Technical Note

# Hyphenation of thermal analysis to ultra-high resolution mass spectrometry (FT-ICR MS) using atmospheric pressure chemical ionization (APCI) for studying composition and thermal degradation of complex materials

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# Hyphenation of thermal analysis to ultra-high resolution mass spectrometry (FT-ICR MS) using atmospheric pressure chemical ionization (APCI) for studying composition and thermal degradation of complex materials

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## Abstract

In this study, the hyphenation of a thermobalance to an ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometer (UHR FT-ICR MS) is presented. Atmospheric pressure chemical ionization (APCI) is used for efficient ionization. The evolved gas analysis (EGA), using high resolution mass spectrometry allows the time-resolved molecular characterization of thermally induced processes in complex materials or mixtures, such as biomass or crude oil. The most crucial part of the setup is the hyphenation between the thermobalance and the APCI source. Evolved gases are forced to enter the atmospheric pressure ionization interface of the MS by applying a slightly over-pressure at the thermobalance side of the hyphenation. Using the FT-ICR exact mass data, detailed chemical information is gained by calculation of elemental compositions from the organic species, enabling a time and temperature resolved, highly selective detection of the evolved species. An additional selectivity is gained by the APCI ionization, which is particularly sensitive towards polar compounds. This selectivity on the one hand misses bulk components of petroleum samples such as alkanes and does not deliver a comprehensive view, but on the other hand focuses particularly on typical evolved components from biomass samples. As proof of principle the thermal behavior of different fossil fuels: heavy fuel oil, light fuel oil and a crude oil, and different lignocellulosic biomass, namely beech, birch, spruce, ash, oak and pine as well as commercial available softwood and birch-bark pellets were investigated. The results clearly show the capability to distinguish between certain wood types through their molecular patterns and compound classes. Additionally, typical literature known pyrolysis biomass marker were confirmed by their elemental composition, such as coniferyl aldehyde ($C_{10}H_{10}O_3$), sinapyl aldehyde ($C_{11}H_{12}O_4$), retene ($C_{18}H_{18}$), and abietic acid ($C_{20}H_{30}O_2$).

## Introduction

Evolved gas analysis (EGA) has become a powerful and widely used tool for the analysis of products generated by thermally induced processes, such as vaporization or pyrolysis.[1–3] Besides the hyphenation of spectroscopic techniques such as infrared spectroscopy[4] and separation via fast gas chromatography (GC) or mass spectrometry (MS) is often used[3,5]. Thermally induced processes, such as pyrolysis and reforming of heavy crude oil distillation fractions or thermal degradation of lignocellulosic biomass, lead to very complex evolved gas mixtures with several hundred up to thousands of components. These materials are studied with increased effort due to several reasons, as the increasing demand of energy needed by mankind, the limited availability of light fuel and the climate change as well as health aspects related to fossil fuel combustion. As a result it is necessary to understand the underlying processes and reactions.

A variety of different thermal analysis/mass spectrometry hyphenations are available commercially or used in research. The sample inlet is either based on a heated transfer capillary[6] or a skimmer system for low volatile species.[7–9] Most often electron ionization (EI) is used to fragment the evolved compounds and receive structural information.[1,2] Early work for soft ionization was done by Zoller et al. in 1999, using thermogravimetry (TG) photo ionization (PI) MS for characterization of the pyrolysis of different rank coals.[10] Recently single photon ionization (SPI) and resonance enhanced multiple photon ionization (REMPI) utilizing time-of-flight (TOF) systems have been presented.[11–14] These soft ionization approaches were applied for the thermal induced EGA of polymers,[8,15–17] crude oil,[18–20] biomass,[21,22] coffee[23] and tobacco[6].

