

Detection of the molecular composition of pyrolysis gases in **thermal analysis** (TA) using **photo ionization TOF MS** for evolved Gas Analysis (EGA): Instrumental set-up and first results on tobacco and cigarette materials

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Detection of the molecular composition of pyrolysis gases in **thermal analysis** (TA) using **photo ionization TOF MS** for evolved Gas Analysis (EGA): Instrumental set-up and first results on tobacco and cigarette materials

Content:

- Single photon ionisation-MS with EBEL VUV light source
- TG-SPI-MS: Evolved gas analysis in Thermogravimetry
- TG-SPI-MS Applications: Polymers, bio-mass, crude oil
- First application of TG-SPI-MS to tobacco/ cigarette material
- Summary

Thermogravimetry (TG): Thermoanalytical method, measures weight loss as a function of temperature

TG - Evolved gas analysis (TG-EGA): Analyzing evolved gases from TG by FT-IR, MS or GC

TG-EGA drawback: Standard on-line EGA technology (MS, FT-IR) → only limited information on organics

EGA by gas chromatography (GC) → slow and only covers a selected fraction during TG run.

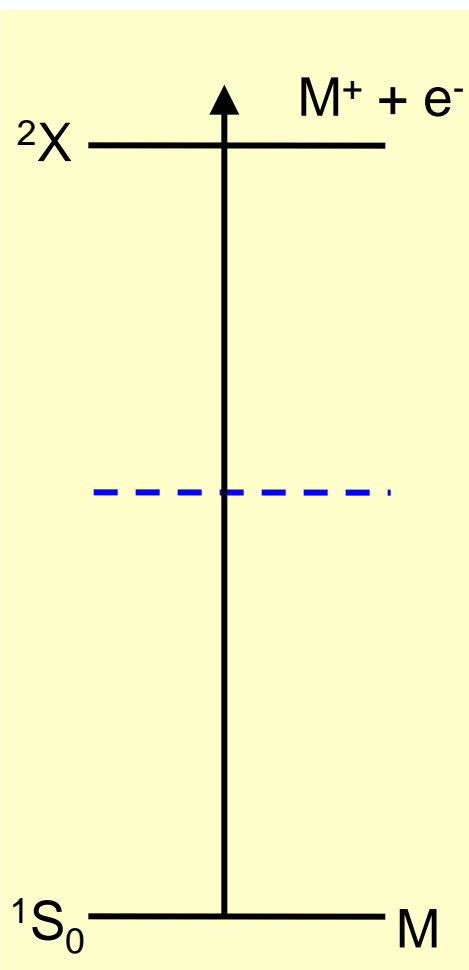
→ This work: TG-EGA using mass spectrometry with soft photo ionisation for organic profiling

Single photon ionisation (SPI) for soft ionisation on-line mass spectrometry

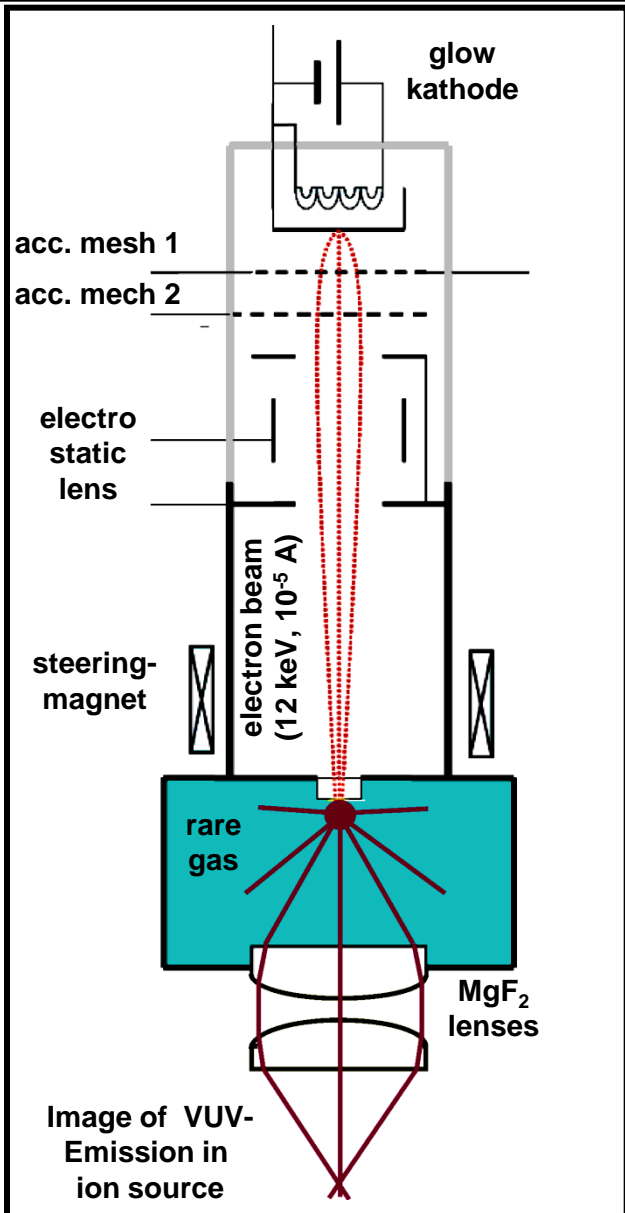
Mass spectrometry with soft photo ionisation: SPI-MS

Single Photon Ionisation (SPI):

- photon energies 8 - 12 eV (**VUV range**)
- **soft ionisation** (molecular ions, no/few fragments)
- **matrix suppression** (small molecules/carrier gas)
- **universal** ionisation of organic compounds
- VUV photon generation:
 - conventional VUV lamps (discharge lamps)
 - **novel VUV light source (EBEL)**
 - third harmonic generation with UV laser pulses (Nd:YAG 355 nm \rightarrow 118 nm)

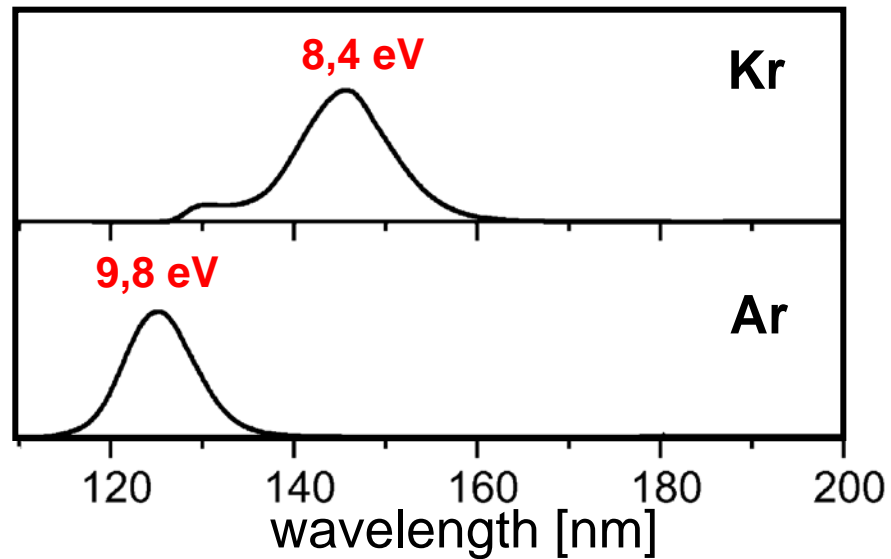


EBEL – An innovative VUV-light source for SPI-MS



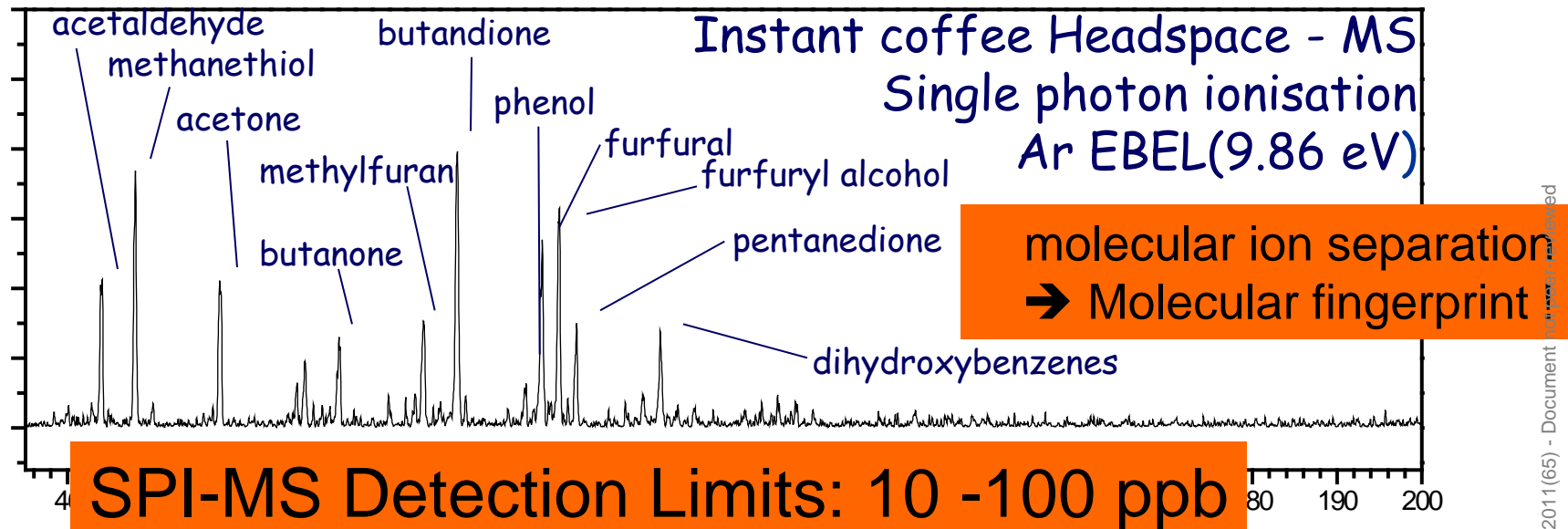
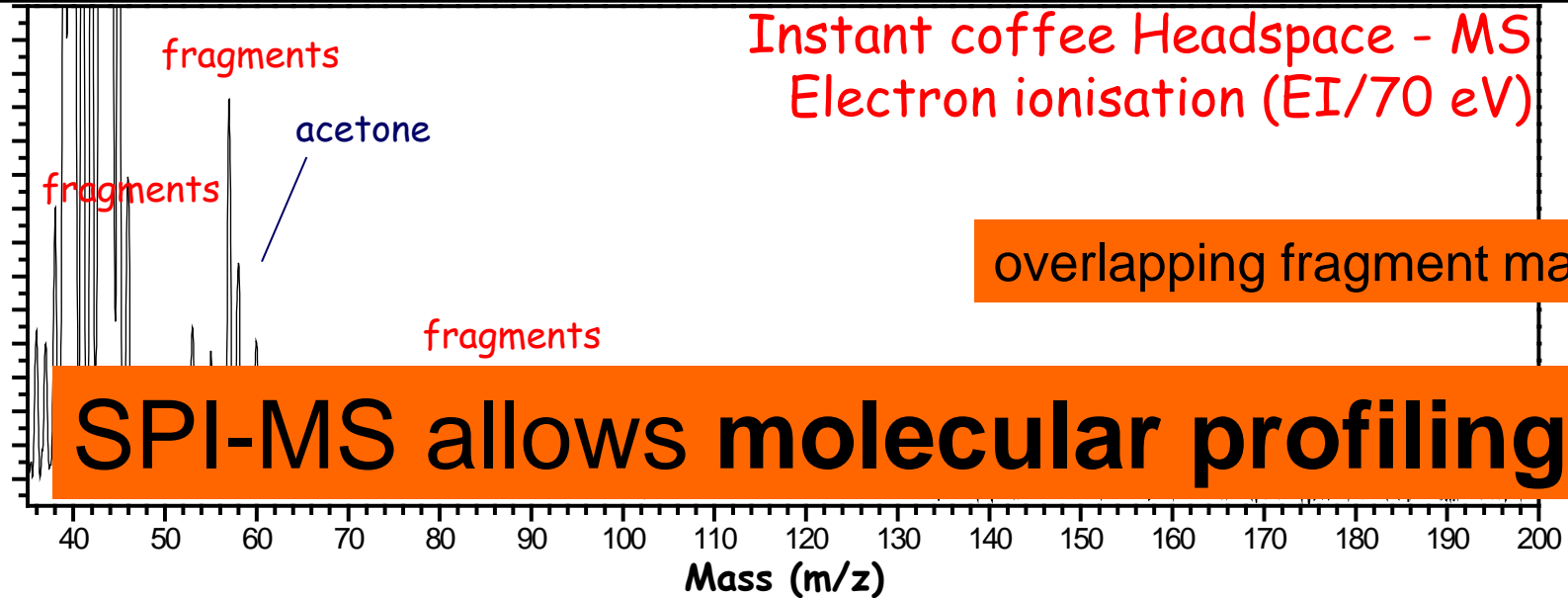
Patented VUV-light source for single photon ionization MS

Electron Beam pumped rare gas Excimer Light source → EBEL

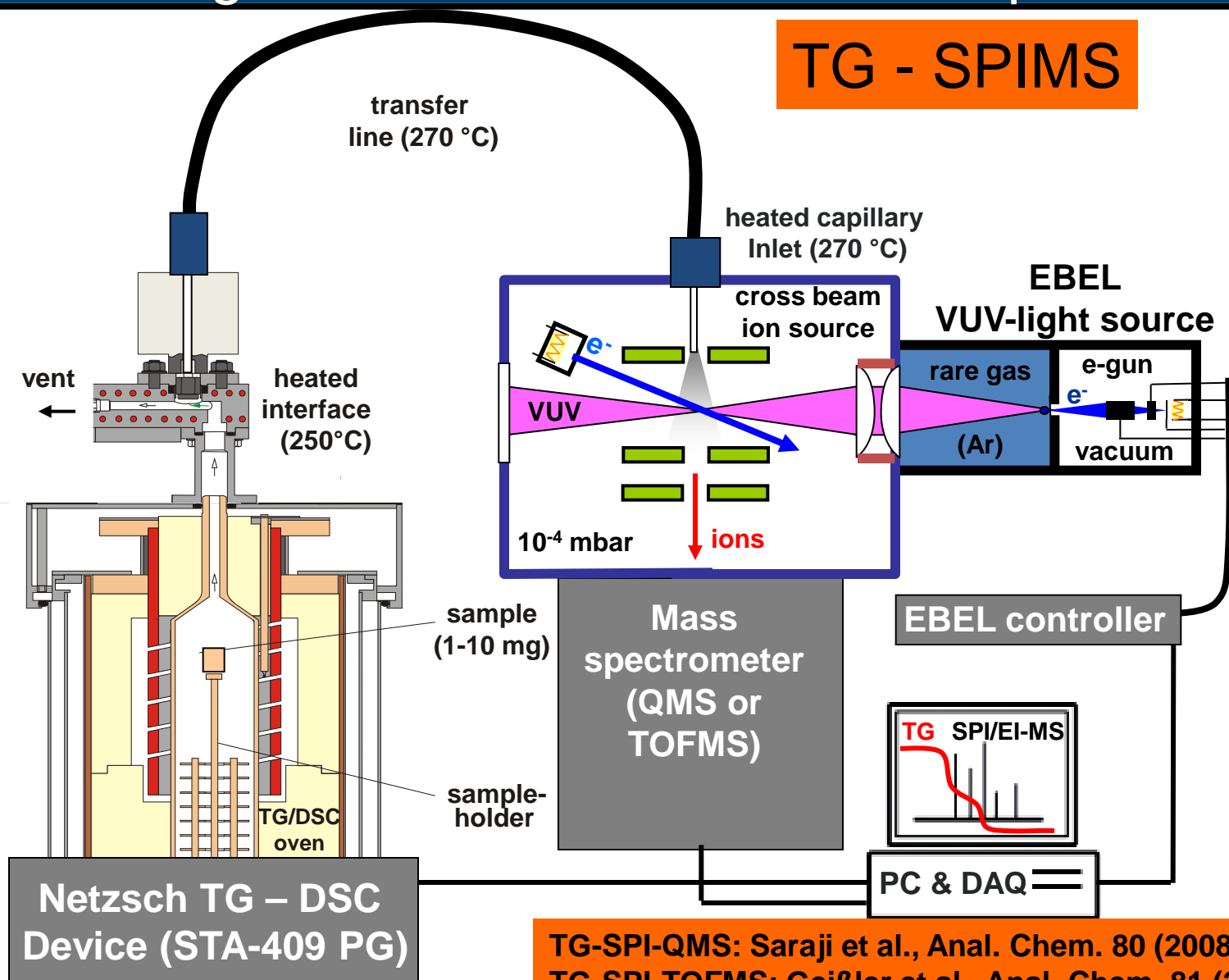


Ulrich, Wieser, Salvermoser, Murnick; Physik. Blätt. 56 (2000) 49.
Mühlberger, Wieser, Ulrich, Zimmermann; Anal. Chem. 74 (2002) 3790.

