Hyphenation of Thermogravimetric Analyzers (TGA) with MS, FTIR and GC-MS

Optimizing the Transfer Line and Interface to Ensure Qualitative and Quantitative Data

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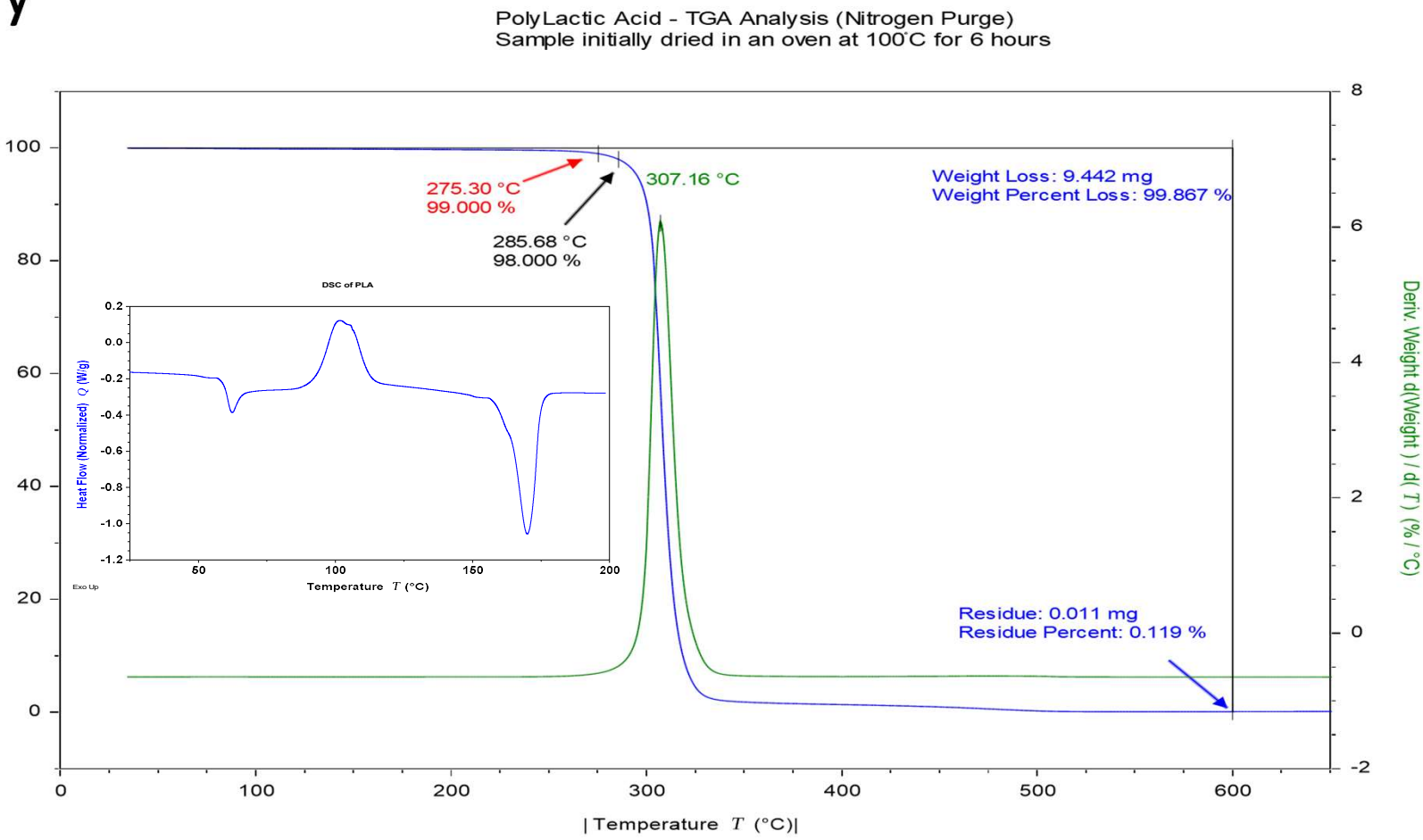
Thermogravimetric Analysis (TGA)

- Measures weight/mass change (loss or gain) and rate of weight change as a function of temperature or time, in controlled atmosphere

Thermal Stability

Upon degradation, typical property changes include:

- Reduced ductility and embrittlement
- Chalking
- Color changes
- Cracking
- General reduction in most other desirable physical properties