The mass analyzers, most often quadrupole or TOF systems, usually lack in resolving power to distinguish between different species with a very small difference in exact mass. One approach to overcome this issue was shown by Saraji-Bozorgzad et al. in 2010 using a TG-GC-setup.[17] Nevertheless the vast complexity of pyrolysis gas lead to the limitation that in many cases isobaric molecules with the same nominal mass are not separable. Another approach is the hyphenation of a thermobalance to an ultra-high resolution MS system with a soft ionization source, which enables the characterization of high complex mixtures at the molecular level by means of elemental composition. However Prime et al. [24] and other [25] have described a atmospheric pressure chemical ionization (APCI) quadrupole mass spectrometer already in the 80s and early 90s. Besides this, pyrolysis mass spectrometry utilizing high resolution mass analyzer, i.e. Fourier transform ion cyclotron resonance devices, was carried out in the 90s, e.g. for the characterization of polymer additives [26] and brominated fire-retardant polymers [27].

For the identification and quantification of marker compounds from biomass decomposition as vast variety of instruments exists. Most often gas chromatographic instruments with and without derivatisation are used, optimized for separation power and sample preparation. They deliver structural confidence and good quantification results, nonetheless they can be seen as targeted approach and miss a high percentage of the complex emissions. Furthermore, if no flash pyrolysis system is utilized, the evolved gas have to be

sampled/trapped and a temperature resolved information is hardly feasible or only available within larger intervals. [28] [29]

In this study we demonstrate the hyphenation of a thermobalance to a Fourier transform ion cyclotron resonance (FT-ICR) MS with positive APCI. The main motivation of the study is to extend the capabilities of pyrolysis evolved gas analytics by utilizing high resolution mass spectrometry, in spite of the system being rather expensive and bulky compared to classical pyrolysis GC-MS devices. Nonetheless the thermobalance allows a controlled and reproducible pyrolysis with various heating rate and gas mixture variabilities as well as the possibility for high sample mass input. The later may lower the effect of introducing inhomogeneous solid biomass matter. For method validation and evaluation complex matrices such as lignocellulosic biomass and crude oil were exemplary investigated. APCI was chosen as ionization technique since it is commonly applied for complex matrices in petroleomics and pyrolysis oil investigation [30] [31]. Even if some major drawbacks are described in literature, e.g. adduct formation processes, non-universal ionization and water vapor pressure dependencies, a high variety of compounds can be analyzed, a high sensitivity towards oxygenated species is observed and it constitutes a robust setup. [32] [33] Customized data interpretation tools for time resolved calculation of elemental composition were applied and characteristic molecular patterns as well as typical marker species described in literature are shown.

## Material and Method

**Instrumentation.** A commercial thermobalance (STA 409 PG Luxx, Netzsch Gerätebau GmbH, Selb, Germany) was utilized for this study. The temperature in the oven was ramped from 50 to 600 °C with a heating rate of 10 K/min using an $Al_2O_3$ sample pan and applying an inert $N_2$ atmosphere. The summed gas flow through the thermobalance was set to 80 mL/min comprising 20 mL/min protective gas and 60 mL/min purge gas. A custom interface, which was used in previous studies and described elsewhere,[6] was heated to 300 °C and the evolved gas flow was split into two parts: one flows through a heated deactivated capillary (TSG: 320450-D-10, 2.5 m, 320 µm ID, 450 µm OD) via a GC-oven into the MS and the other vented into the waste. A known, constant overpressure at the thermobalance side was obtained by adjusting the vent line restriction by a needle valve. For ionization an APCI source with a specialized gas phase inlet was used.[34] The ion source worked under atmospheric pressure and with nebulizer gas flow and drying gas flow set to 3 L/min at 320 °C and 2 L/min at 220 °C, respectively. The corona current was set to 3 µA. Accurate mass measurement was done using a commercial 7 T high resolution Fourier transform ion cyclotron resonance mass spectrometer (Apex Qe series II, Bruker Daltonics, Billerica, MA, USA / Bruker Daltonics GmbH, Bremen, Germany) in positive ion mode. The entire setup is shown schematically in Figure 1 as well as photographically in the supporting information (Figure S-1).