On-line SPI-MS: Difference of soft and hard ionisation

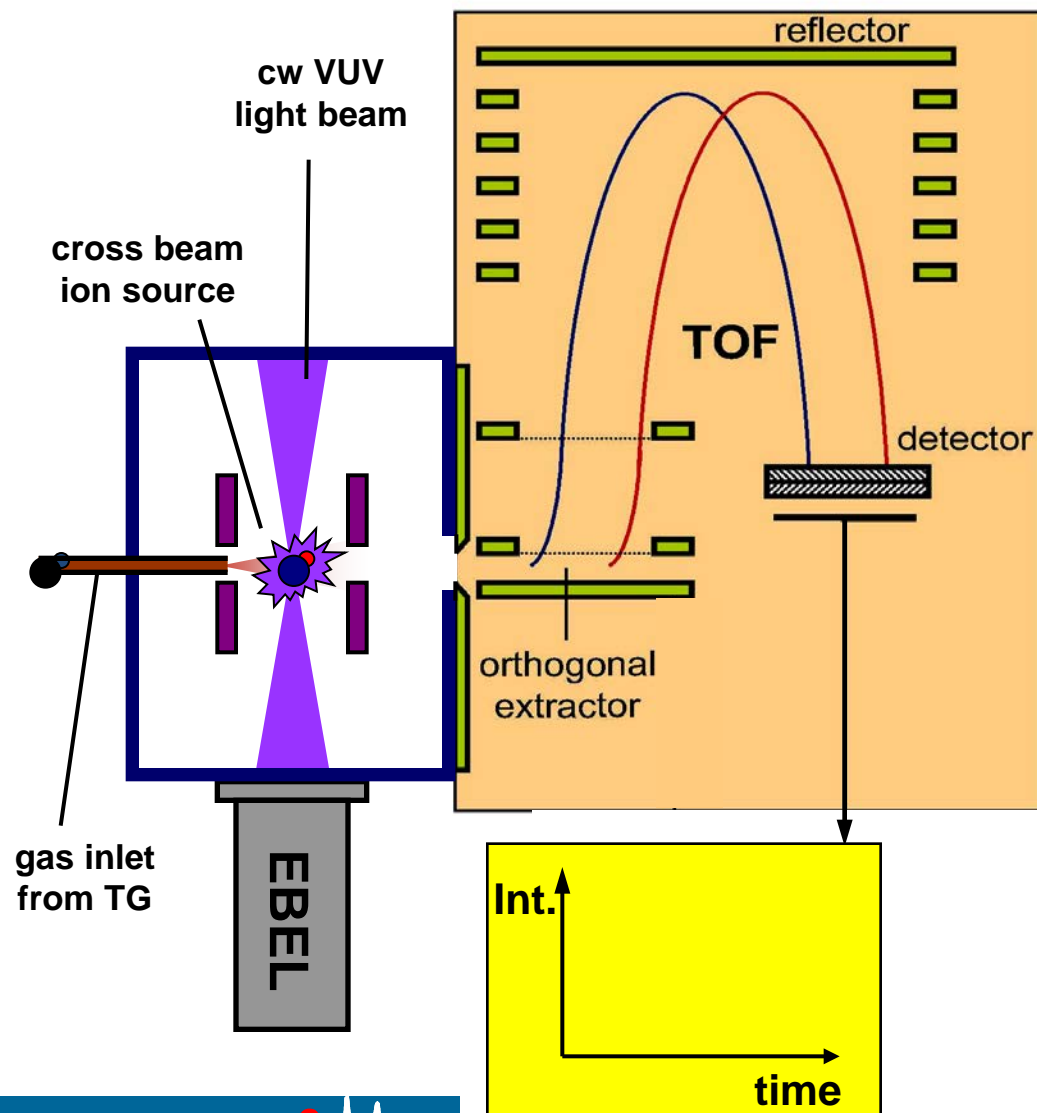


Thermogravimetry - Single Photon Ionization-Mass Spectrometry



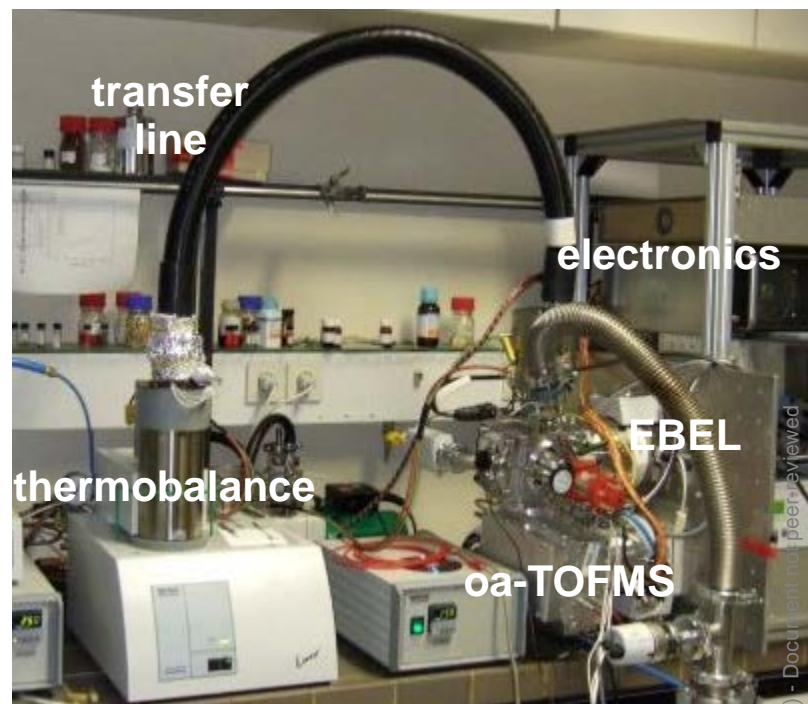
TG-SPI-QMS: Saraji et al., Anal. Chem. 80 (2008) 3393
TG-SPI-TOFMS: Geißler et al., Anal. Chem. 81 (2009) 6038

Thermogravimetry – Single photon ionization - oaTOFMS



Orthogonal acceleration TOF:

- fast (50 kHz rep. rate)
- scan-free

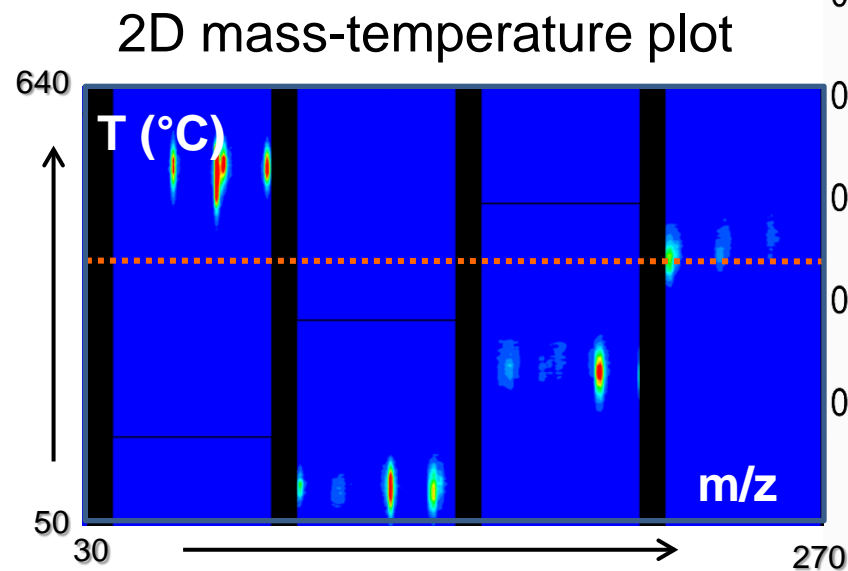
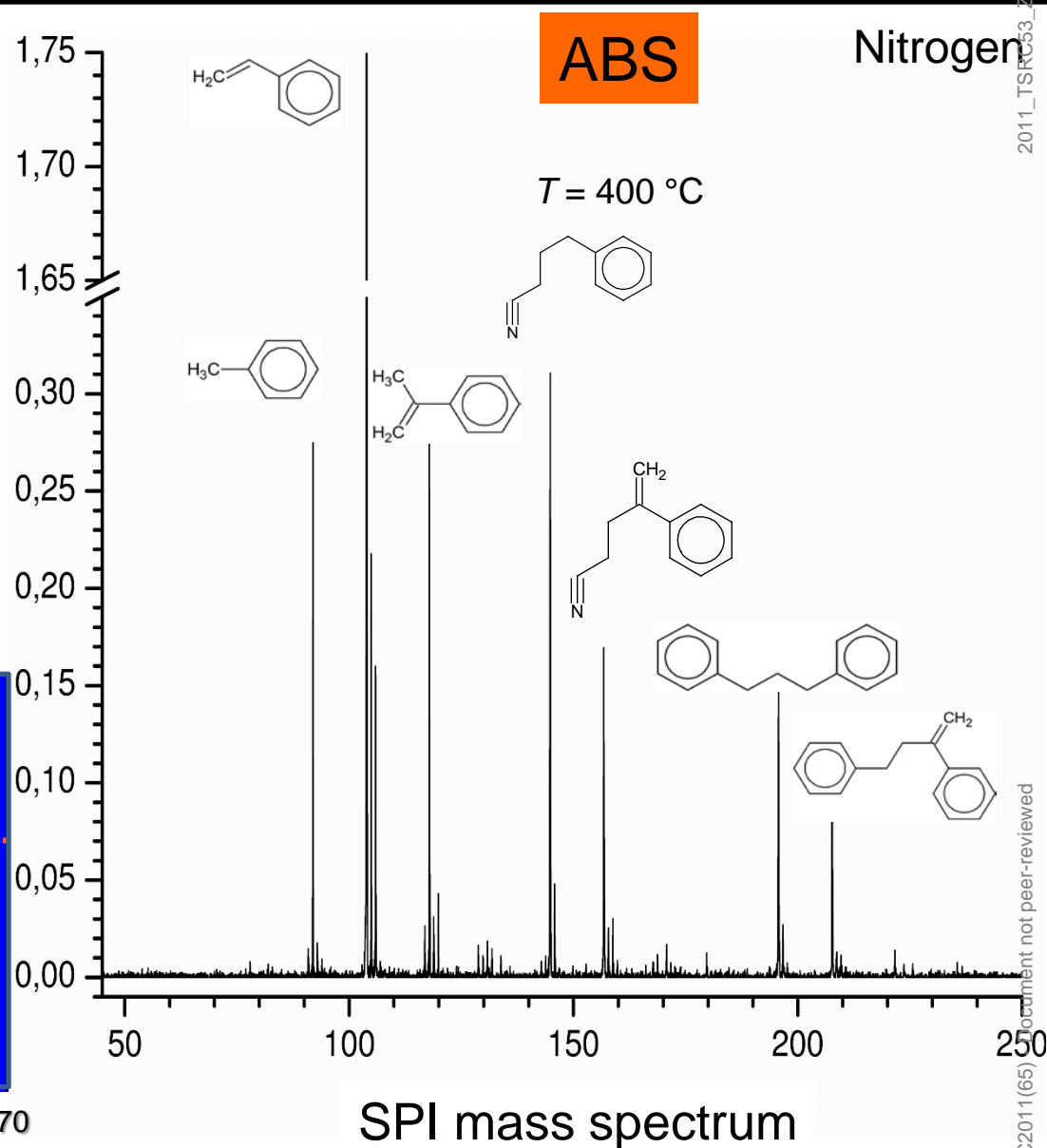
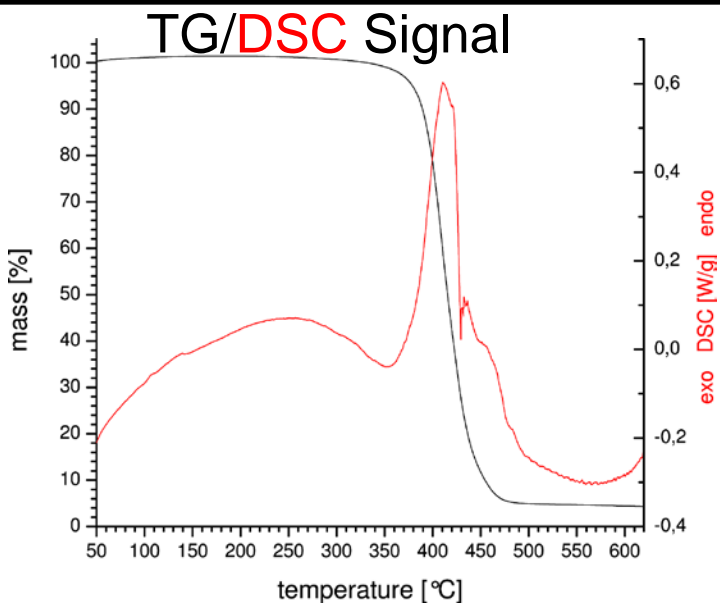


Thermogravimetry - Single Photon Ionization-Mass Spectrometry

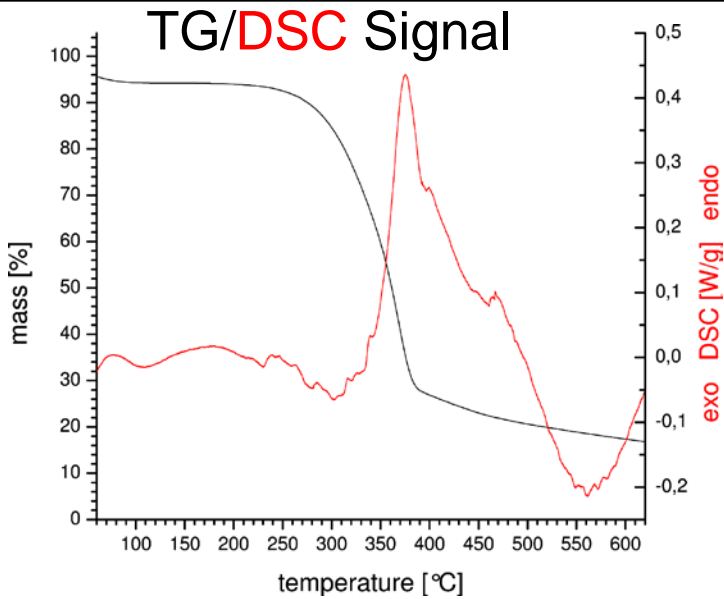
Application: SPI-MS for
gas analysis in Thermogravimetry



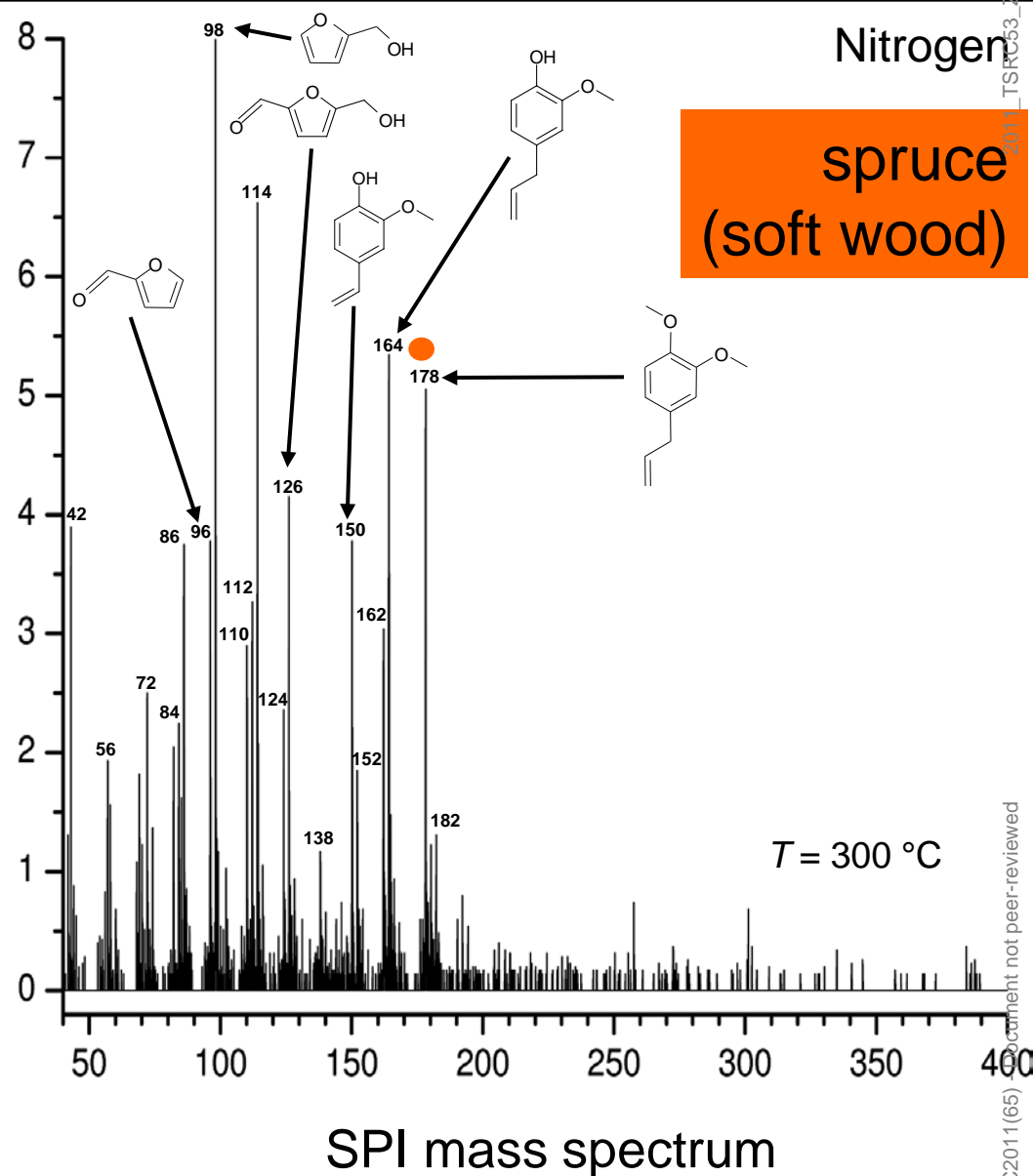
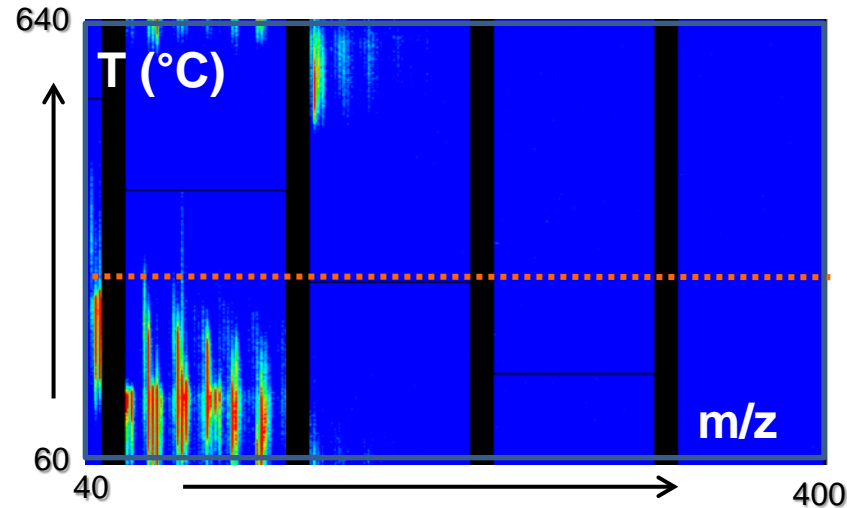
TG-SPI-MS Applications: Polymers