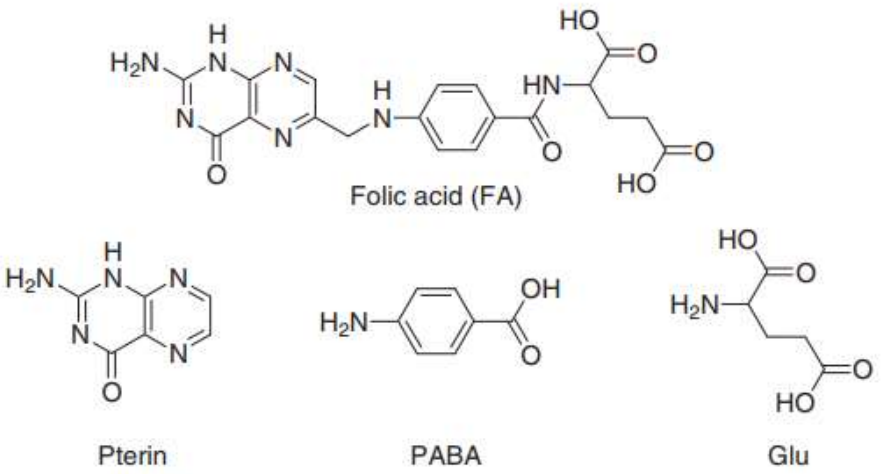
Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer.

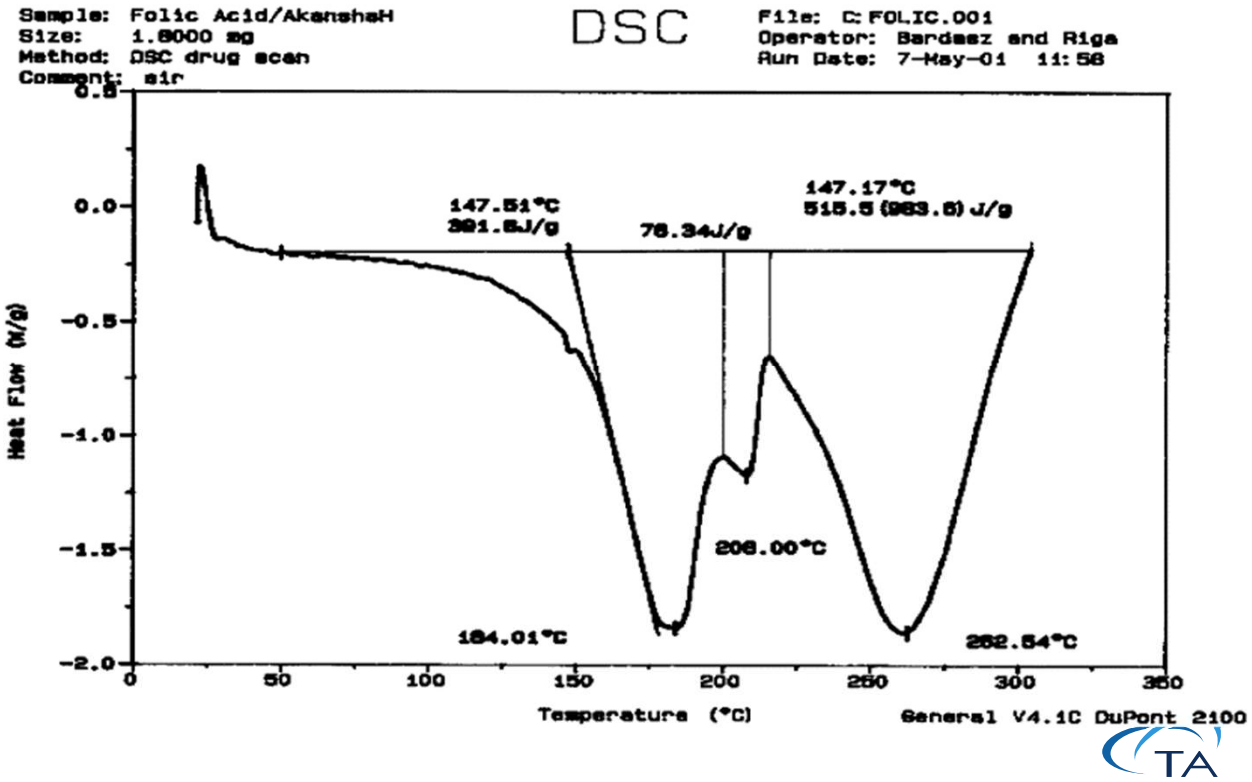
Thermal Stability by TGA

Solid - State Folic Acid Degradation

*1% per year under normal conditions (20°C and 65% relative humidity.