The observable mass range was limited to m/z 107.5 - 1000 Da. Transient length per spectra was set to 2.097 s corresponding to four million data points resulting in a resolving power of roughly 280,000 @ m/z 400. Four spectra were accumulated per scan to enhance signal-to-noise-ratio and improve sensitivity, resulting in a time resolution of roughly 10 s.

**Material.** For purpose of method validation and evaluation different petroleum related samples as well as lignocellulosic biomass based samples were analyzed. Briefly, three different petroleum related samples: heavy fuel oil (HFO), diesel fuel, according to DIN EN ISO 590 (LFO), and a North Sea crude oil (NSO); and nine different biomass samples: beech, birch, oak, ash, pine, spruce log wood as well as commercial birch-bark pellets and two charges of softwood pellets, were investigated.

**Data analysis and spectral interpretation.** Spectral interpretation of the acquired raw spectra was carried out using Bruker Daltonics Compass Data Analysis 4.0 SP 5 and MATLAB R2010b. Accurate mass measurement was calibrated externally using a mixture of fatty acid methyl esters ($C_{10}$ – $C_{24}$ FAME). A mass accuracy better than 1 ppm was obtained by internal calibration using mass signals of typical marker compounds for biomass decomposition and of alkylated rows of characteristic $CHO_x$- as well as CH-species for the petroleum samples (Table S-1 - S-4). Result lists including exact mass and intensity for signals with a signal-to-noise ratio (S/N) ≥ 6 were exported in ASCII-format for each spectrum, saved in a separate data file and imported to MATLAB. Automatic feature detection, of so called "region of interest", was carried out applying self-build MATLAB algorithms based on the approach of Tautenhahn et al. using a m/z-window of 5

ppm.[35] Generation of elemental compositions was performed using the following restrictions: $C_cH_hN_nO_oS_s$, c ≤ 100, h ≤ 160, n ≤ 3, o ≤ 10, s ≤ 2 and a maximum error of 1 ppm. For further validation, intensities of the $^{13}C$-isotope and existence of the $^{34}S$-isotope was used. Remaining features with more than one elemental composition for a measured m/z-value was finally limited by applying the "Seven golden rules" and common data analysis approaches from the field of petroleomics (e.g. DBE: -10 – 80, nitrogen rule, number of heteroatom's < 6, mass error). [36–40] The final output of the algorithm is a list of filtered elemental compositions and their time/temperature traces.

## Results and Discussion

In the following, the characteristics and most crucial aspects of the novel hyphenation are shown. The transport of evolved gases is realized by the pressure difference between thermobalance and ionization source, which is usually given when combining a vacuum ionization source at roughly $10^{-4}$ mbar, with a thermobalance, operating at atmospheric pressure conditions. Thereby only capillary length, diameter and temperature limit the total flow rate, so that it is assumed that a constant aliquot of the homogenous mixed evolved gas is transported and further ionized. Obviously this advantage is not given when coupling to an atmospheric pressure ion source. Operation of the ion source at reduced pressure was dismissed, since the ionization cell was designed and optimized for atmospheric pressure conditions.[34] Therefore, to obtain a driving force for the evolved gas to enter the sampling line, the pressure in the thermobalance was slightly enhanced. It turned out that a setting of 50 mbar gained the best results for the quality of mass spectra and sensitivity. Nevertheless, already 7 mbar of over pressure lead to sufficient signals in the mass spectrometer. An over pressure below this value showed almost no signals, whereas a higher pressure could cause condensation in sample room and balance. Pyrolysis characteristics, such as thermal effects, can be changed by applying higher operating pressures as shown by Basile et al. for various biomass samples [41]. Nonetheless effects were observed at several bars over pressure. Therefore it can be assumed that the here applied value of 50 mbar is much too low to influence the emission characteristics significantly.

