coupled with an additional fast-GC step. Eschner et al. reported direct injection online puff-resolved isothermal fast-GC measurements of cigarette smoke. Amirav et al. used fast-GC technology for open probe analysis of various samples.[10,11] Romano et al. coupled a fast-GC to proton transfer reaction - mass spectrometry (PTR-MS) for preselection and to gain additional separation power for wine analysis. Saraji et al. performed modulated evolved gas analysis to get additional chromatographic separation.[6,12]

Our new ultra-fast-cycling gas chromatography module (fast-GC module) can be adapted easily into hyphenations with online or offline gas sources. In the following section, we demonstrate the advances by coupling it to thermal analysis - mass spectrometry (TA-MS) to reach a TA-GC-MS system.

The continuously evolving gas of the TA was modulated in 30 s cycles to preserve the online character of the TA and to obtain additional chromatographic information. Previously, Saraji et al. and Wohlfahrt et al. presented a hyphenation of TA-GC-MS, using a modulated fast-GC step with a modulation cycle of 30 s at a TA heating rate of 10 K/min.[12,13] They state that in TA, gases evolve over a longer time period and therefore, a time resolution of 30 s or 5 K, respectively can be defined as quasi-online. One major drawback of the reported setup is caused by the use of a normal GC oven. The applied slow temperature ramp in the GC oven causes heterogeneous GC conditions throughout one measurement. This results in different separation behaviors of the same molecules, leading to shifting retention times. Based on this particular circumstance, the need for a fast-GC that offers a whole and unchanging temperature program for every single modulation cycle arose.

EXPERIMENTAL SECTION

Fig. 1 shows the construction from the uncovered fast-GC module and a photograph of the inside components. The entire construction including details of the used accessories (blower, power supply, control unit) can be found in the supporting information (Fig. S-1). Inside the metal framework in Fig 1A, a gold-coated quartz glass protection cylinder (1) (Netzsch-Geraetebau, Selb, Germany) is placed. The coating improves reflection of the IR radiation. Through a hole in the glass cylinder, along the heated transfer path (2), the capillary is guided to the analytical system. The core of the device inside the glass cylinder is depicted in Fig. 1B: A halogen lamp (3) as heat source in the center of the column stack (4). The thermal mass is again reduced and a nearly unobstructed airflow through the glass cylinder is provided. This leads to the effective cooling of the column stack with ambient air. The integral column stack was built using an embedded design. If the required bending radius (3 cm) can be achieved, different capillary parameters, e.g., other dimensions and coatings, are possible. In the present work, a Rtx-50 capillary column (Restek, Bad Homburg, Germany) with an inner diameter of 250 µm and a film thickness of 0.25 µm was chosen. As reported, a 3 m column is a good compromise between separation power and retention time, to allow all molecules to pass through the column during one isothermal cycle.[12,13] This was verified by test measurements.

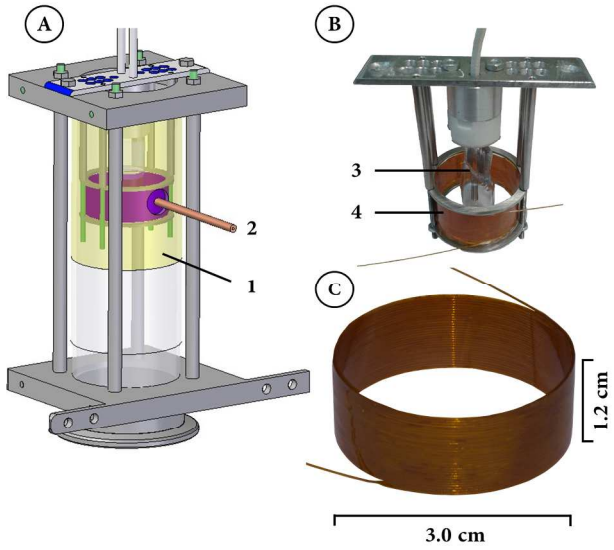

Figure 1. Drawing of the fast-GC oven module (1A) with the gold-coated glass cylinder (1) and the heated transfer path (2). 1B pictures the inner framework with a halogen lamp (3) inside the column stack (4). 1C shows a home-built column stack (3 m of column).