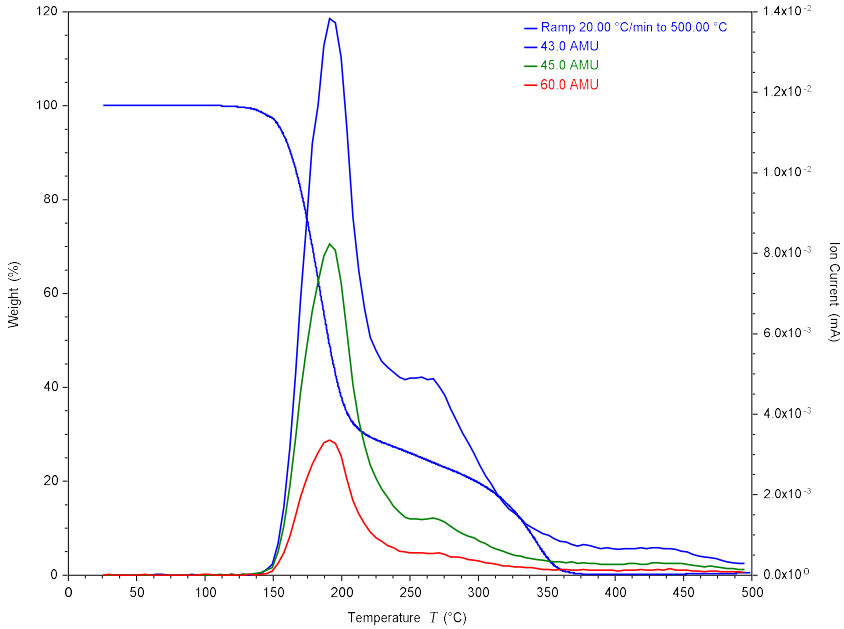
**"Thermal Stability Of Folic Acid in the solid-state"* Journal of Thermal Analysis and Calorimetry 2004, Volume 75, pg 709-717

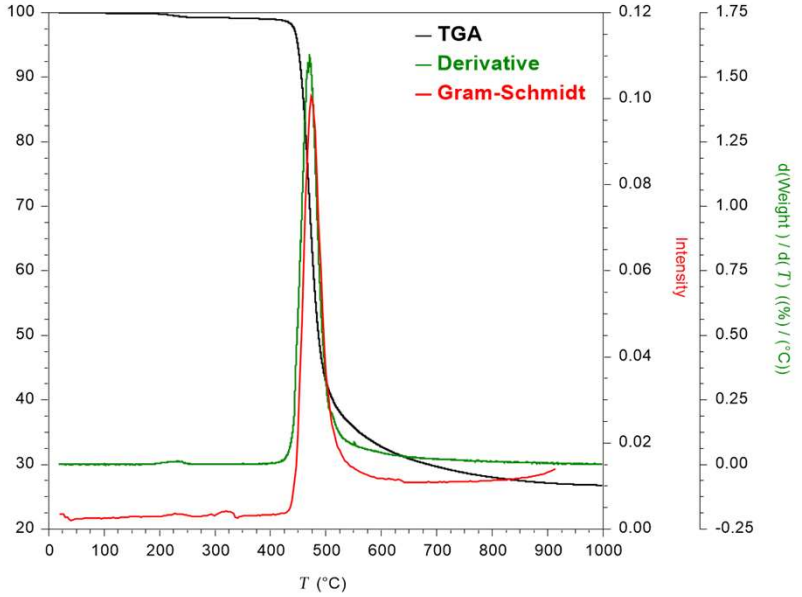




Evolved Gas Analysis

- Commonly referred to as “hyphenated” techniques, TGA is combined with
  - FTIR (TGA/FTIR)
  - mass spectrometry (TGA/MS)
  - gas chromatography and mass spectrometry (TGA/GC-MS)
  - FTIR-MS and FTIR-GC-MS