One characteristic of atmospheric pressure chemical ionization is the specific ionization behavior, which is selective towards polar species. For example, typically oxygenated compounds and aromatic compounds are ionized, whereas e.g. alkanes are not. Thus important analyte classes are readily ionizable, while other compounds are suppressed. Therefore the characterization of trace components in a non-polar matrix is feasible. Concerning the ionization process mostly protonated ions were found. Evaluation of the ionization source with the FAME standard clearly showed that ionic oxidation, which is common to APCI, is not completely avoided but rather low and only detectable summing up a large number of spectra. As a result of the selectivity towards polar species the curve of total ion count (TIC) in Figure 2a - c does not fit perfectly to the mass loss. Drawback of the reduced sample weight applied is the relatively poor quality of the mass loss curves, mainly caused by the high impact of the upwelling correction. Nonetheless the petroleum samples (diesel, heavy fuel oil and crude oil) show a pure distillation/evaporation behavior with a rather gradual mass loss with increasing temperature. The sharp edge of the TIC trace of the diesel fuel at roughly 220 °C (Figure 2c) clearly points out, that cold spots or condensation, which would cause a massive tailing of the signal, is avoided as possible. In comparison to the diesel, the signal from the heavy fuel oil, a low volatile residue from crude oil, raises later at approx. 210 °C and decrease at higher temperatures of 500 - 550 °C. The TIC from crude oil, which inherently incorporates the distillation fraction from heavy and diesel fuel, spreads over the whole temperature interval from approximately 100 - 500°C.

Two main aspects limit the observed mass/volatility range: On the one hand the lower mass range is given by the mass analyzer itself at roughly 100 m/z due to ion transport optics and geometric setup. As a consequence, small pyrolytic products emerging at temperatures above 350°C are not observed.[18] On the other hand the upper mass boundary is given by the temperature of the sampling line and the interface. Very low volatile species condensate even at 300 °C and slowly re-evaporate from the surface, leading to carryover effects.

The contour plot of temperature versus m/z given in Figure 3a for NSO and in the supporting information for LFO and HFO (Figure S-3), exhibit a rather complex pattern with typical differences of 14.01565 Da and 15.994 Da, which account for $CH_2$- (alkylation) and O-building blocks, respectively. Additionally the distribution reveals a certain maximum in intensity with relatively smooth trend towards the edges which confirms the gradual mass loss of the thermobalance at the mass spectrometer level, although only a minor part of the organic species is ionized. The maximum m/z of roughly 380 observed for diesel fuel is reasonable for this middle distillate. In contrast, the heavy fuel oil reveals only a minor abundance of two ring aromatics, whilst the intensity weighted mean mass is 344 m/z. The crude oil covers species with a DBE from 0 to 15 peaking at 6. The most intense alkylated series originates from benzothiophene derivatives.

For biomass, thermodesorption and pyrolysis processes can be mimicked in the thermobalance. This allows the investigation of wood burning characteristics, since pyrolysis is a first step of wood combustion often overwhelming the oxidation to $CO_2$. It turned out that the major compound classes observed are CH- and $CHO_{1-8}$ (Figure S-2), especially birch-bark pellets showed an obvious high abundance of CH- and $CHO_1$ species. In contrast to wood-pyrolysis the petroleum samples revealed CH, $CHO_{1-2}$ and CHS as major compound classes (Figure S-3). Variance between the compound class patterns of the replicates was found to be between 5 - 15 %. In good agreement with literature the wood pyrolysis exhibit only pure hydrocarbons as well as oxygenated compounds, nitrogen and sulfur containing species were not found or with negligible intensity. Typical mass differences of 30.01057 m/z ($CH_2O$) were found as building blocks between the most intense homologue rows.