The key innovation of the presented fast-GC system is the column stack. Fused silica column is embedded between two layers of polyimide tape. The column was agglutinated with polyimide glue and cured. Polyimide is stable at high temperatures and provides thermal conductivity. Having a column stack as described, the thermal mass is minimal. Fig. 1C shows a column stack with a 3 m capillary column. Moreover, a standardized manufacturing process guarantees that quality, size and performance of the column stacks are reproducible.

A standard 24 V/150 W halogen lamp (Halostar 64465, Osram, Munich, Germany) was used as heat source in the fast-GC. The temperature of the column stack was controlled by a remote-controlled power unit supervised via a USB-module using custom software (Roth ITK, Munich, Germany). After receiving an external trigger signal, the described control unit initializes the programmed sequence. Sequences can be adapted to specific needs, leading to individual temperature programs. In the present work, three different sequences were used. The cooling begins when the heating current drops below a certain threshold that causes relay switching. The blower

cools the inside of the cylinder with a maximum airflow of 102 m³/h.

The fast-GC module was integrated into an evolved gas analysis setup (Fig. S-2), similar to the setup described by Wohlfahrt et al.[13] Evolved gases from the thermal analytical device (recent work), STA 449 F3 Jupiter (Netzsch-Geraetebau, Selb, Germany), were guided via a heated transfer path to the GC×GC (Thermo Trace GC×GC, Thermo Fisher Scientific, Waltham, USA), used as an interstage oven. Here the modulation of the evolved gases takes place. A modulation cycle of 30 s is provided by a cryogenic dual-jet CO_2 modulator. To eliminate and avoid cold spots, all transfer paths in the entire setup, including the interstage oven, are heated to at least 250 °C. Finally, the evolved gases are detected by an orthogonally accelerated time-of-flight mass spectrometer (CTOF, Tofwerk, Thun, Switzerland) with electron ionization (EI) at 70 eV. Please note, the analyte gases evolve within the TA at ambient pressure. The pressure difference between the TA the high vacuum (10^{-5} mbar) present in the mass spectrometer is the only driving force for analyte transport. No additional pressure is applied to the fast-GC module.

To demonstrate the advantages of the rapid fast-GC module cycling compared to an isothermal GC step, TA-GC-MS measurements were carried out using a mixture of several selected substances. This mixture contained the following substances: o- and p-xylene (isomers), nonane and naphthalene (isobars), hexane, dodecane and pentadecane (alkanes). This standard mixture was heated in the TA at 10 K/min in N_2 atmosphere (20/180 ml/min protective/purge gas flow). On the one hand, previous experiments with 3 m 250 µm Rtx-50 column showed that separating volatiles like xylenes requires lower temperatures than larger and less volatile molecules, e.g., naphthalene or pentadecane. On the other hand, higher temperatures are necessary to avoid peak broadening or if analytes cannot pass the column within one modulation cycle, so-called wrap-around. These drawbacks can be overcome by using the fast-GC and conducting complete temperature sequences within 30 s instead of isothermal GC steps. By application measurements using tobacco as very complex natural sample the performance of the developed technology could be proved (Fig. 5 and 6). Detailed information about the sample and the TA settings are given elsewhere.[14] Differing from the described settings were the gas flow (20 ml/min protective, 60 ml/min purge gas flow), the ionization (electron ionization at 70 eV) and the sample weight (10 mg). The fast-GC module was equipped with 3 m of250 µm Rtx-5 or a BPX35 column.

The acquired chromatograms were processed and the associated figures were prepared using the post-processing software Tofware (Tofwerk, Thun, Switzerland).

RESULTS AND DISCUSSION

Three 30 s-temperature programs with a maximum temperature of 285 °C were tested (Fig. 2). Corresponding heating and cooling rates are given in Tab. 1. Details regarding the applied power and time steps can be found in Table S-1. Please note that beside these examples any other desired sequence is programmable. Maximum temperature limitations depend only on the manufacturer's specification of the employed column, the polyimide tape and the applied heating power. With a 150 W halogen lamp temperatures up to 350 °C were possible. Temperature data were gathered using a column stack, prepared as described in the experimental section, with an integrated 0.25 mm type K temperature sensor at an acquisition rate of 50 Hz. As the temperature is controlled by the power of the halogen lamp, the program was adapted empirically to the desired temperature profiles. The profiles in Fig. 2 differ in their characteristics and their field of application. Profile A (40–255 °C, Fig. 2A) is suitable for more volatile samples, while profile B (70–285 °C, Fig. 2B) is shifted +30 °C and covers lower volatile compounds than A. Profile C (95–280 °C, Fig. 2C) can be considered to be a universal application profile due to its higher starting temperature, a long heating duration and very short cooling time.