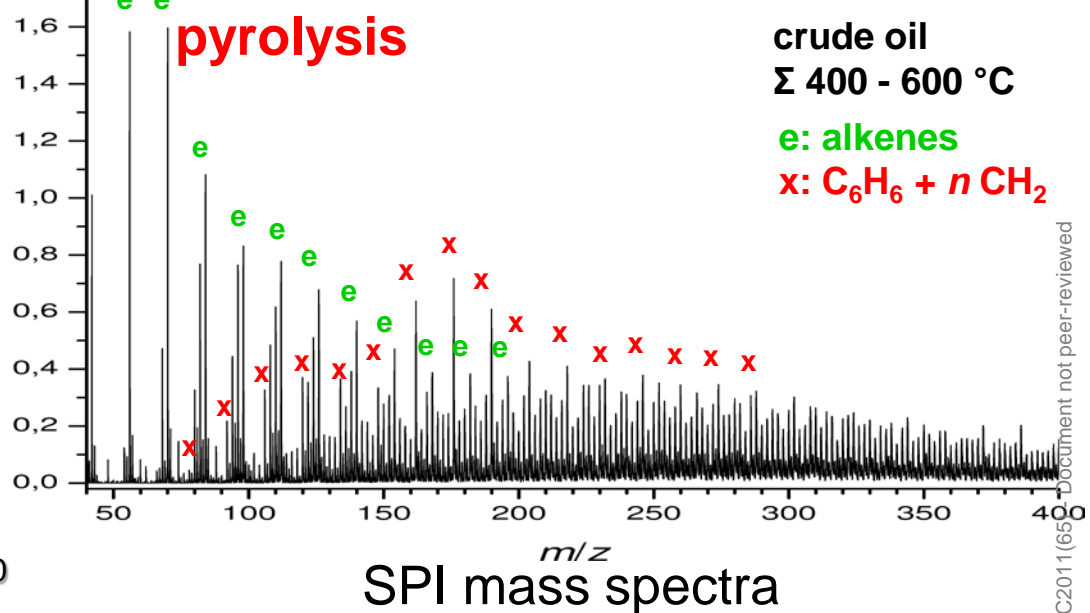
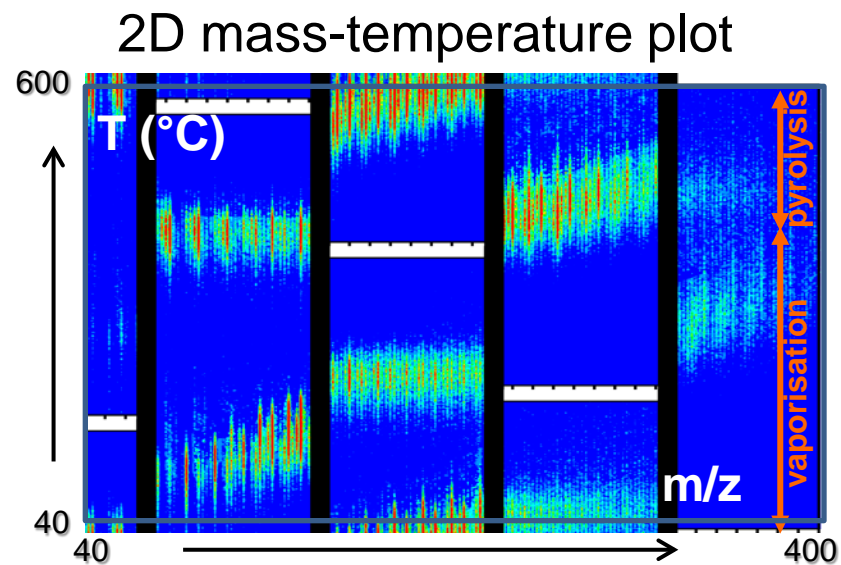
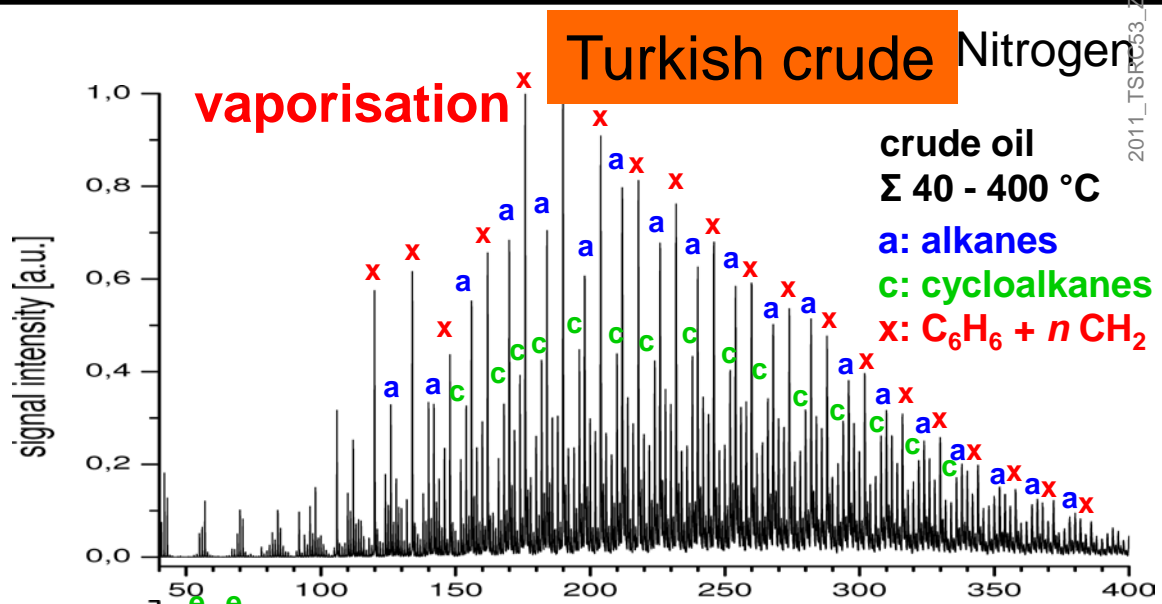
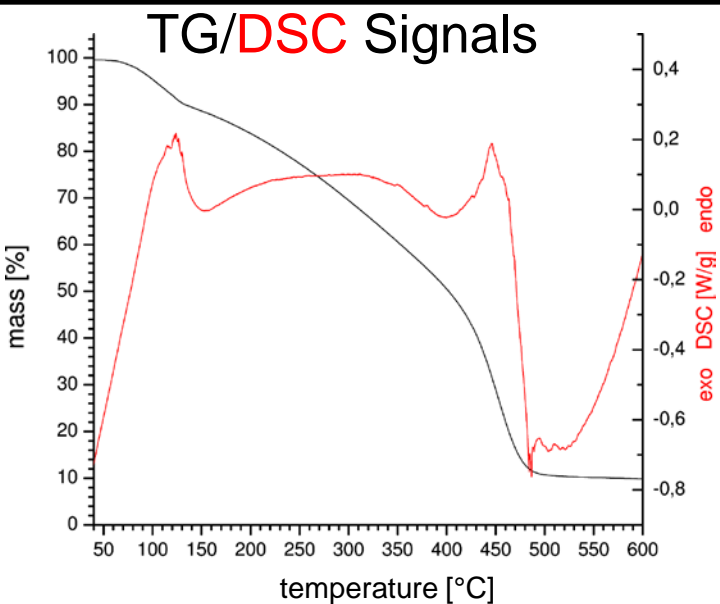
TG-SPI-MS Applications: Biomass



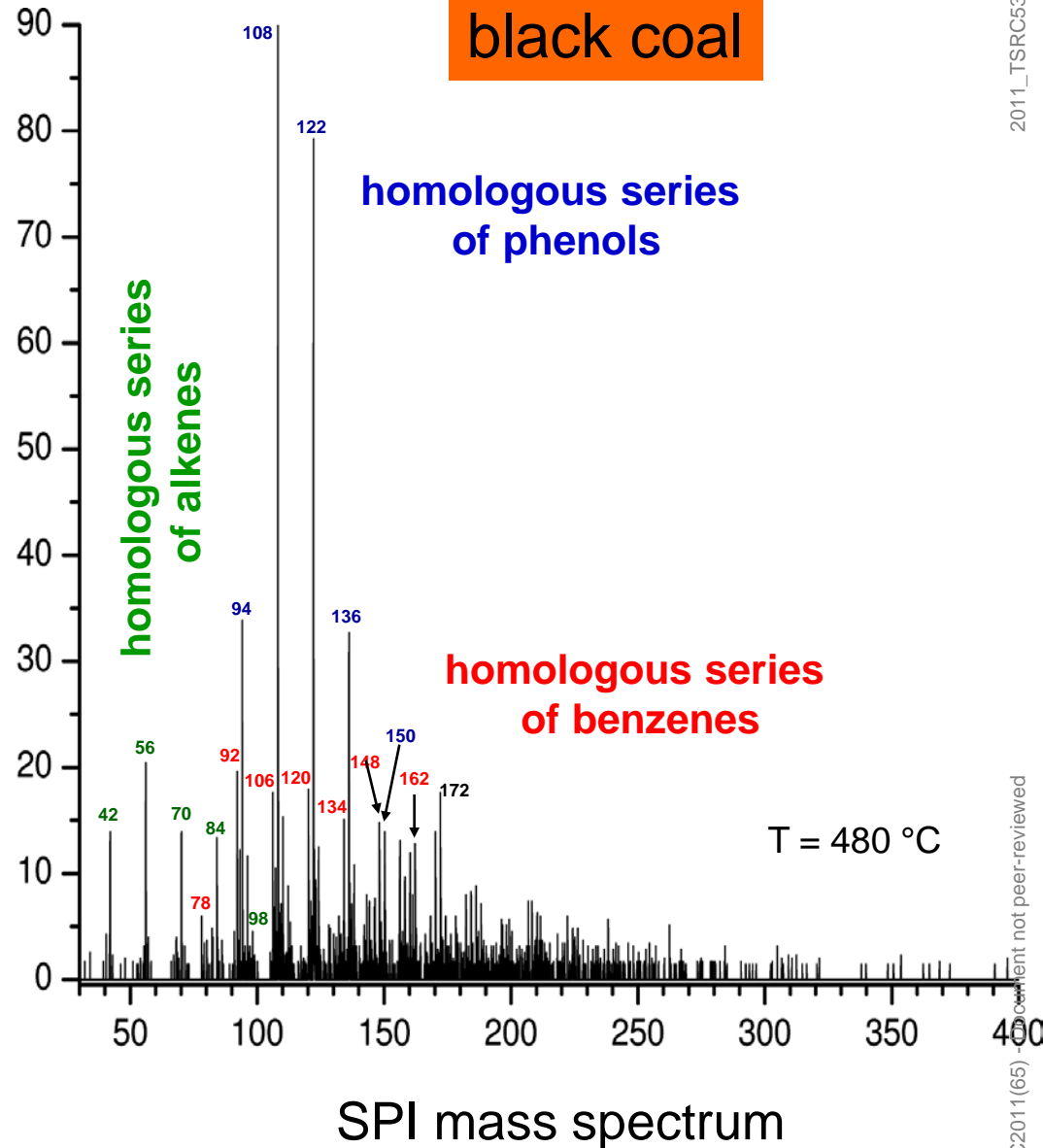
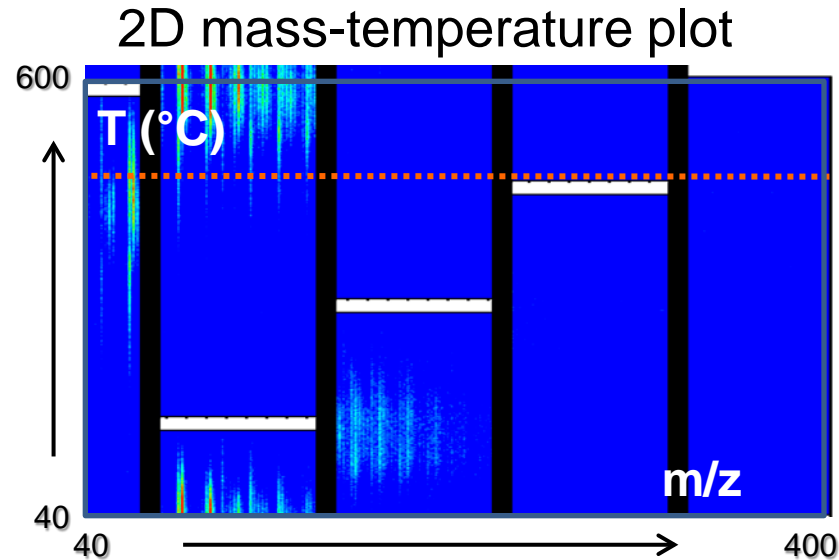
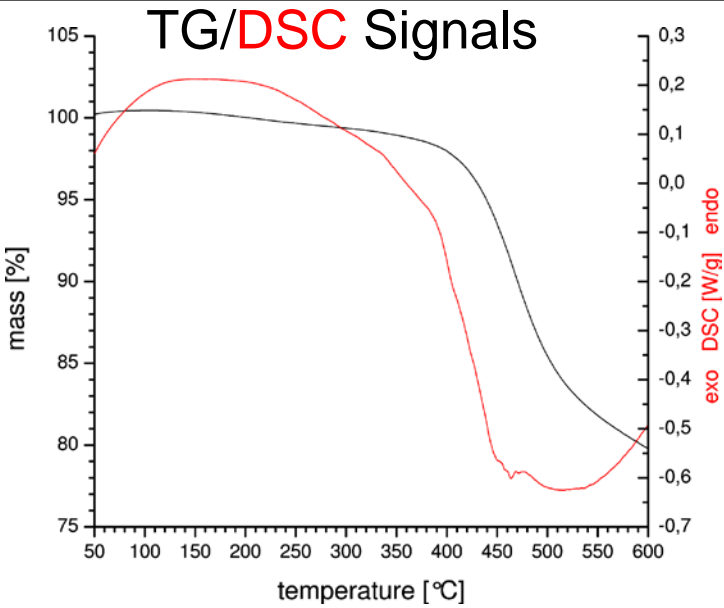
2D mass-temperature plot



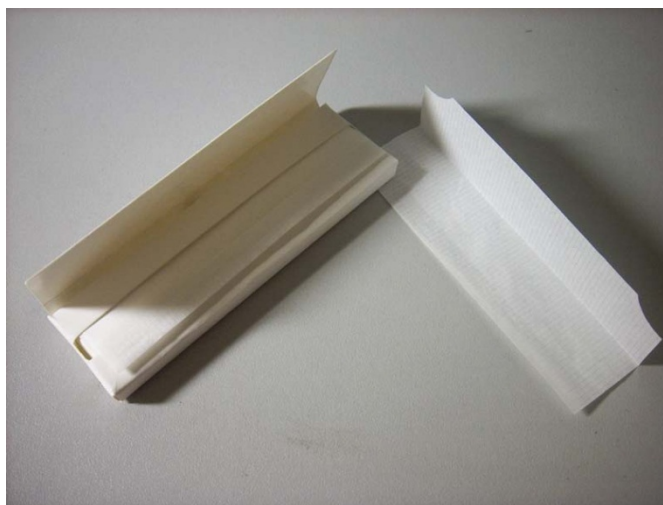
TG-SPI-MS Applications: Crude oil



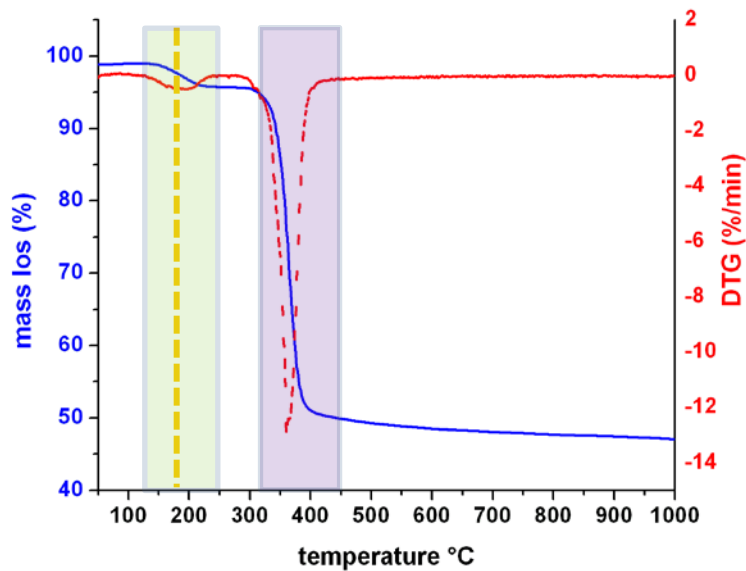
TG-SPI-MS Applications: Coal



First application of **Thermal Analysis - Photo Ionization TA-SPI-TOFMS** on tobacco and cigarette materials

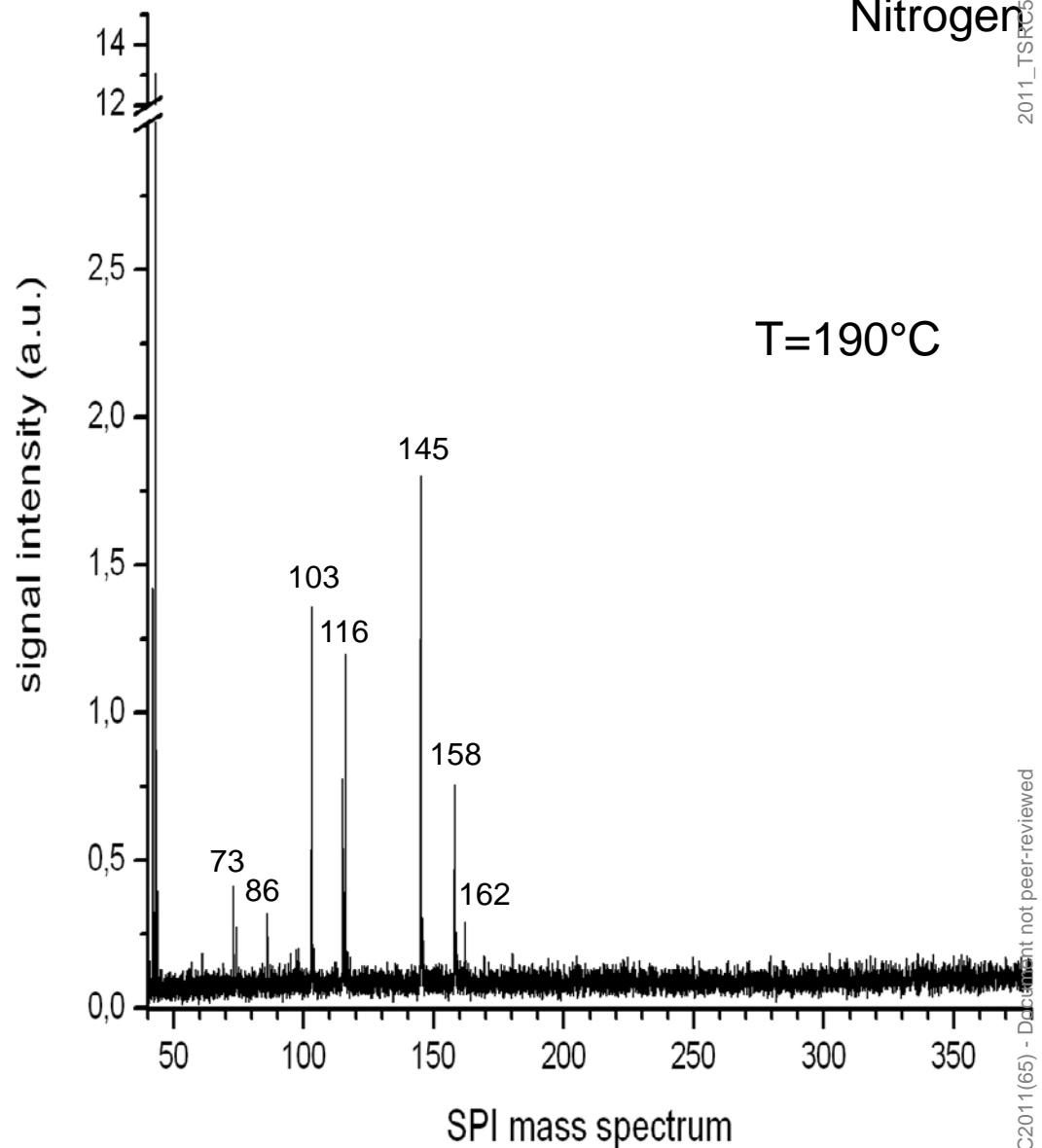
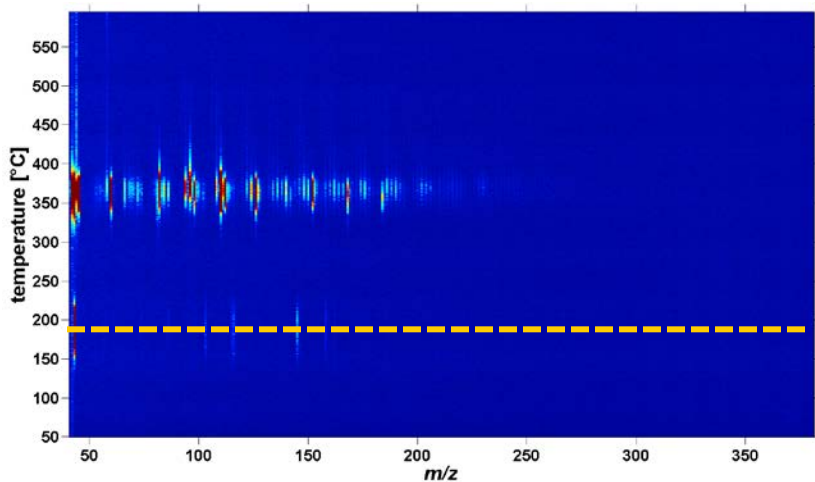