At the molecular level typical literature known wood combustion marker compounds were found.[42–45] These are mainly phenol derivatives and thermal degradation products of resin acids, with most likely sinapyl aldehyde ($C_{11}H_{12}O_4$), coniferyl aldehyde ($C_{10}H_{10}O_3$) and retene ($C_{18}H_{18}$) being the most important ones. It is important to highlight that these markers are here identified only by their elemental composition and existence in literature. $C_{18}H_{18}$ was only detected in the pine, spruce and softwood samples, but due to the relatively low ionization efficiency of hydrocarbons rather less abundant. From the softwood pellet manufacturer it is known that the softwood pellets consists partly of pine and spruce, which is consistent with the data. The concept of using the ratio between coniferyl aldehyde as typical softwood marker and sinapyl aldehyde as typical hardwood marker to differentiate between hard and soft wood can also be

applied here.[42,45] It turned out that the softwood pellets, pine and spruce reveal ratios of 17, 19 and 21, respectively. Whereas ash, beech, oak and birch bark pellets showed ratios below one. With this concept coniferous and deciduous wood types were clearly separated from each other. The birch bark pellet exhibit some unique characteristics clearly observable in Figure 3b. The molecular pattern is shifted towards higher m/z-values compared to the other biomass samples, such as oak (Figure 3c) and pine (Figure 3d). The signals can mainly be assigned to relatively saturated (low DBE) CH-class species, the most prominent one is $C_{30}H_{48}O$, most likely dehydro betulin, which might be the product of water loss from betulin ($C_{30}H_{50}O_2$).[46] In contrast the petroleum samples revealed a significant higher number of detected features with 2060 and 3099 for the crude oil and the heavy fuel oil, respectively, compared to the biomass samples with a spread of 200 - 700 (~ 200 birch bark pellets, ~ 640 pine and ~ 550 oak) identified features, and diesel with 487.

Time resolved calculation of elemental compositions along the temperature gradient revealed that different compound classes occur at different temperature intervals. Exemplary the pine log wood pyrolysis showed two distinct regions (Figure 3d and Figure S-5): one thermodesorption like phase, where mainly CH and $CHO_{1-3}$ species were detected, and a thermal degradation like phase, where higher oxygenated classes, i.e. $CHO_{4-8}$, were most abundant. This outlines the unique opportunity compared to classical TG-MS-hyphenations or even pyrolysis gas chromatographic approaches. Besides marker studies these pyrolysis processes, which are comparable to wood burning in a stove, make the technique applicable for studying the complex mixture composition of the evolved gas in more detail which is to the best of the authors' knowledge not feasible with other techniques. The main advantages compared to classical instrumentation are the selective soft ionization by APCI, the high resolving power and the high mass accuracy. Even when considering disadvantages, such as the comparable low scan rate, the lack of structural information and the need for creating a driving force for the evolved gases to enter the ionization chamber, the hyphenation exhibits novel opportunities.

## Conclusion

The hyphenation of thermal analysis (i.e. a thermobalance) to high resolution mass spectrometry applying soft chemical ionization at atmospheric pressure for evolved gas analysis was firstly shown in the presented work. The setup is feasible to analyze the complex gas mixtures evolving from the thermal process at the molecular level (i.e. with assignment of the elemental composition). Solid and liquid samples were studied covering petroleum samples and biomass. Compared to TOF systems the acquisition rate is somewhat lower, but the ICR offers an unbeaten mass resolving power. However, as the heating rate in thermal analysis mostly is quite slow the achievable scan speed of the FT-MS of ~ 0.1 Hz is sufficient for typical applications.

Alternative techniques such as pyrolysis gas chromatographic approaches can identify markers with structural evidence for targeted and semi-targeted approaches, but usually fail for a more screening-like and comprehensive view. Despite the fact that the here presented hyphenation is bulky and expensive untargeted analytics within the chemical space ionized by APCI is one major advantage The main advantage was shown by confirming literature known marker species from biomass decomposition by their elemental composition. Additionally high complex mixtures such as crude oil were fully resolved at the m/z-scale. As data interpretation is a crucial step misinterpretation due to the selective view of the APCI is not completely avoided. Nonetheless APCI is capable of ionizing a high proportion of the species typically emitted by lignocellulosic biomass decomposition. In conclusion it is likely that this novel technique can enable valuable contribution to actual research on thermally induced processes and complex samples.