Temperature program C (95–280 °C) was chosen to demonstrate the benefits of the developed fast-GC module in TA-GC-MS with the aforementioned standard mixture. To prove the reproducibility of repeating sequences, the temperature was recorded for 60 sequences (30 s each).

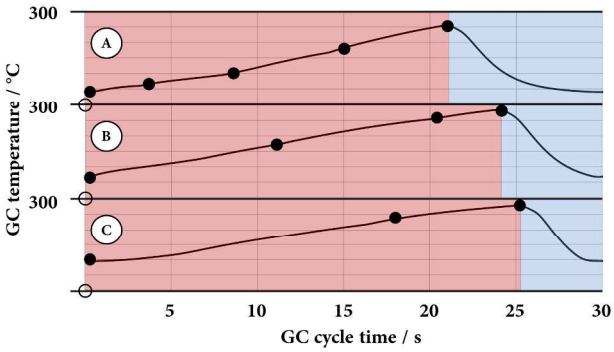

Figure 2. Three fast-GC temperature profiles with the black dots tagging the time steps when the control unit sets new power values (see Tab. S-1 for details).

The standard deviation of the average minimum (93.63 °C) and the average maximum temperature (280.35 °C) are only ± 0.74 °C (0.79%) and ± 0.81 °C (0.29%), respectively. In addition to the temperature stability between sequences and complete runs, we compared the temperature profiles of different fast-GC modules of the same type. The data revealed similar temperature profiles, demonstrating the high reproducibility of this technique (Fig. S-3).

Table 1. Heating and cooling rates of the measured temperature profiles A, B, and C.

Profile	Effect	Rate [K/s]	Time [s]
A	Heating	10.3	21.0
	Cooling	24.3	9.0
B	Heating	9.1	24.0
	Cooling	37.3	6.0
C	Heating	7.4	25.3
	Cooling	39.2	4.8

In Fig. 3A, the separation of the standard mixture using temperature program C (95–280 °C) is depicted. The graph is a two-dimensional projection with the TA temperature on the x-axis and the corresponding retention time of the analytes on the y-axis. This type of graphical representation is similar to

those used in GC×GC. The set of n-alkanes, i.e., hexane (1), nonane (2), dodecane (5) and pentadecane (7) as well as the isomers p-xylene (3) and o-xylene (4) are baseline separated. Even naphthalene (6) passes the fast-GC without extensive peak broadening or other restraints. The peak widths (full width at half maximum, FWHM) are quite similar and nearly independent of the component properties due to the rapid temperature ramping. For example, the hexane peak (1) in Fig. 3B has a peak width of 240 ms compared to 280 ms and 290 ms of p-xylene (2) and naphthalene (6), respectively.

In GC and fast-GC one major performance benchmark is the retention time repeatability. The variance should be as small as possible within one (intra-run) and between several (inter-run) measurements to ensure the reliability of gathered retention times (RT) for specific analytes. For the here presented fast-GC module a set of three measurements has been evaluated. Fig. 3C illustrates the RTs for three sample measurements. The error bars represent the intra-run standard deviation of the respective peaks. Values between 0.09-0.18 s have been achieved. The inter-run repeatability ranges from 0.30 to 0.40 s (details are given in Tab. S-2). The higher inter-run deviation is mainly caused by an overall time shift of about 0.5 s between measurements C1 and C2/C3. Even though this circumstance ascribed to internal or external factors cannot be explained by the authors, they like to emphasize that the relative RTs remain constant.