TG-SPI-MS Applications: Cigarette Filter

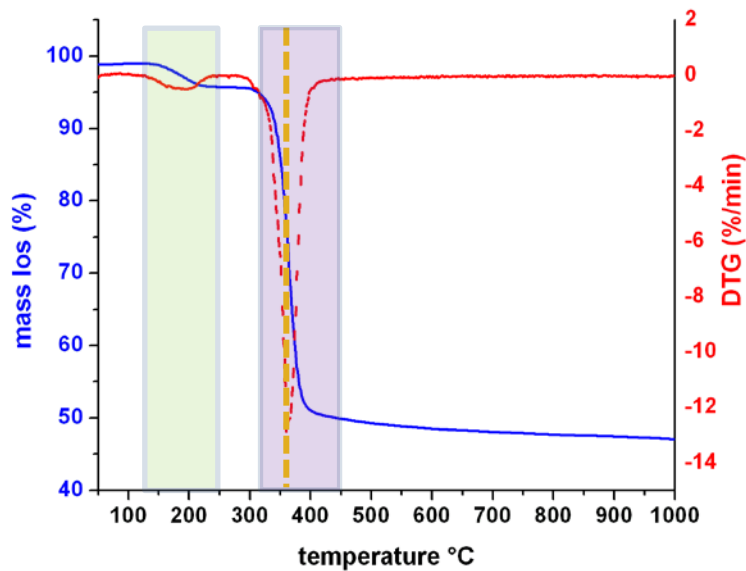


Nitrogen

T=190°C

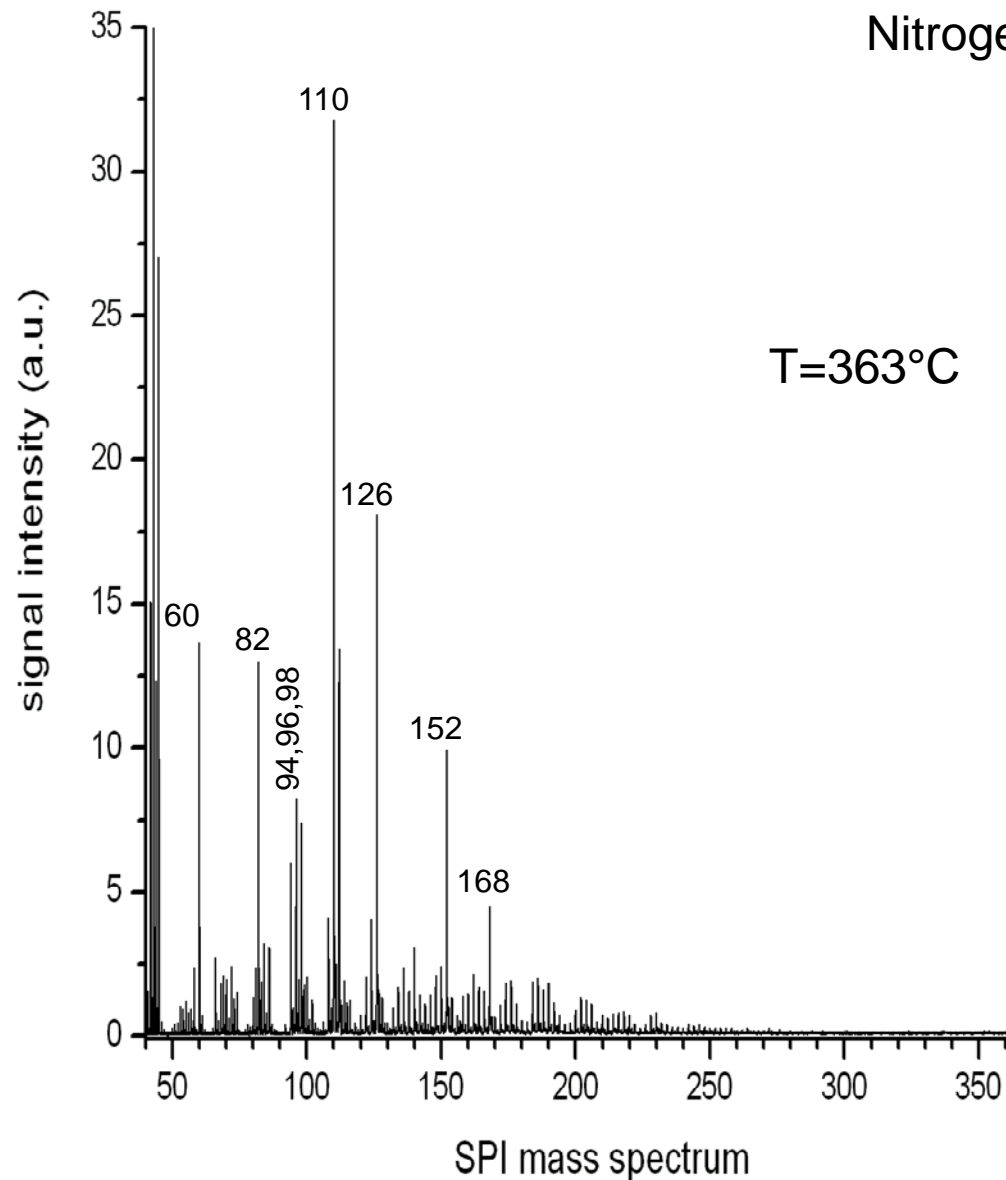


TG-SPI-MS Applications: Filter



Nitrogen

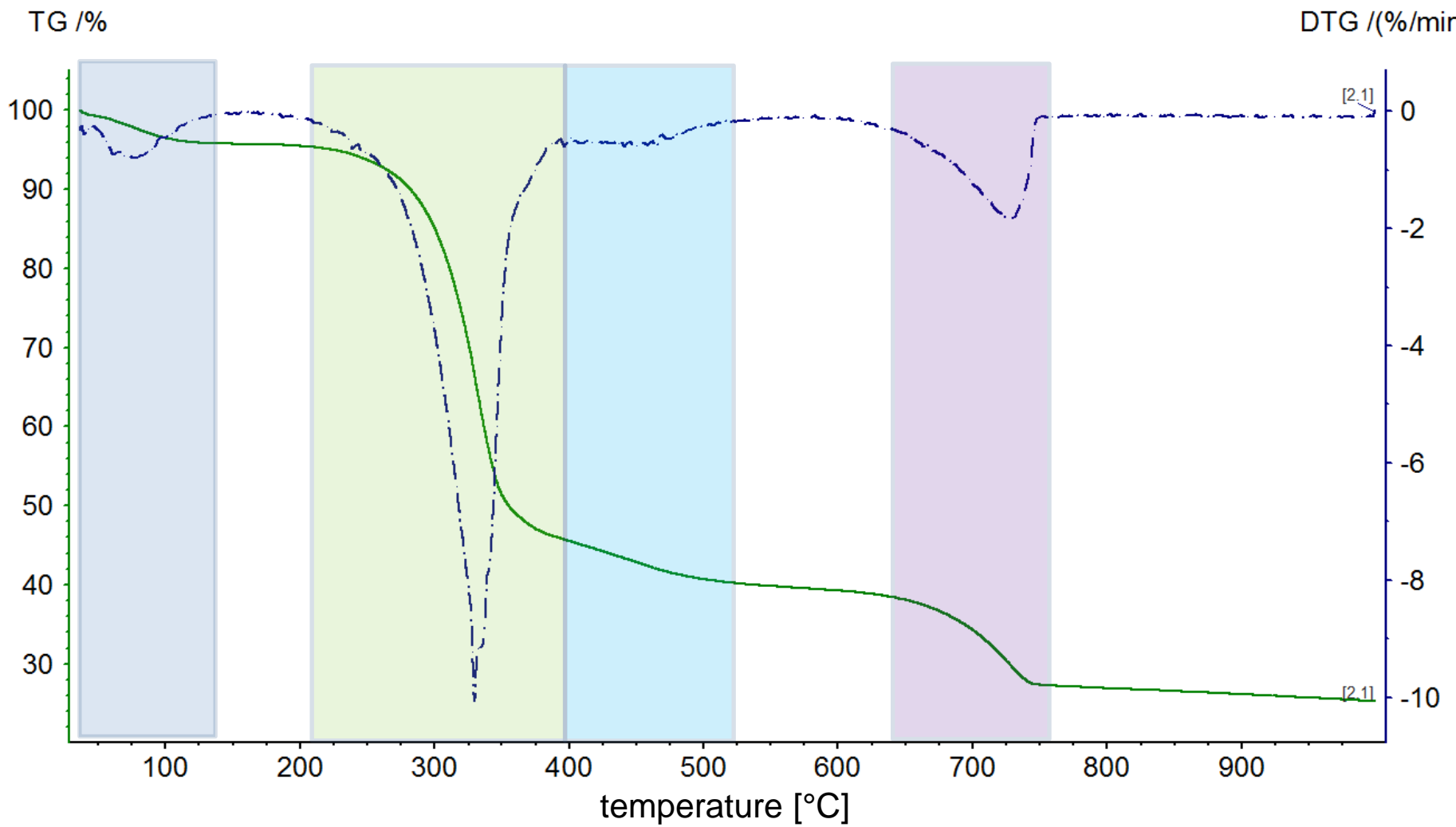
T=363°C



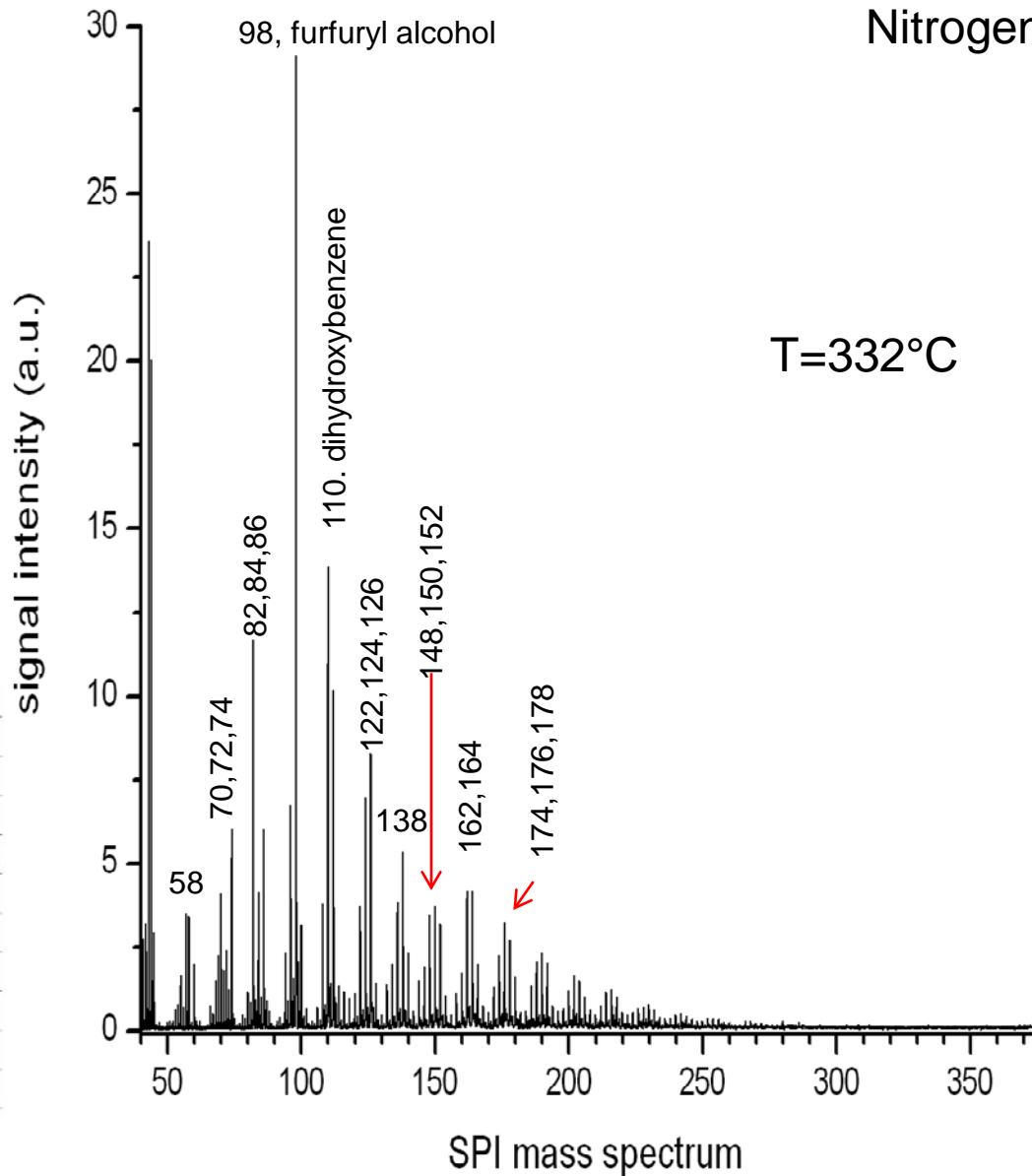
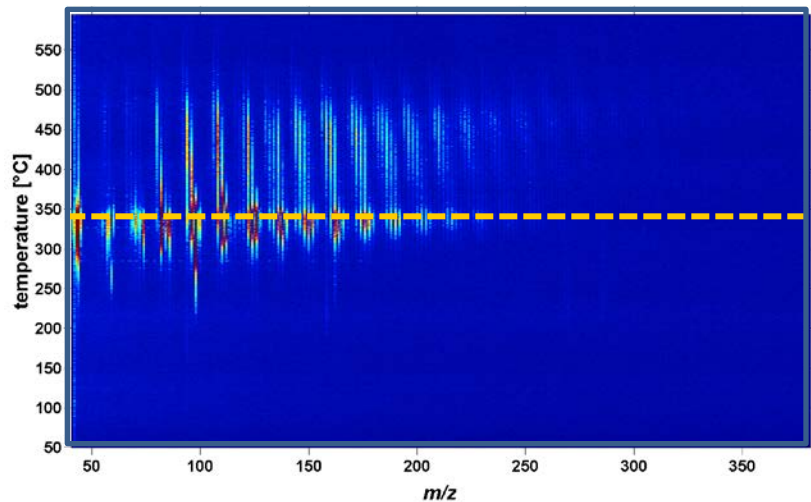
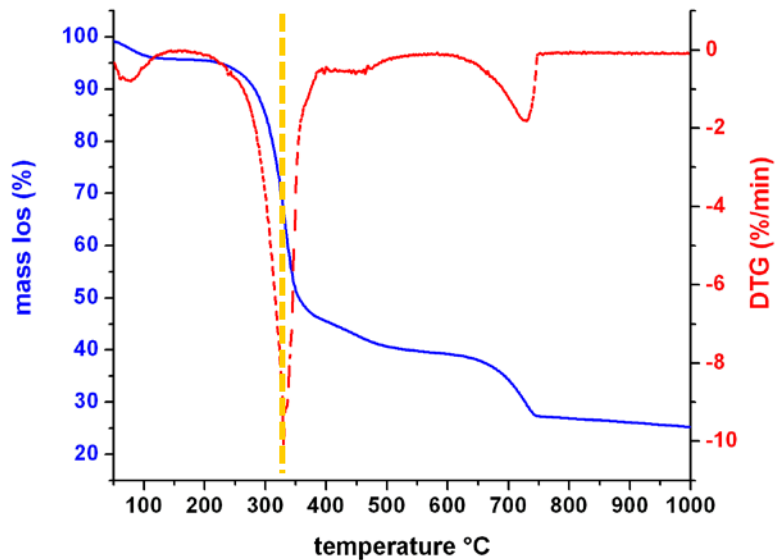
TG-SPI-MS Applications: Paper

Nitrogen

DTG /(%/min)



TG-SPI-MS Applications: Paper

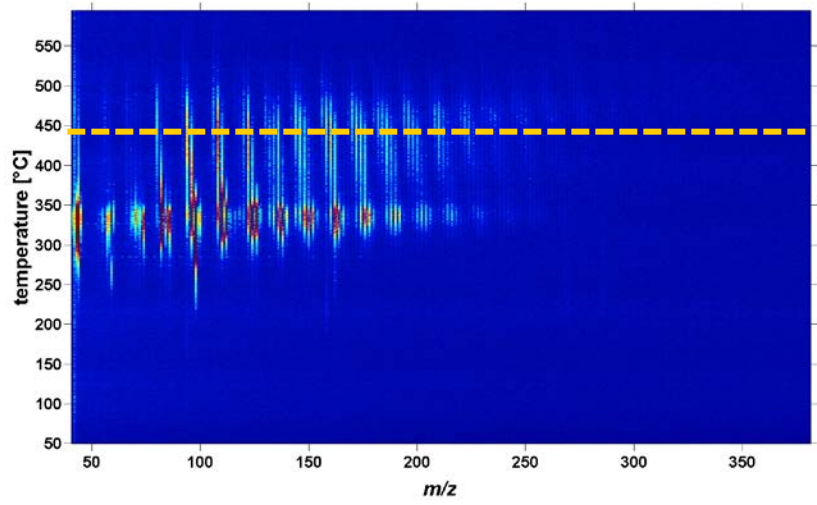
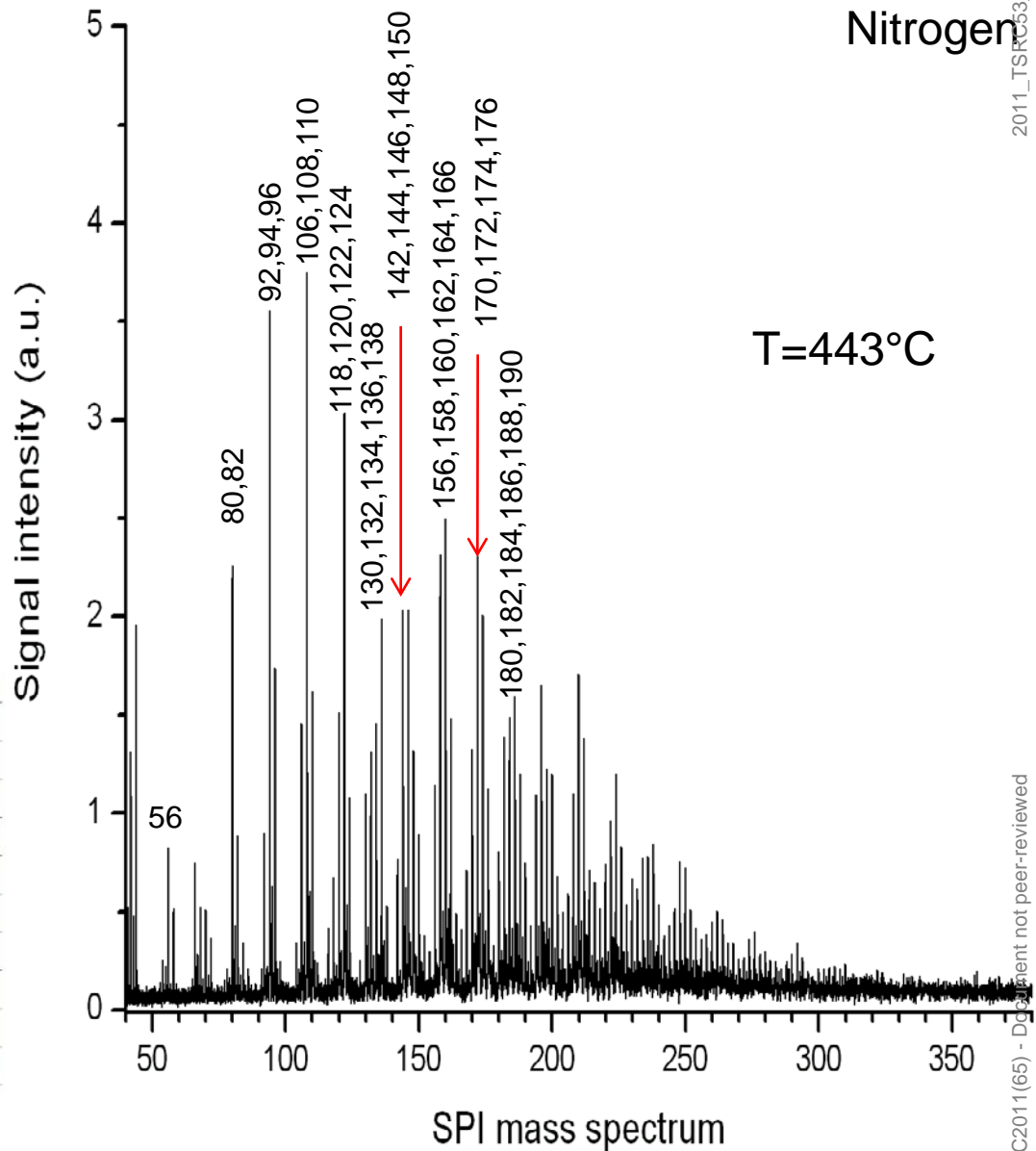
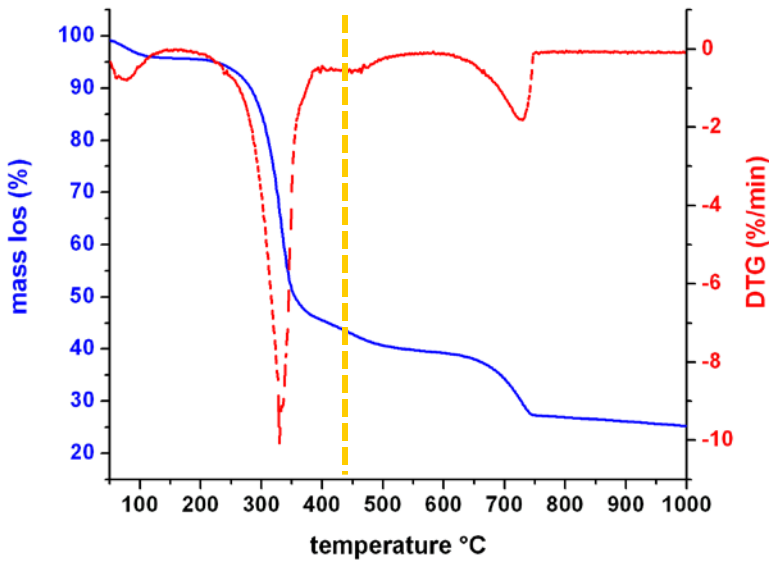