## Supporting Information

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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**Figure 1** Scheme of the coupling between thermobalance and ultra-high resolution mass spectrometer equipped with atmospheric pressure chemical ionization via a GC oven. Only "direct mode" was applied, "GC mode" is reserved for future work.

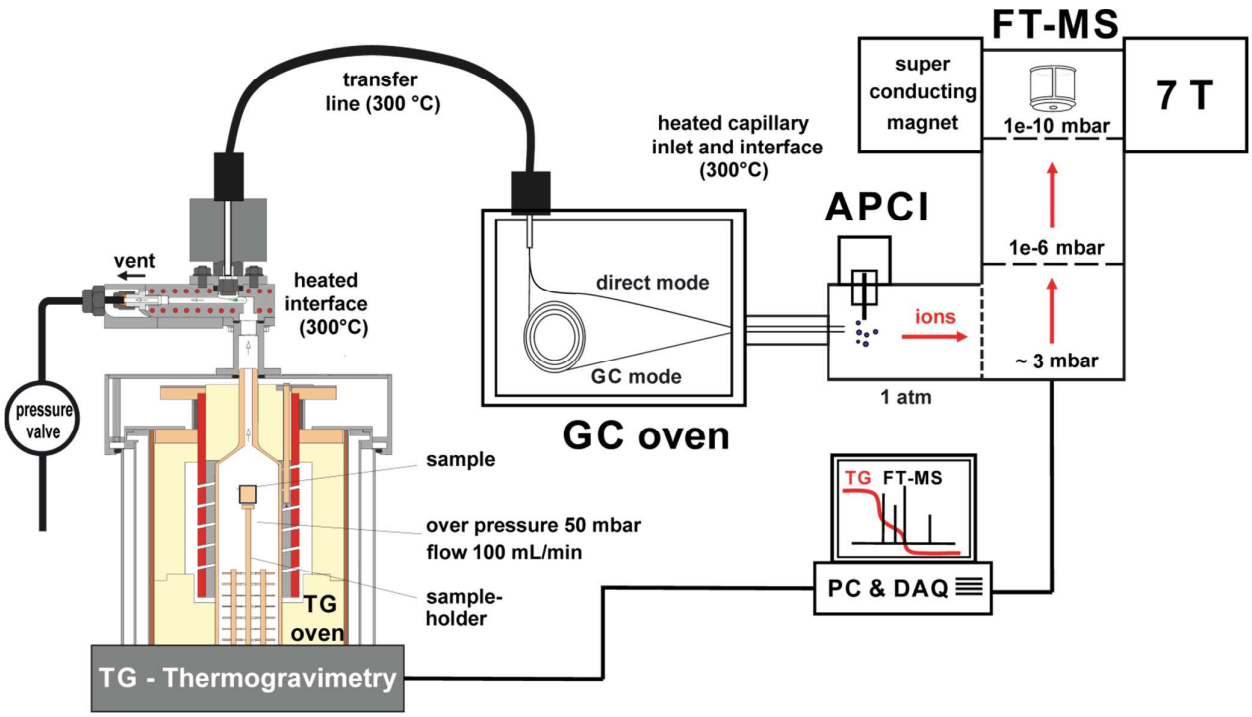


**Figure 2** Temperature resolved TG-signal and the corresponding total ion count (TIC) and basepeak ion count (BIC) of the evolved gas analyzes from different petroleum samples, a) North Sea crude oil, b) heavy fuel oil, c) light fuel oil. Please note that the BIC signal is enhanced by a factor of 10.