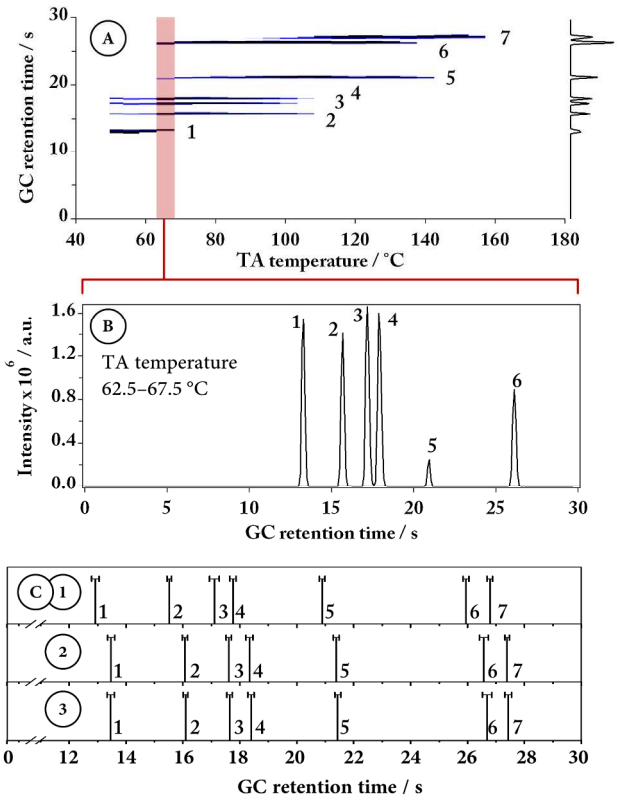

Figure 3. Two-dimensional plot of the standard mixture (hexane (1), nonane (2), p-xylene (3), o-xylene (4), dodecane (5), naphthalene (6), pentadecane (7)) with the TA temperature (40–180 °C) on the x- and corresponding fast-GC retention times on the y-axis. 3B:One-dimensional chromatogram from the TA temperature range between 62.5 and 67.5 °C. 3C: Inter-run (C1-3) and intra-run retention time repeatability (error bars). For details see Tab. S-2 in the supporting information.

One major advantage of the fast-GC is its independence from the TA. This becomes obvious when a direct comparison is made to the former work of Saraji et al.[12] (Fig. 4; enlarged version available in Fig S-4). They noted difficulties for compounds that are released from a Diesel fuel sample over a larger TA temperature range. The GC temperature is not constant (Fig. 4E) and thus, the GC retention times shift. This is shown in Fig. 4G: the rising GC temperature leads to a severely decreased retention time for naphthalene. The main achievement of the new fast-GC module is the maintenance of constant GC conditions in every cycle throughout the entire TA run. The GC temperature course of the fast-GC is presented in Fig. 4F. In comparison to Fig. 4G, this results in constant retention times for naphthalene and nonane (Fig. 4H).

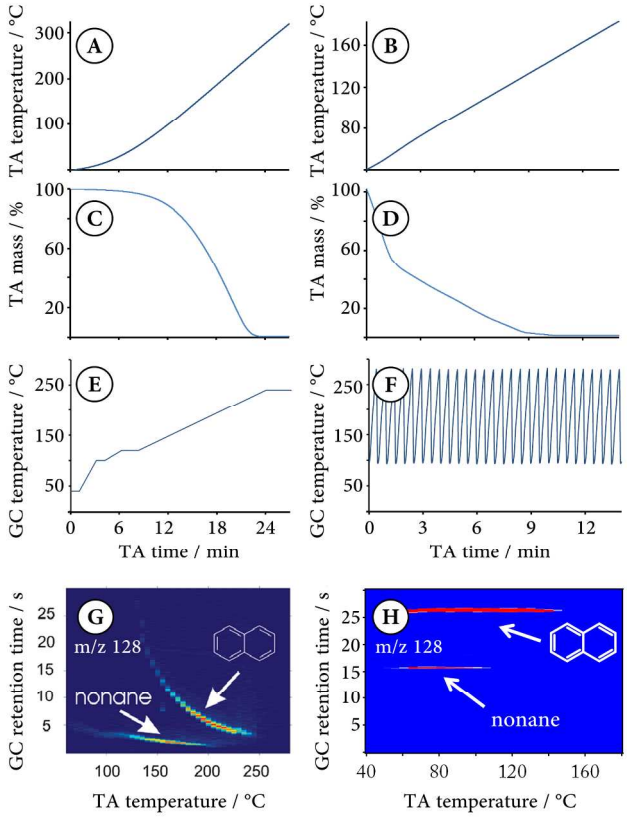

Figure 4. The left column shows parameters and results from a ramped TA-quasi isothermal fast-GC-MS analysis of a diesel sample[12]. The right column depicts parameters and results from the here introduced TA-GC-MS analysis of the standard mixture (Fig. 3). 4A/B: TA temperature program: 4C/D: TA mass loss curve. 4E/F: Quasi-isothermal[12]/fast temperature cycling GC temperature profiles. 4G/H represent a comparison of the two-dimensional contour-plots of m/z 128 (assigned to naphthalene and nonane). 4G was reproduced from Saraji et al.[12], ©2010 American Chemical Society.