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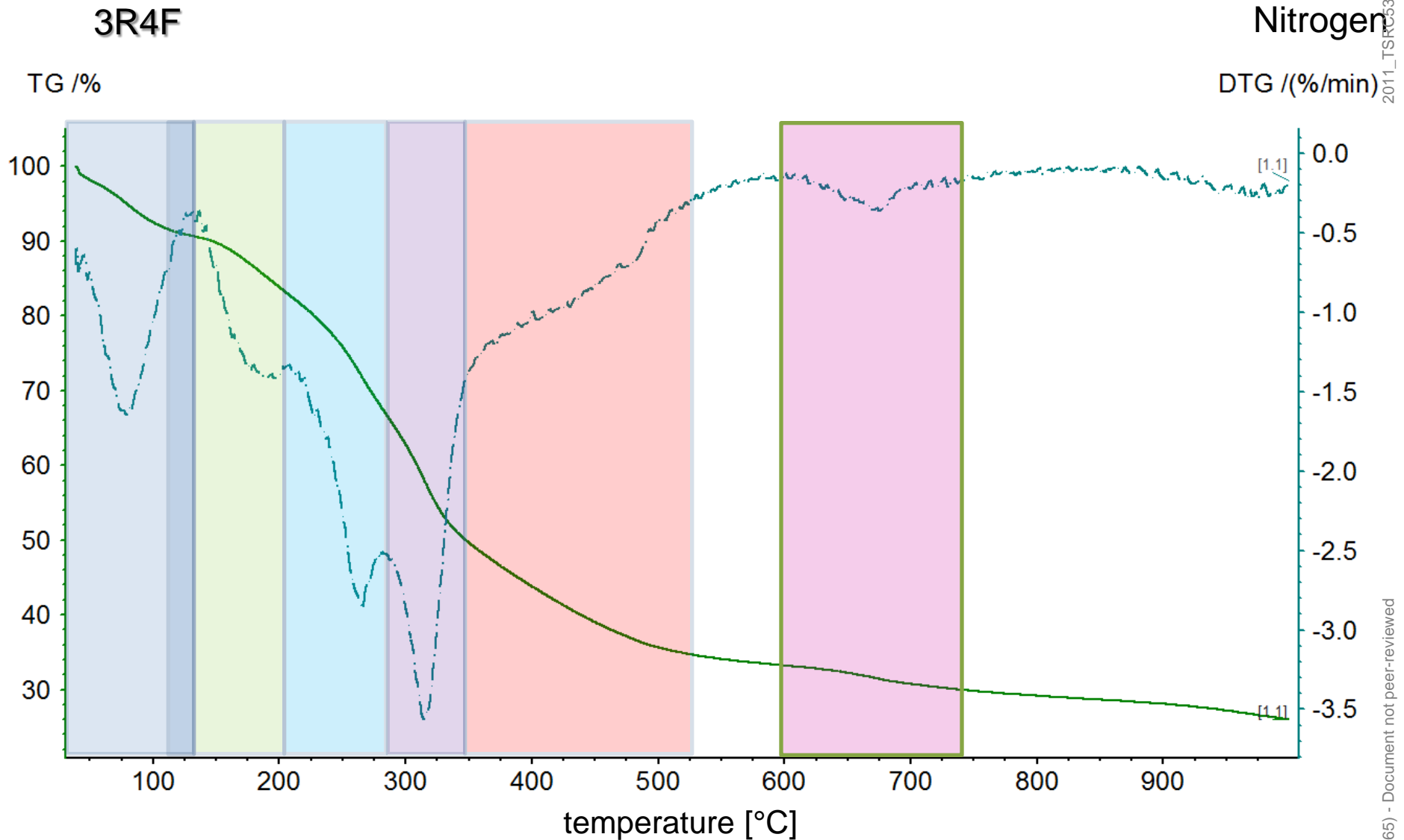
T=332°C

TG-SPI-MS Applications: Paper

Nitrogen

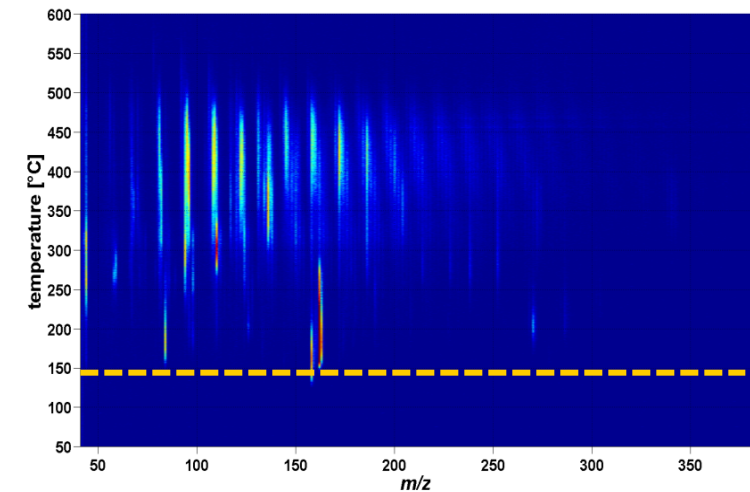
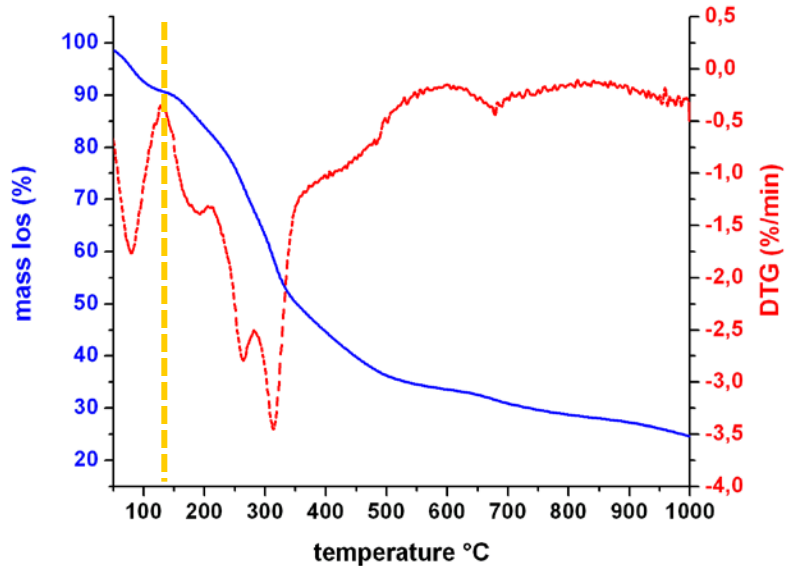


TG-SPI-MS Applications: Tobacco

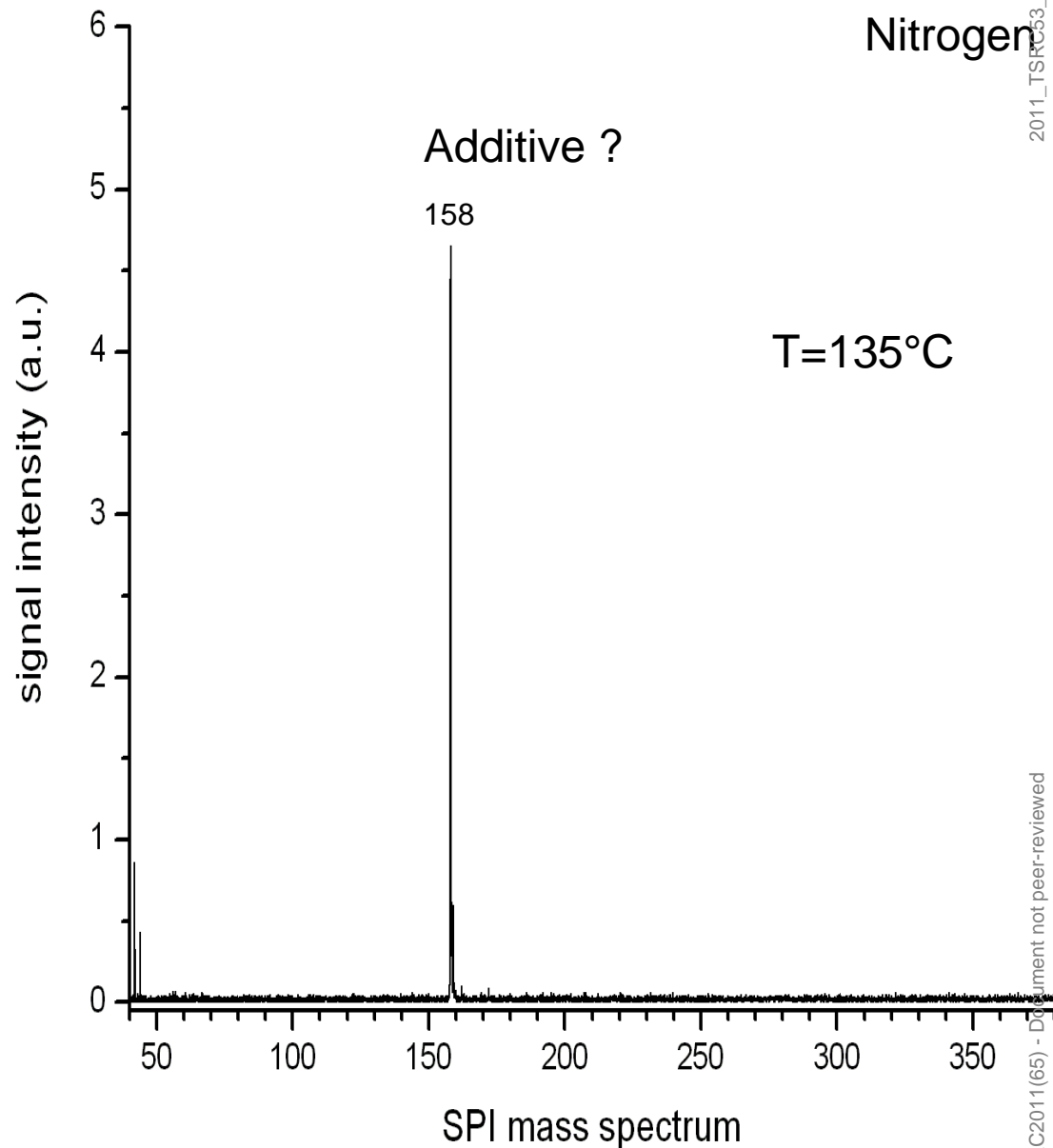


TG-SPI-MS Applications: Tabaco

3R4F

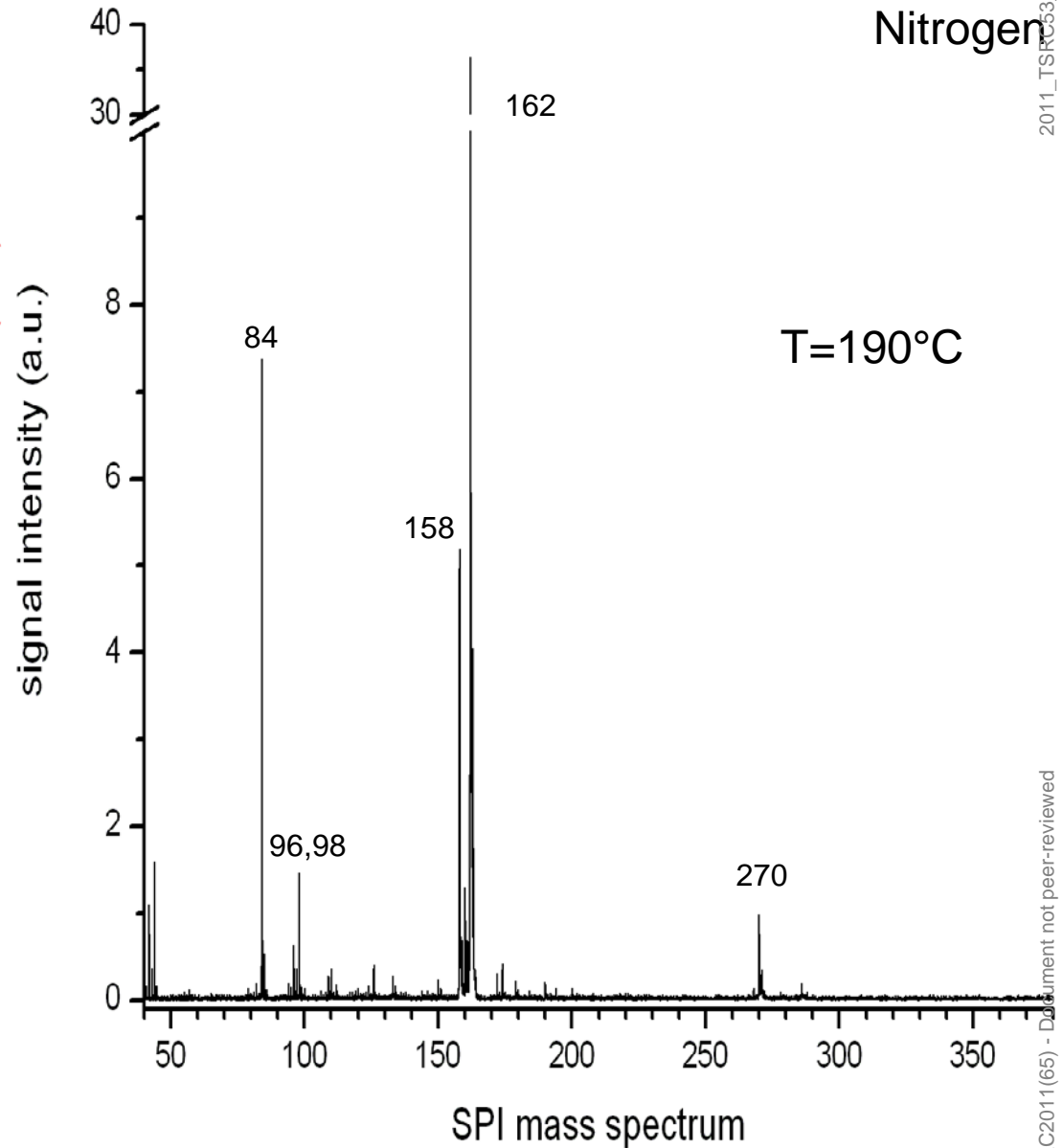
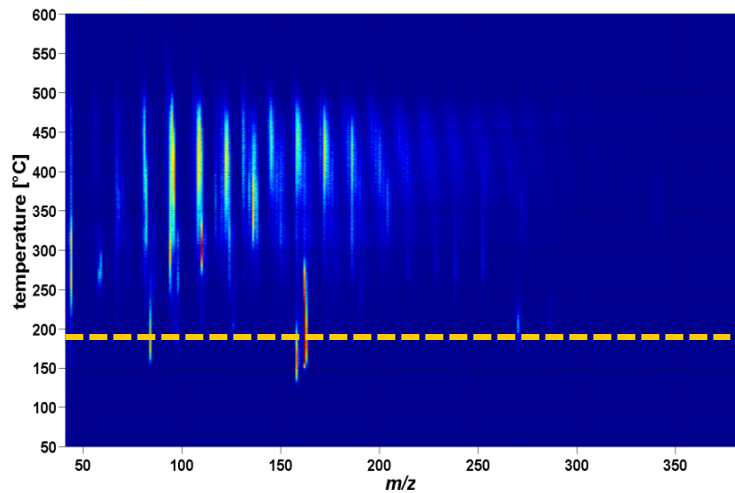
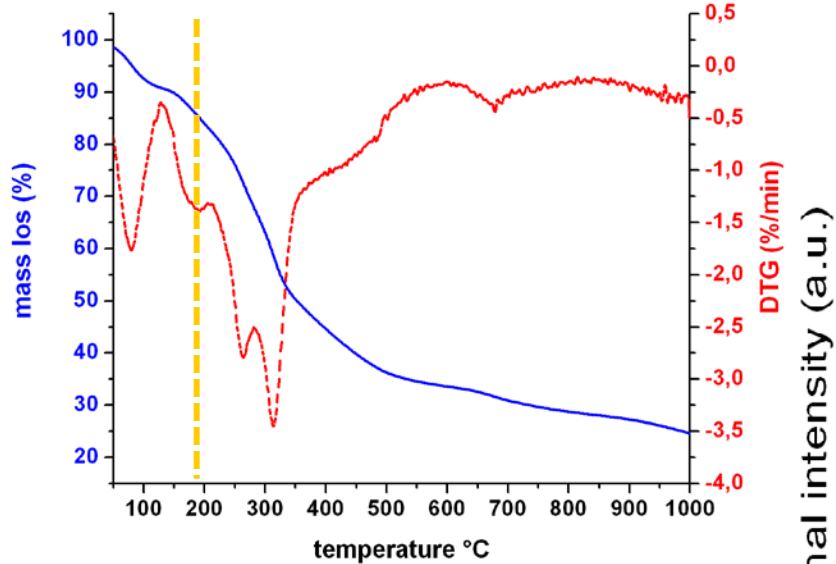