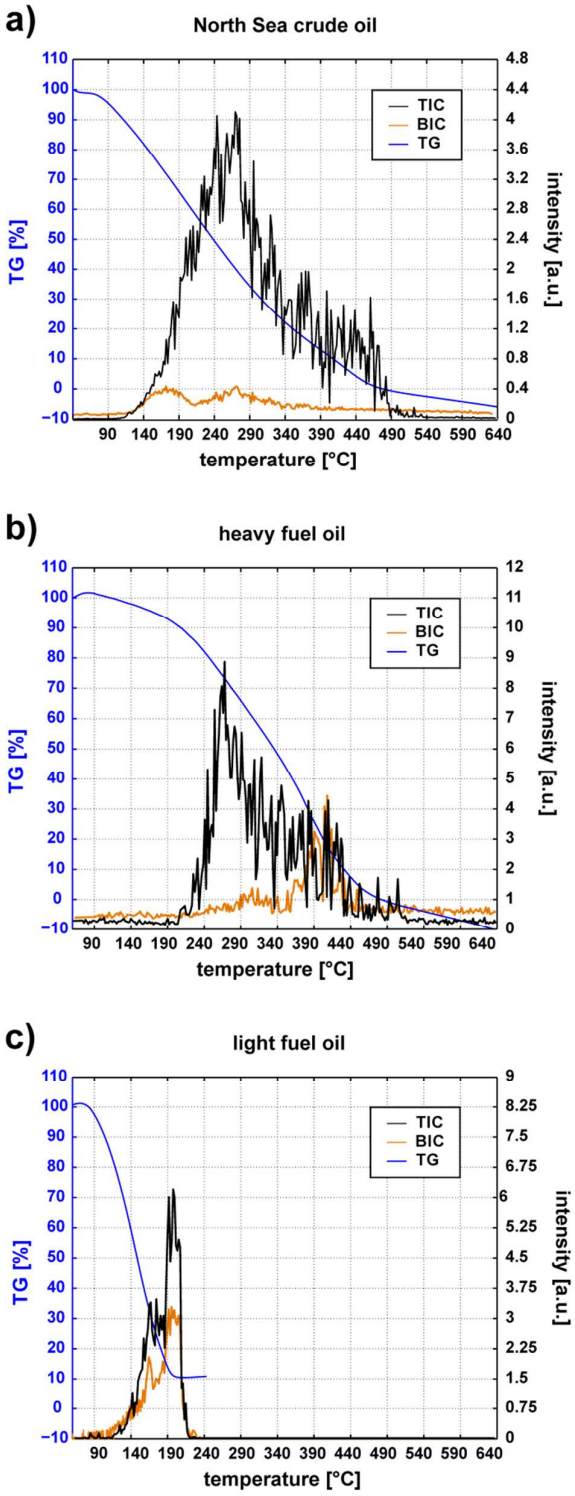
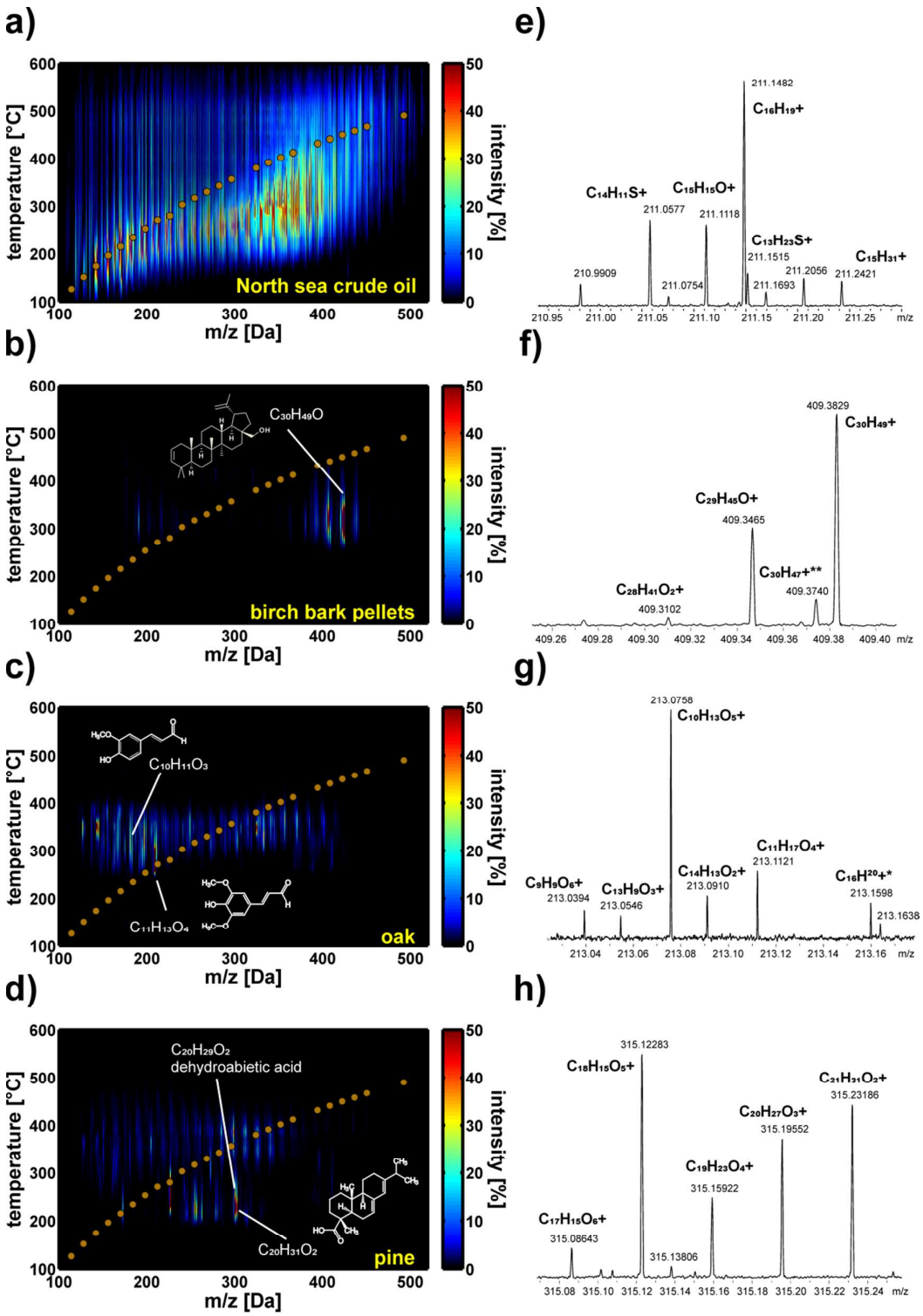