To evaluate the performance of the fast-GC module with real world complex samples, thermal analysis of bio mass (here tobacco) was chosen for demonstration purposes. The authors reported earlier on tobacco, investigated with TA-MS.[14] They elucidated three significant TA temperature steps (180–210,

250–280 and 290–320 °C) showing different chemical compositions of the evolved gases. The first and the second temperature step showed high abundances at m/z 162, which were assigned to nicotine, according to literature.[14] Fig. 5 presents the TA-GC-MS results of the same tobacco sample (3R4F). With the achieved separation, additional retention time information is obtained. This assists a more comfortable and confident peak assignment. We determined a RT of 24.04 s (±0.08 s, N=10) for pure nicotine. As m/z 162 in the tobacco sample shows also a RT of 24.10 s (±0:15 s, N=43) it could be assigned to nicotine. Additionally, the chromatographic separation allowed peak assignment according to its EI fragment pattern with the NIST chemical data base.

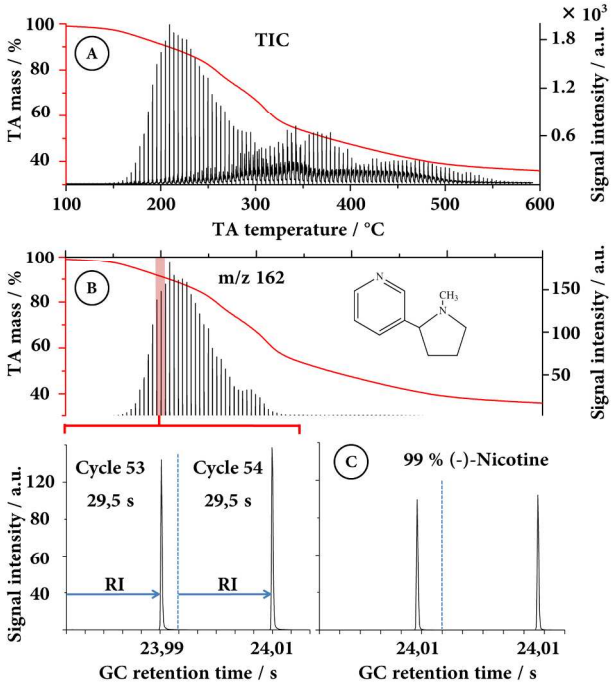

Figure 5. Mass loss (red line) of 3R4F-tobacco during thermal decomposition and the corresponding total ion current (TIC). The modulated single ion count of m/z 162 is depicted in 5B and a zoom shows two modulation cycles. The retention times are similar to those of pure nicotine in 5C.

Furthermore, the authors discussed m/z 94 to represent most likely phenol, a typical thermal degradation product of hemicelluloses, sugars and lignin. The presence of the monoterpene limonene was also assumed.[14] In this study, similar measurements applying the fast-GC module prove these suggestions and emphasize the technical advantages.

Fig. 6A shows the single ion count (SIC) of m/z 94 extracted from the TG-GC-MS measurement presented in Fig. 5A. Three cycles at different TA temperatures are enlarged in Fig. 6B-D. Peaks with RTs of 15.35, 15.74 and 15.55 s could be assigned to phenol according to their EI fragment pattern. Please note, that the RT stays the same (with a certain deviation) within the complete measurement independently from the present TA temperature. The arising second signal in Fig. 6D at 16.53 s could be assigned to limonene, also through library search. Therefore, the suggested presence of phenol and limonene was proven.