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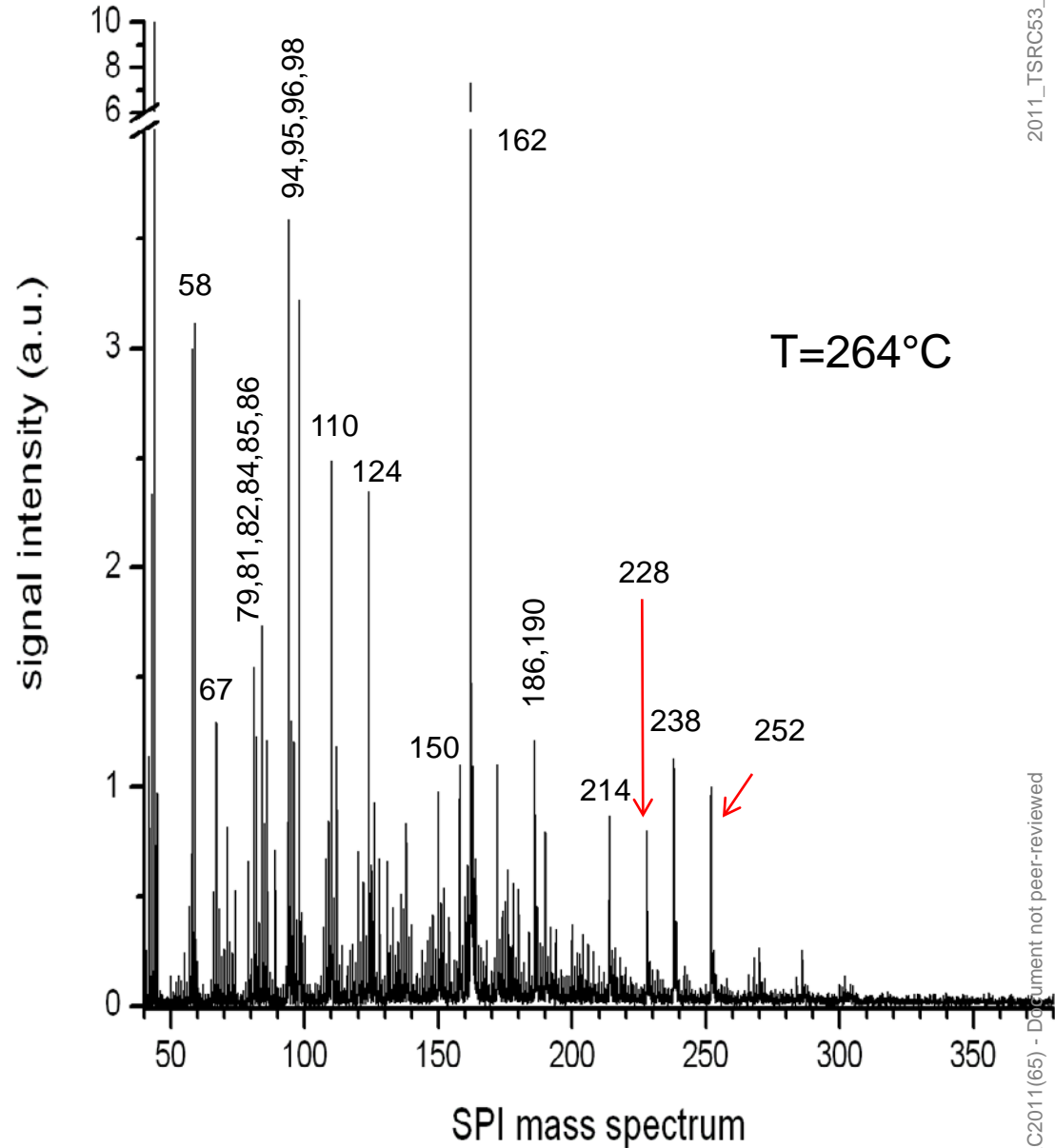
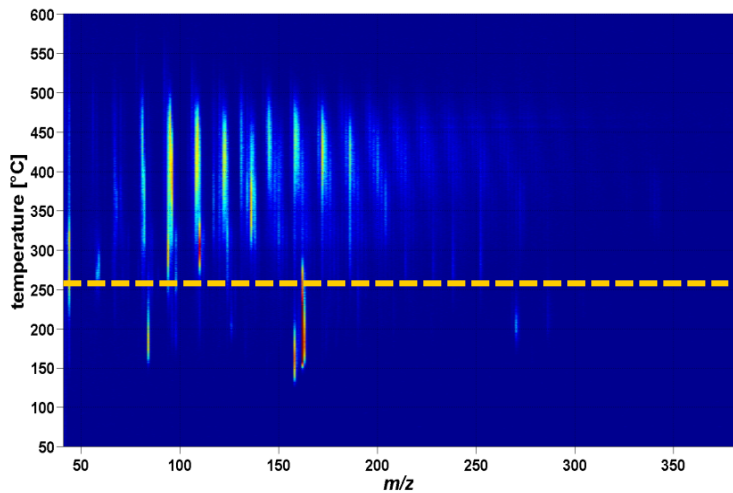
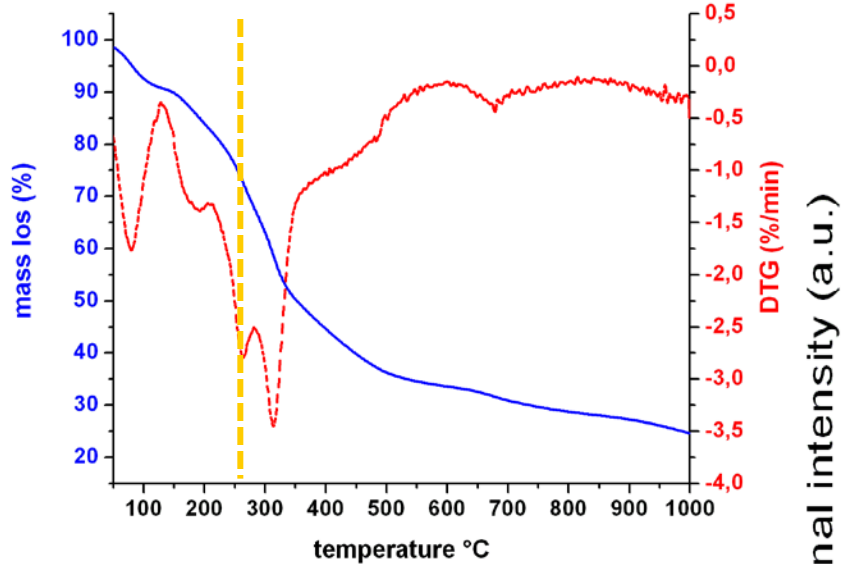
TG-SPI-MS Applications: Tobacco

3R4F



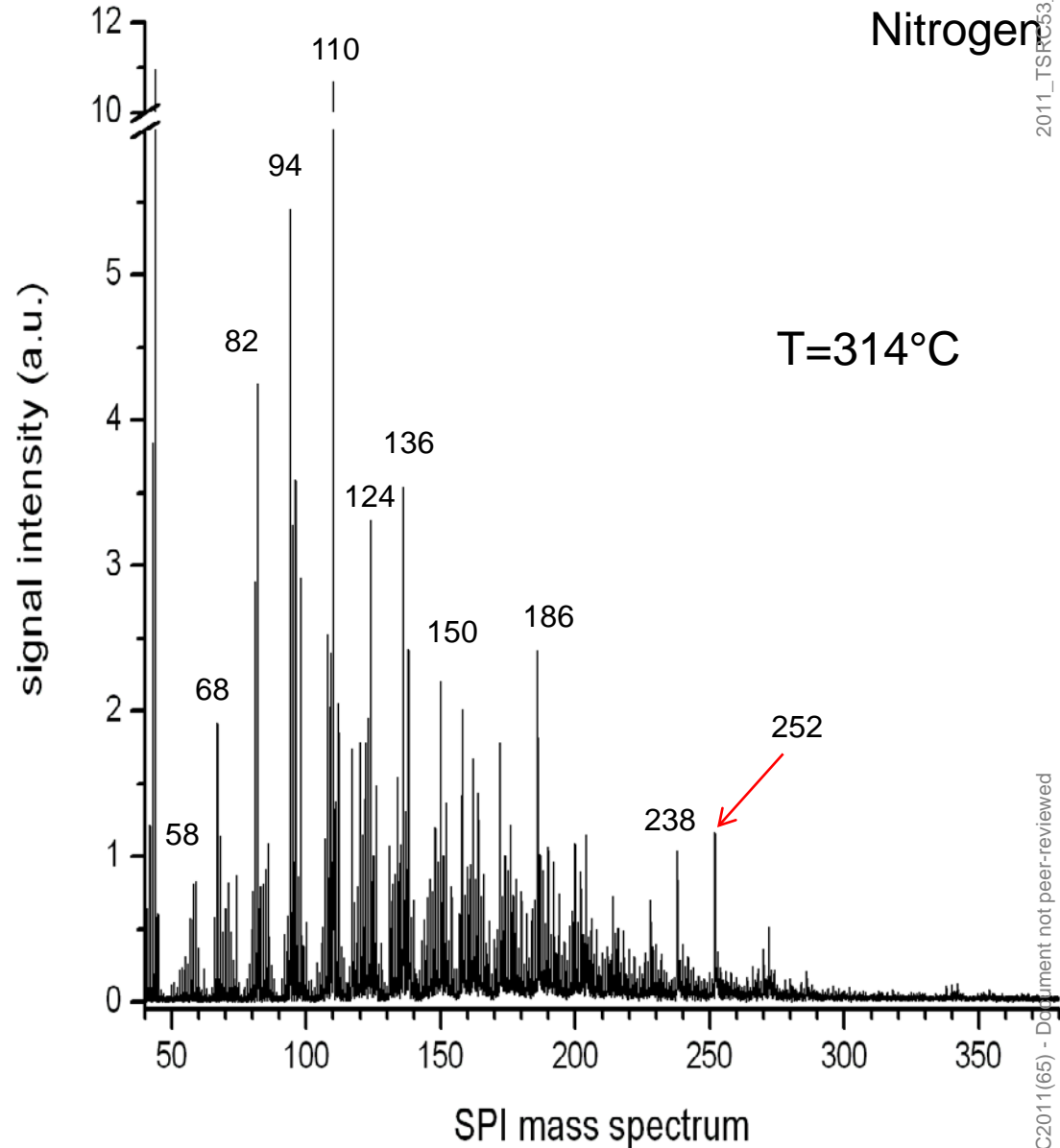
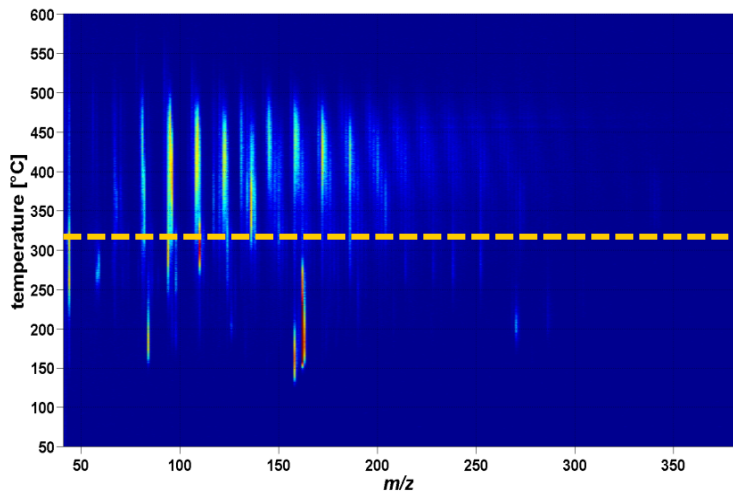
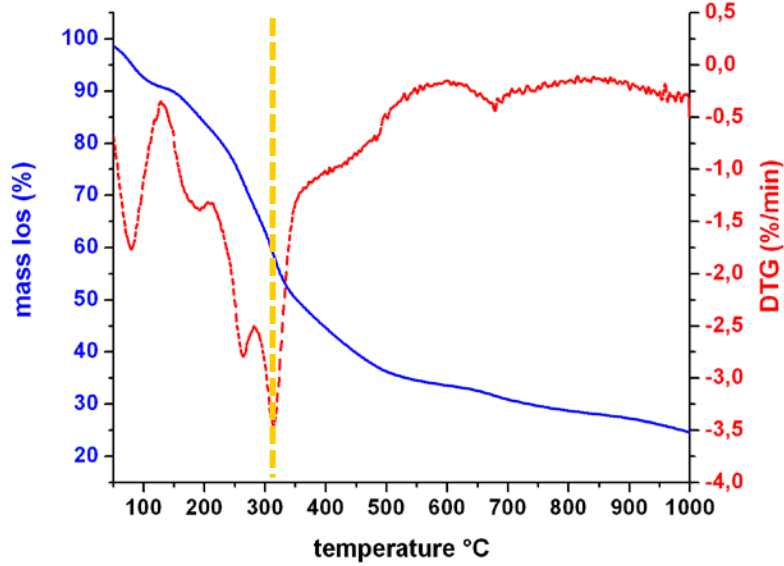
Nitrogen

TG-SPI-MS Applications: Tobacco



TG-SPI-MS Applications: Tobacco

3R4F



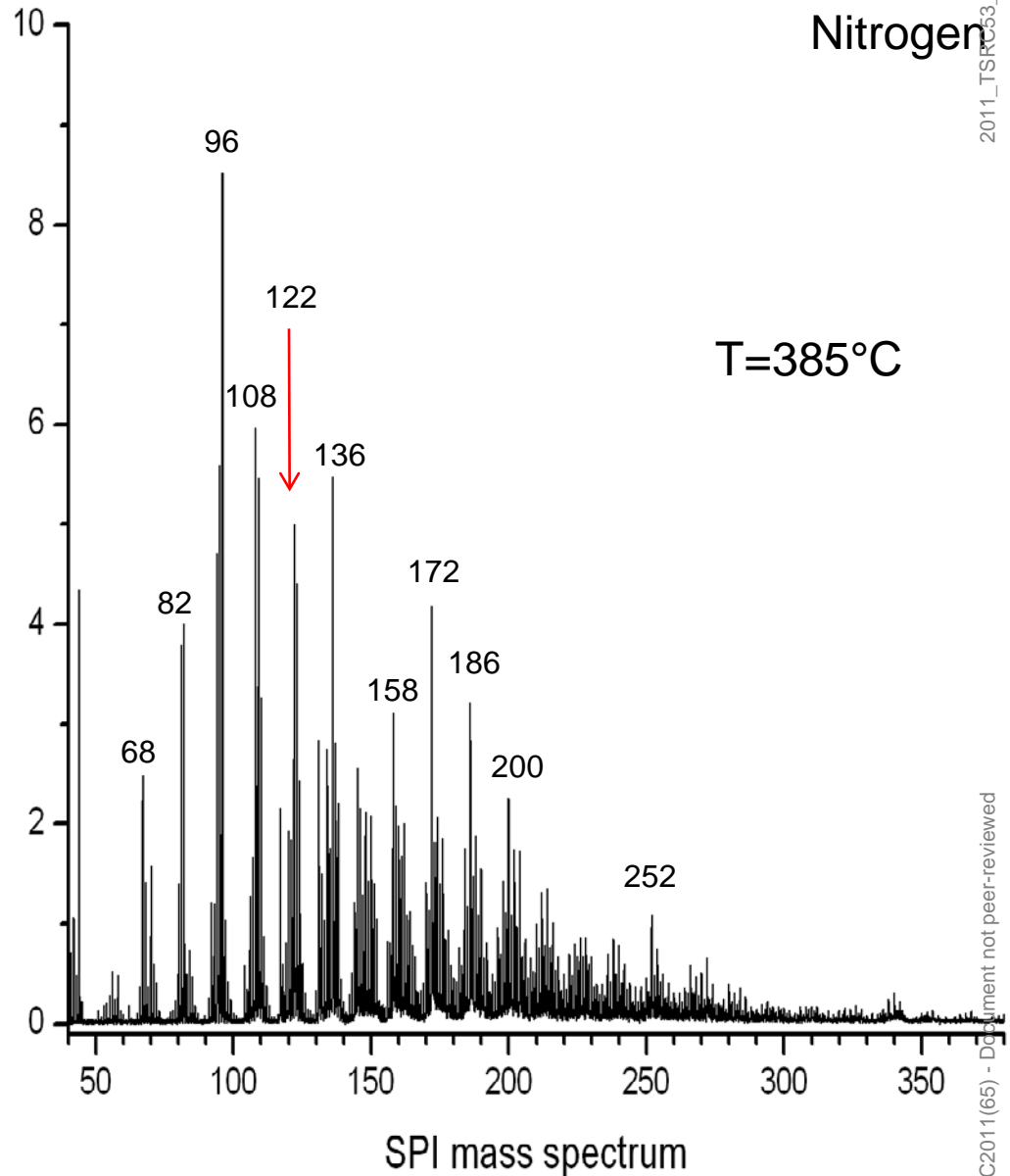
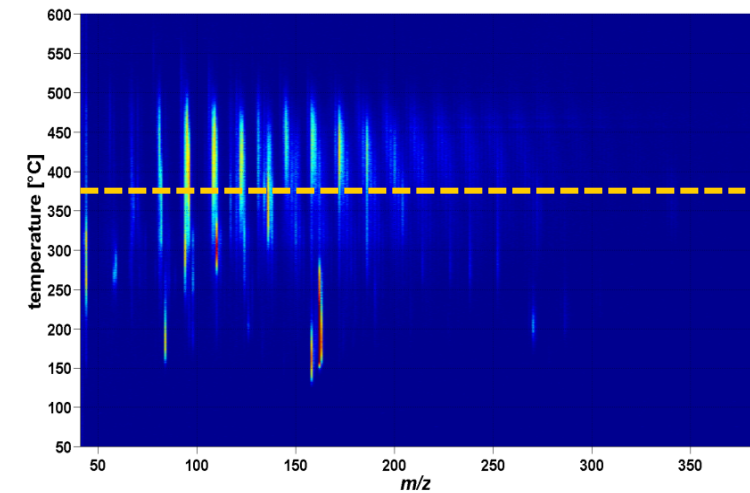
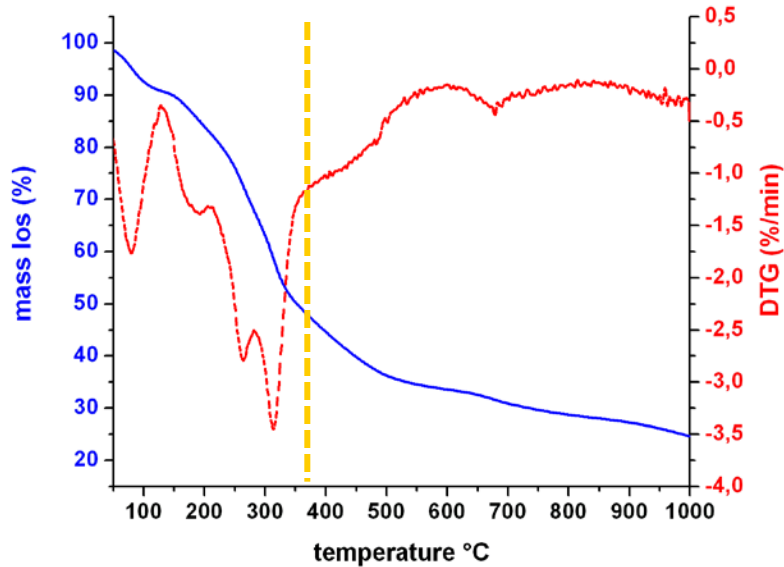
Nitrogen