**Figure 3** Image plot of the evolved gas measurements from three different biomass and one petroleum samples, the orange dotes indicate the boiling temperature of respective alkanes, a) North Sea crude oil, b) birch bark pellets, c) oak log wood, d) pine log wood, selected feasible structures are highlighted using their protonated molecular ion; e) – h) corresponding mass spectra enlarged to an exemplary nominal mass with assigned elemental compositions (*-1$^{st}$ $^{13}$C-isotop, **-2$^{nd}$ $^{13}$C-isotop).



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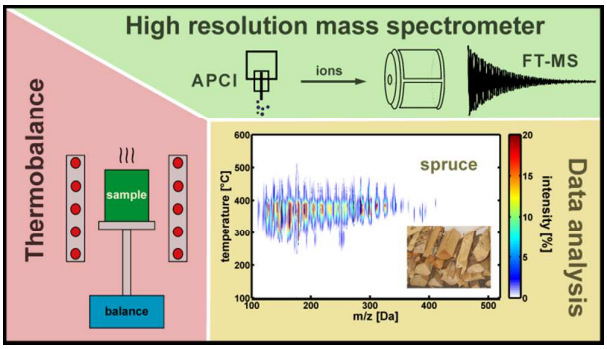
**for TOC only**


High resolution mass spectrometer
APCI
ions
FT-MS
Thermobalance
sample
balance
spruce
temperature [°C]
m/z [Da]
intensity [%]
Data analysis