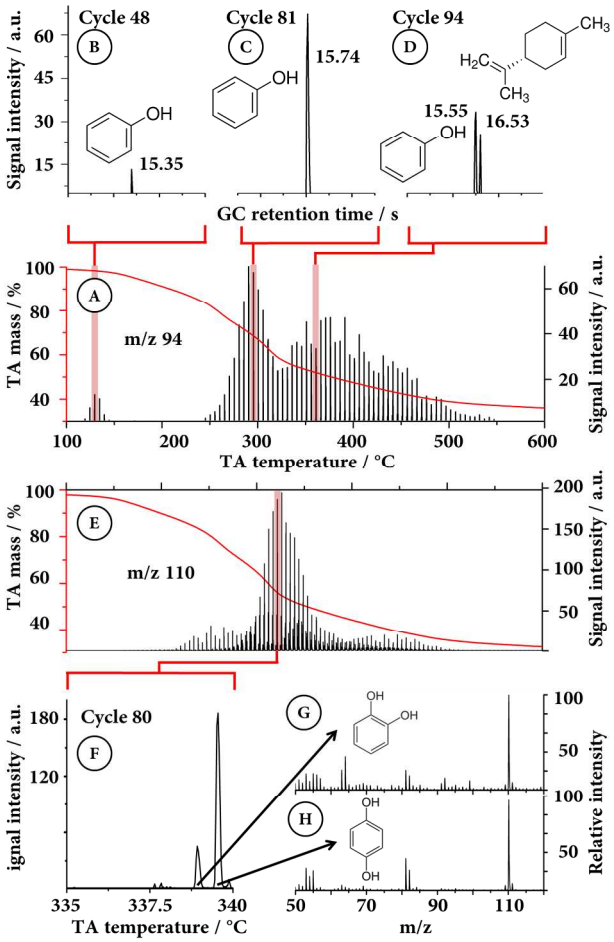

Figure 6. SICs of m/z 94 (A) and m/z 110 (E) during thermal decomposition of tobacco and the respective mass loss (red line). 6B–D show single modulation cycles at different temperatures. The independence of retention time from the TA temperature is emphasized. The center peak was assigned to phenol, the second peak in 6D a fragment of limonene. At the modulation cycle 80 (at 335–340 °C TA temperature) an isomeric separation of o- and p-dihydroxybenzene (catechol 6G, hydroquinone 6H) was worked out.

An example for the separation power of the fast-GC module was given above by separating isobaric (naphthalene/ nonane) or isomeric (e.g. o-/p-xylenes) compounds in a standard mixture. Fig. 6E-H shows a separation of isomers within the tobacco sample. The modulation cycle 80 at 335–340 °C of m/z 110 (Fig. 6F) reveals two major peaks, which can be assigned to o-/p-dihydroxybenzene (catechol/hydrochinone) through comparison of the EI fragment pattern (Fig. 6G/6H). So, despite the ultra-fast-cycling of the fast-GC module and within a very complex natural sample, it is possible to separate isomeric compounds.

SUMMARY AND OUTLOOK

An optically heated low thermal mass fast-GC module was developed and tested successfully. The applicability for evolved gas analysis was demonstrated by standard measurements as well as real world complex samples. The perfor-

mance was compared to previous work in the literature. The particularly rapid cooling rates allow comparatively long heating times for maximum separation performance within each individual sequence. The fast-GC module is an easily adaptable stand-alone module and the parameters of operation (e.g. applied fused silica column, temperature program) can be chosen freely. Therefore, it is possible to include and upgrade other existing systems to obtain more information from complex samples and processes by providing additional separation power. Essentially, the fast-GC module is created for all direct sampling mass spectrometric or spectroscopic on-line methods. The high cycling speed suggests using the principle for realization of a rapid cycling second dimension or in combination with soft ionisation mass spectrometry for multi-dimensional separation.[15,16]

ASSOCIATED CONTENT

Supporting Information

Fig. S-1–4, Tab. S-1–2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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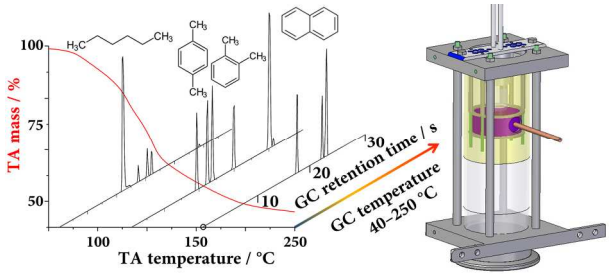

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