T=314°C

SPI mass spectrum

TG-SPI-MS Applications: Tobacco

3R4F

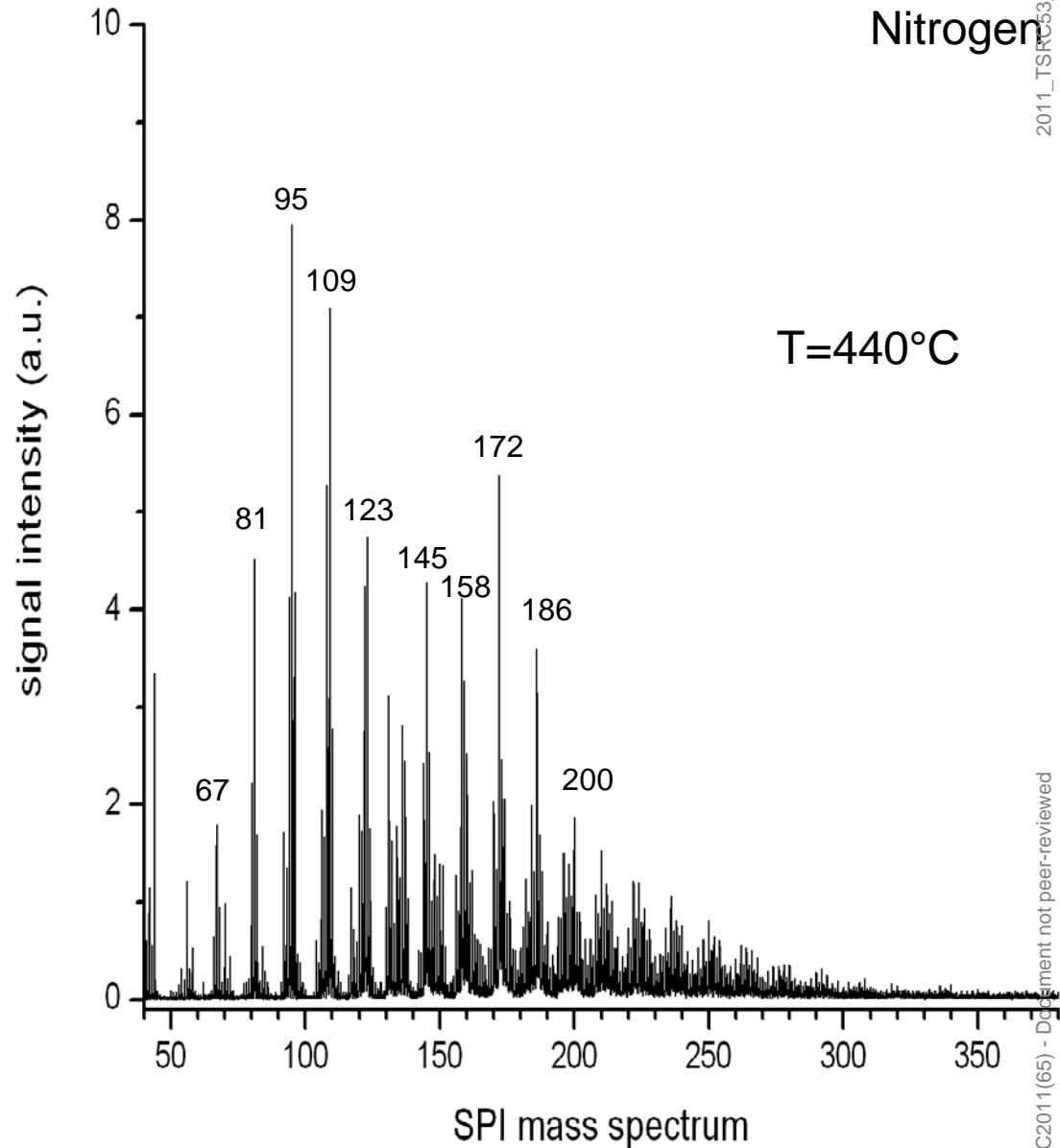
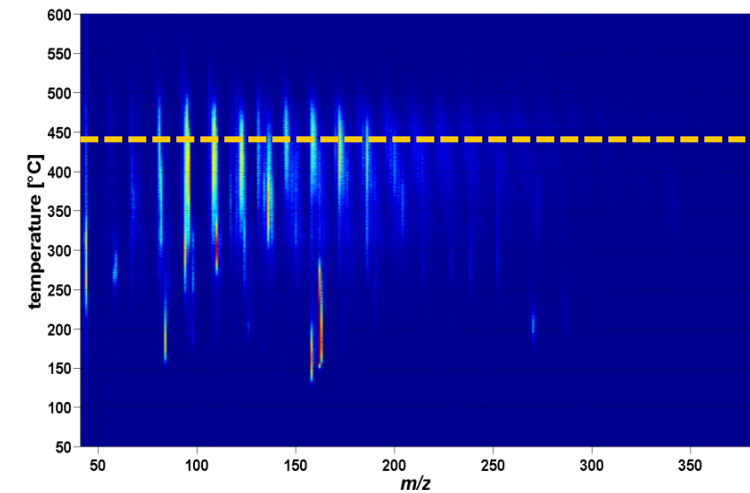
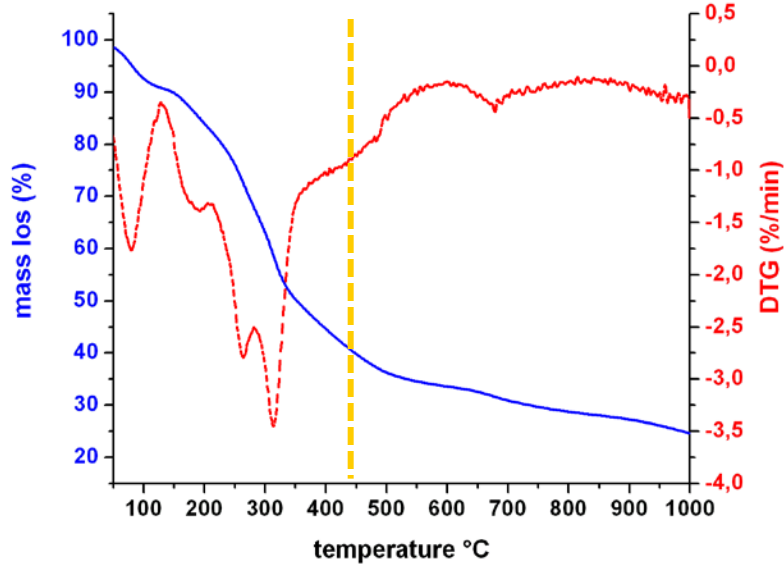


Nitrogen

T=385°C

TG-SPI-MS Applications: Tobacco

3R4F

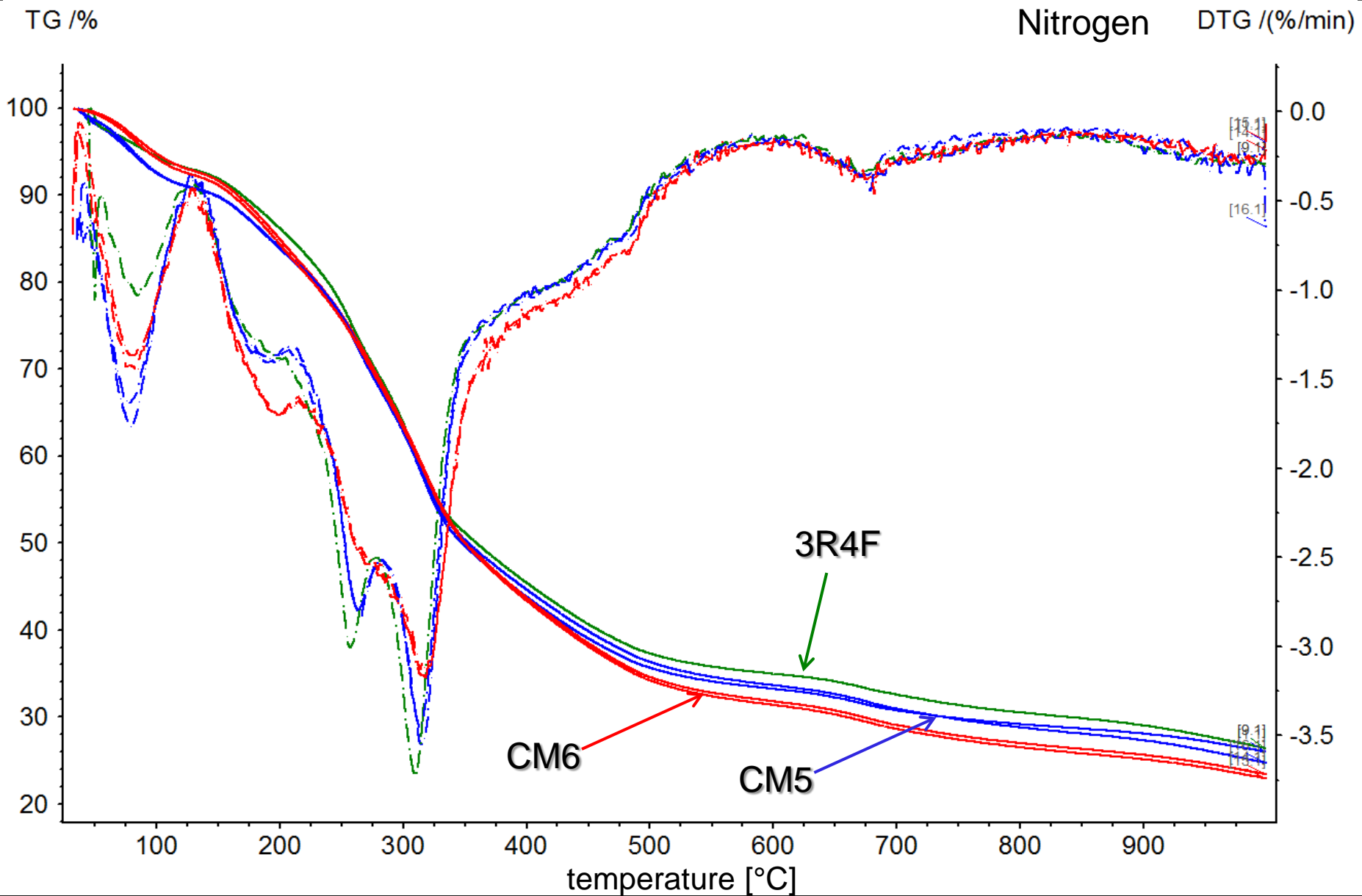


Nitrogen

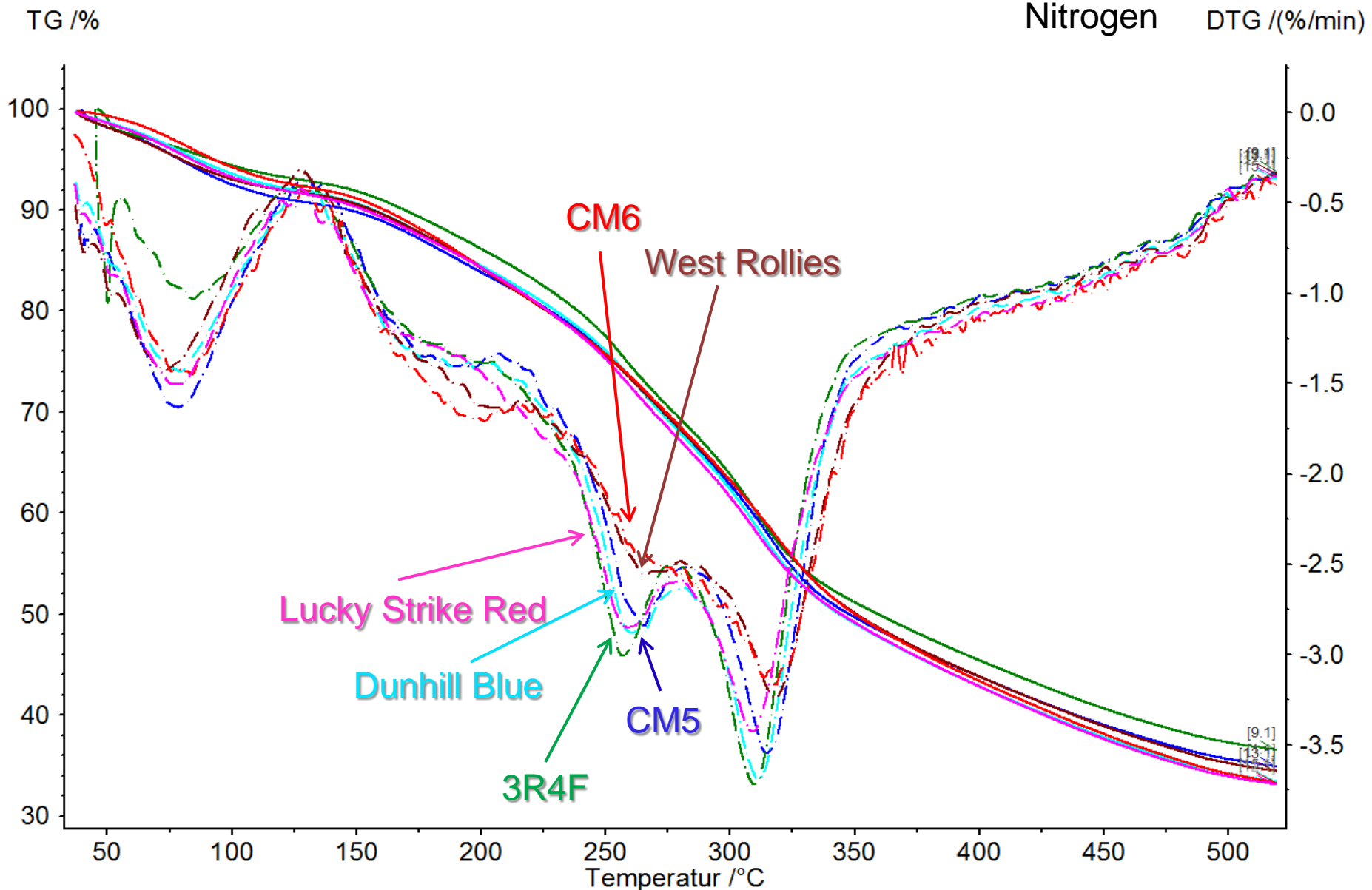
T=440°C

SPI mass spectrum

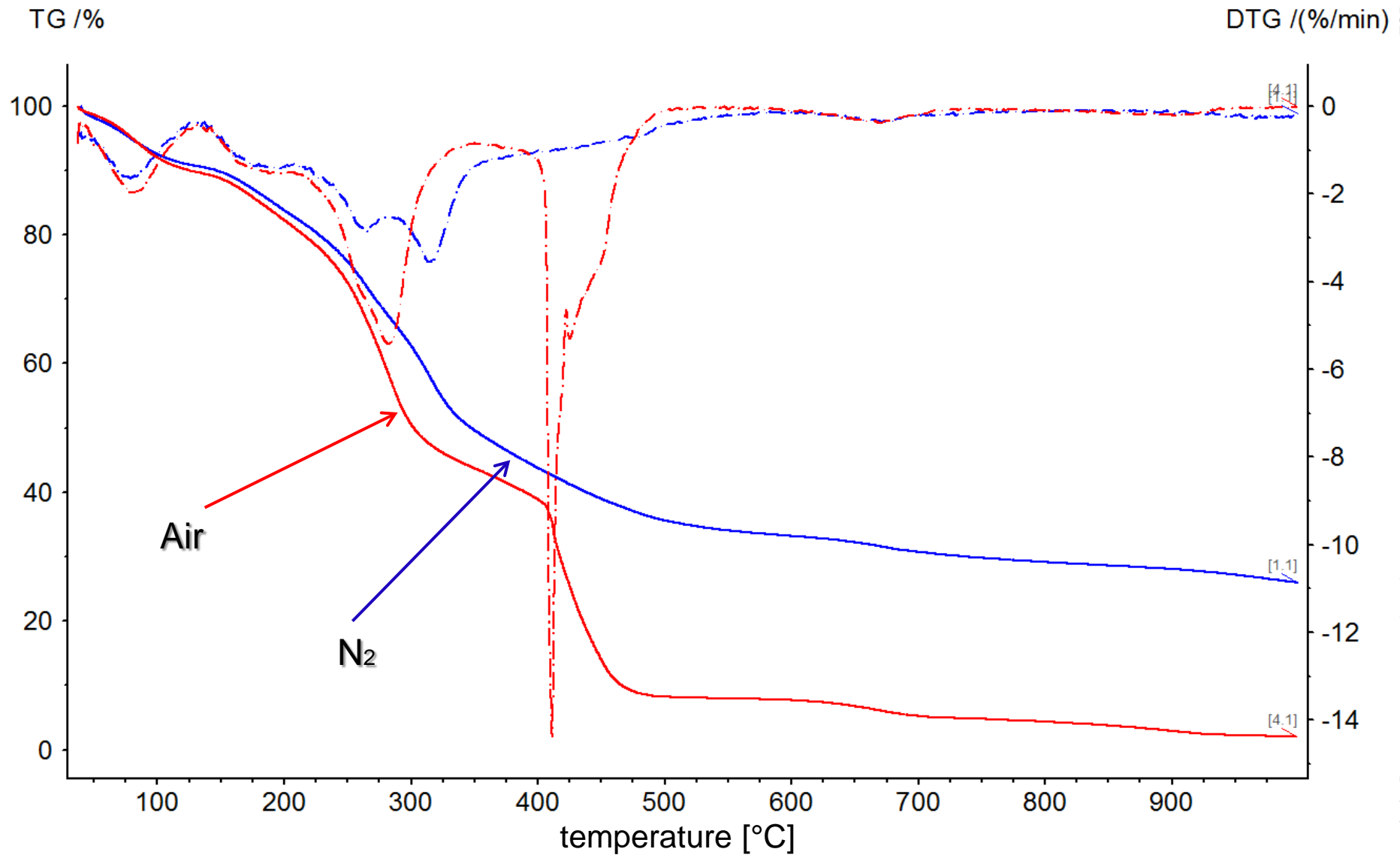
TG-SPI-MS: CM6 vs. CM5 vs. 3R4F



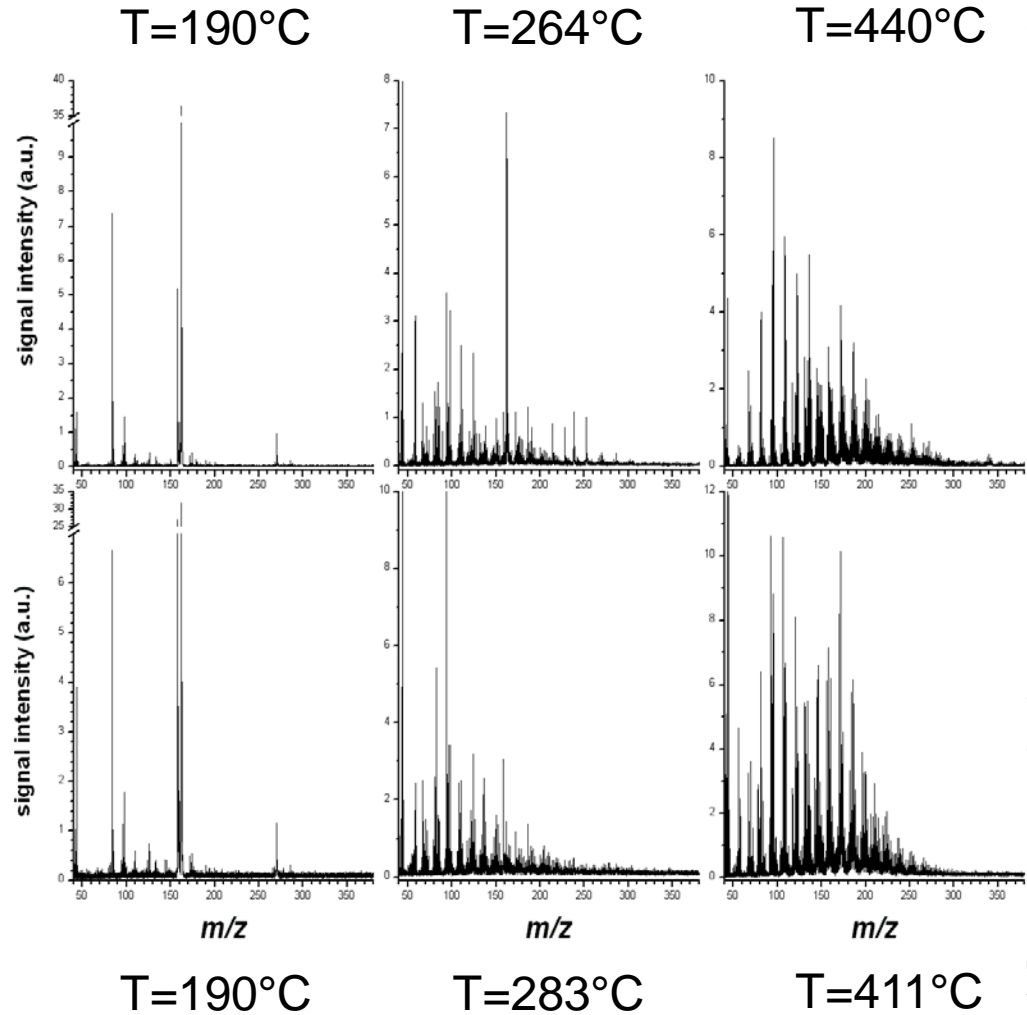
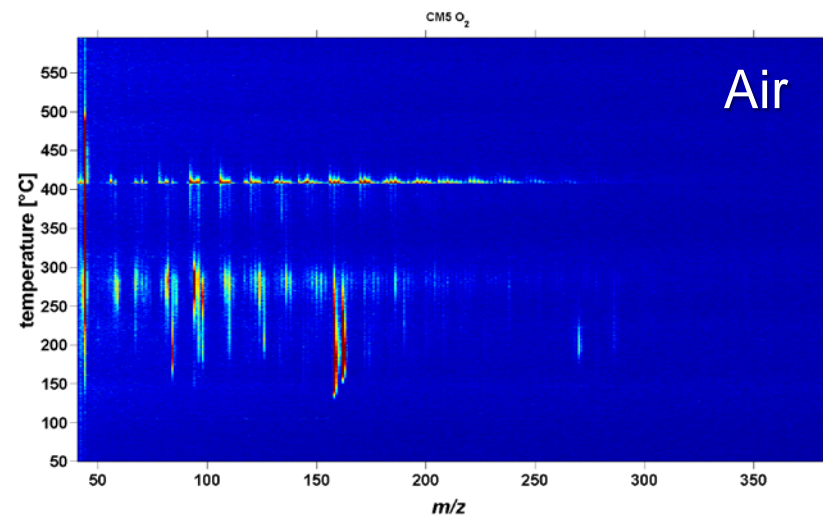
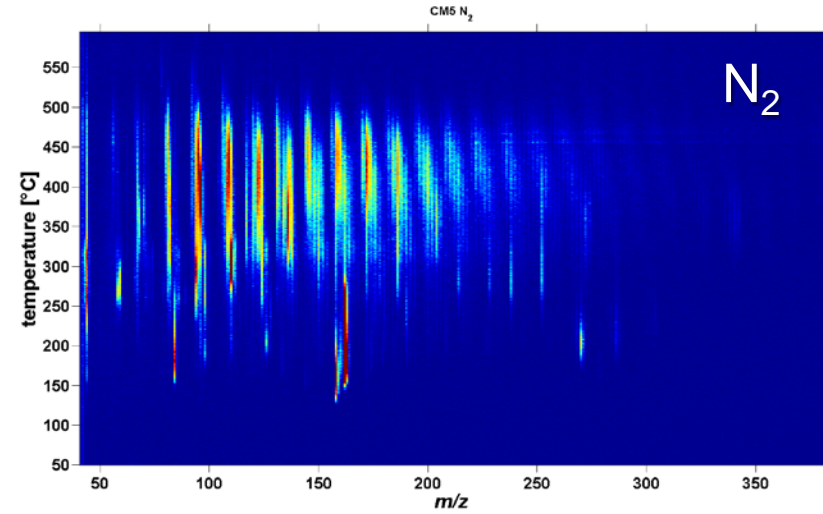
TG-SPI-MS: Commercial brands



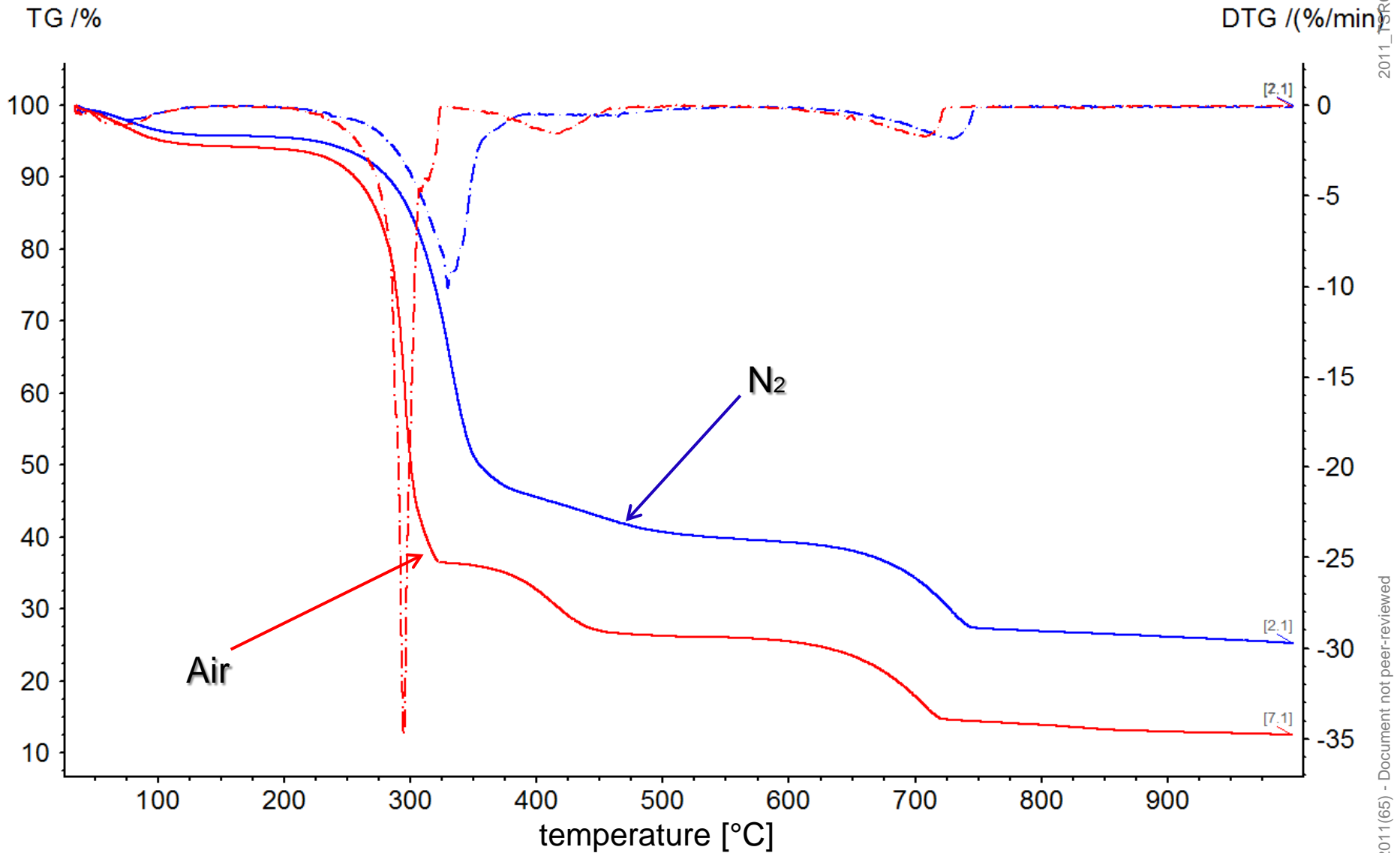
TG-SPI-MS: Tobacco with Air/Nitrogen



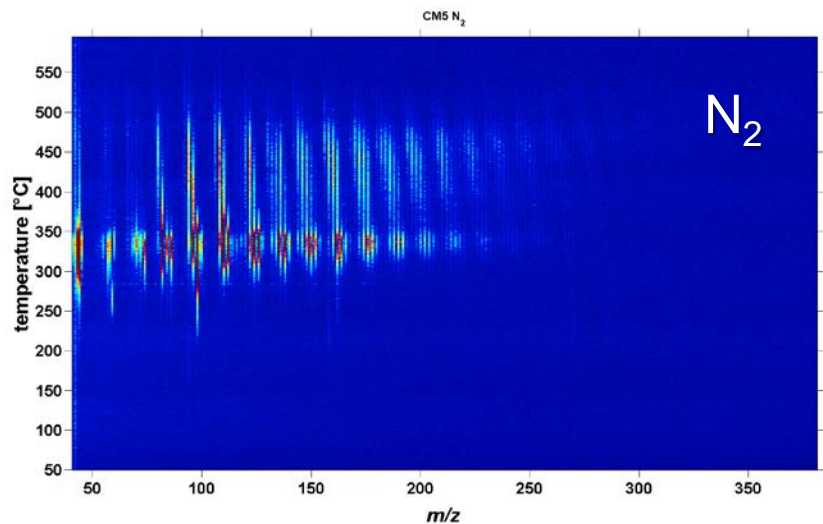
TG-SPI-MS: Tobacco with Air/Nitrogen



TG-SPI-MS: Paper with Air/Nitrogen



TG-SPI-MS: Paper with Air/Nitrogen



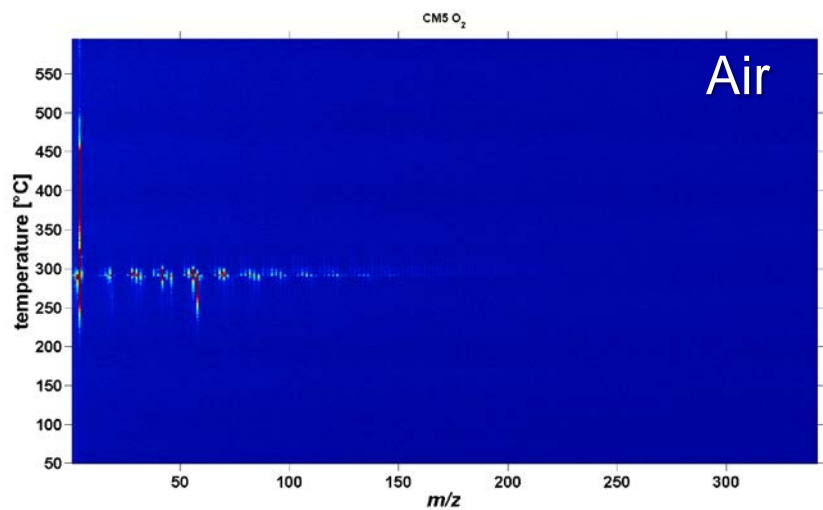
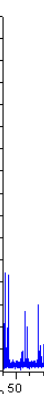
T=332°C

signal intensity (a.u.)



T=443°C

signal intensity (a.u.)



signal intensity (a.u.)



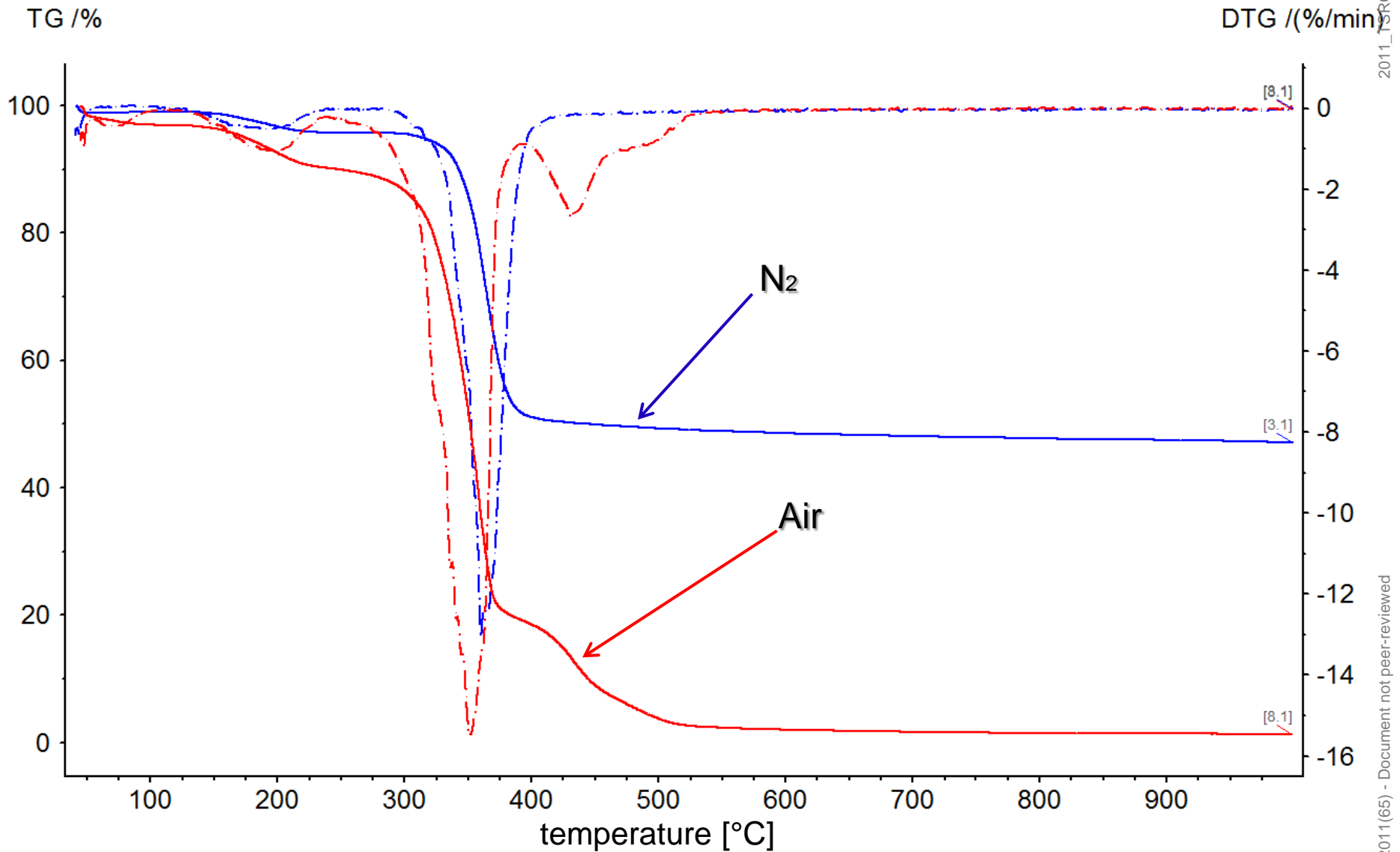
T=293°C

signal intensity (a.u.)

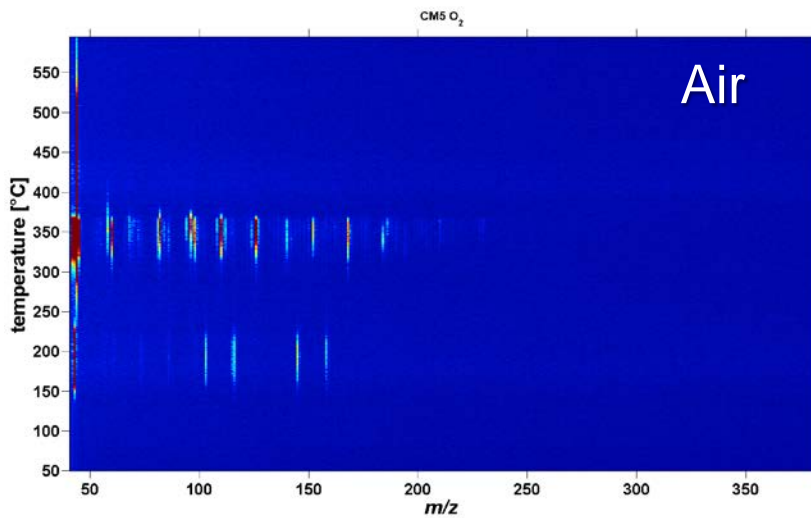
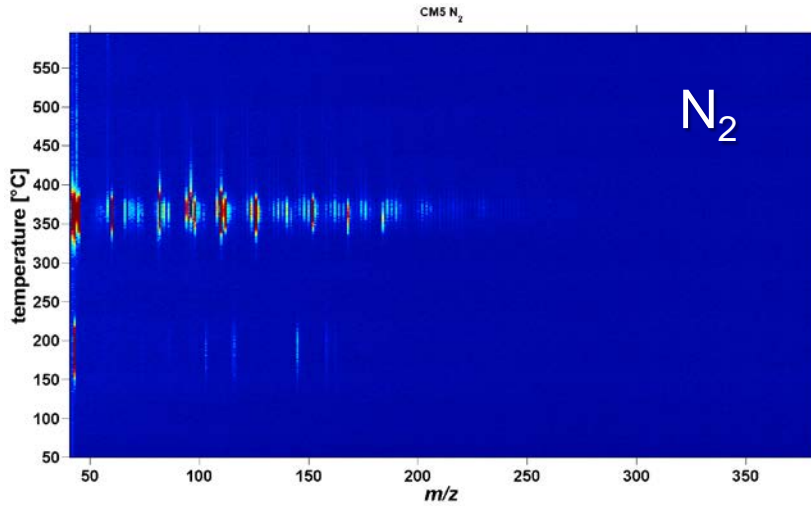


T=410°C

TG-SPI-MS Applications: Filter



TG-SPI-MS Applications: Filter



T=190°C

signal intensity (a.u.)

2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0

50 100 150 200 250 300 350

m/z

T=190°C

T=360°C

35
30
25
20
15
10
5
0

50 100 150 200 250 300 350

m/z

T=352°C

signal intensity (a.u.)

2.5
2.0
1.5
1.0
0.5
0.0

50 100 150 200 250 300 350

Summary

- Advanced **SPI-MS measurement** system for on-line organic profiling in evolved gas analysis (**EGA**) in **Thermal Analysis** (TA)
- **Polymers** as well as **crude oil**, **bio mass** and **coal** samples were successfully investigated by TG-SPI-MS
- First tests of **tobacco** and **cigarette materials** identify tobacco science as well as tobacco product engineering and quality control as interesting & promising applications
- Commercialization of an integrated **TG-SPI-MS** instrument via **Netzsch Instruments GmbH**, Selb, Germany
- **SPI-MS LM2x-TOF-MS tobacco smoke** profiler commercialized via **Borgwaldt KC**, Hamburg, Germany

Commercial Multi-Component Gas Analyzers On-Line Mass Spectrometry with novel EBEL Photoionization Source

Applications



- Flexible Systems for Process and Quality Control: Photo-TOF und Photo-Quad
- Time Resolved Analysis of Cigarette Smoke (LM2X-TOF-MS, Borgwaldt KC)
- Evolved Gas Analysis of Organic Compounds in Thermal Analysis (TG-Photo-Quad, Netzsch GmbH)



Contact: Info@photonion.de