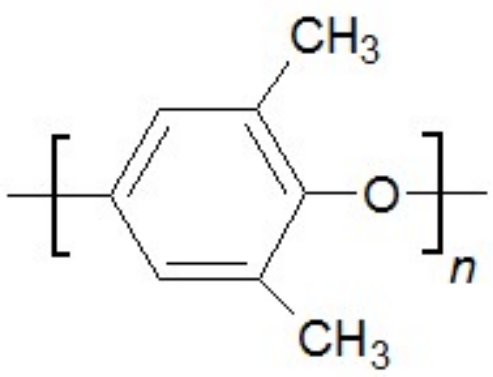


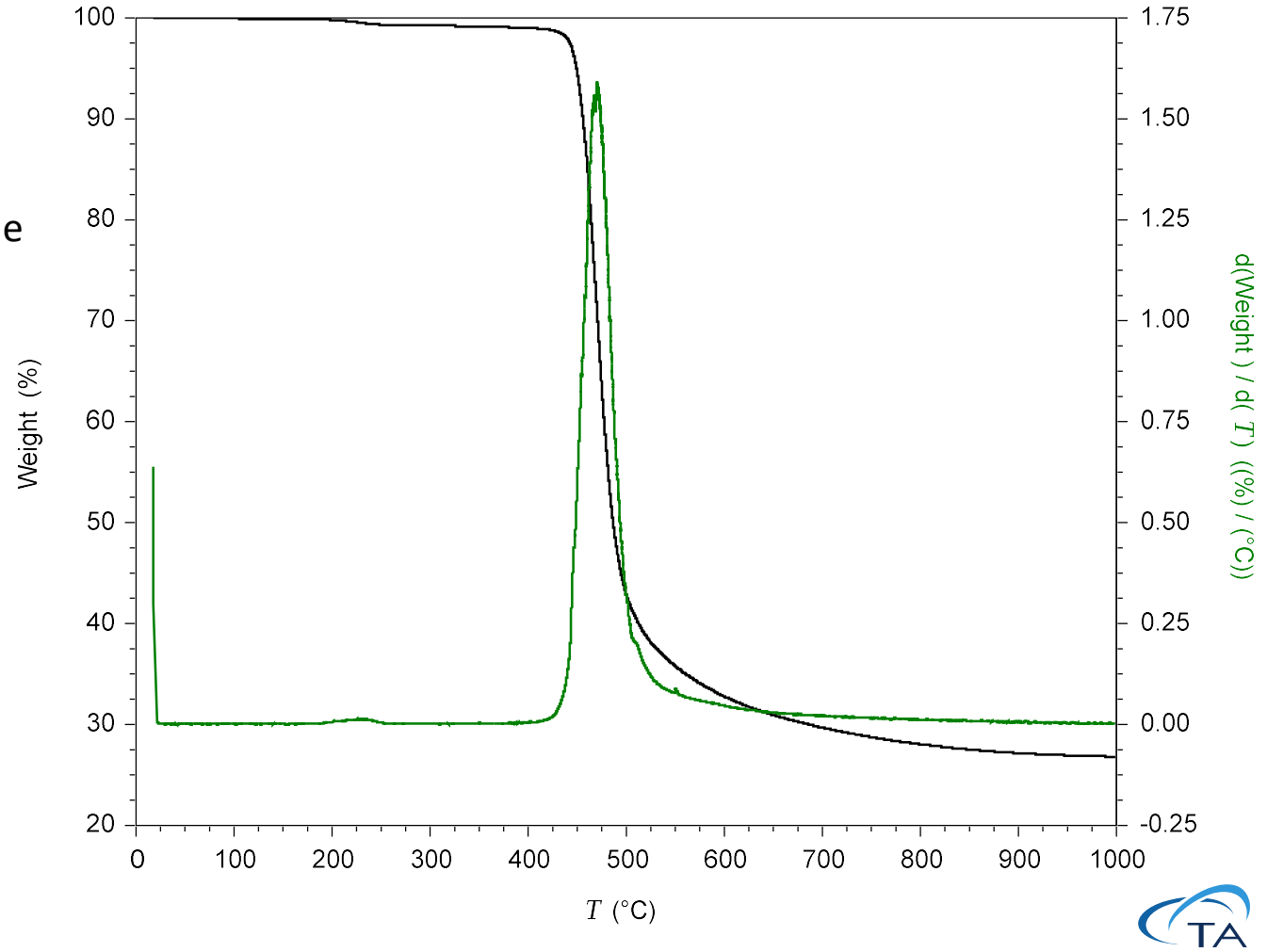


TGA-FTIR: Analysis of Polyphenylene Oxide

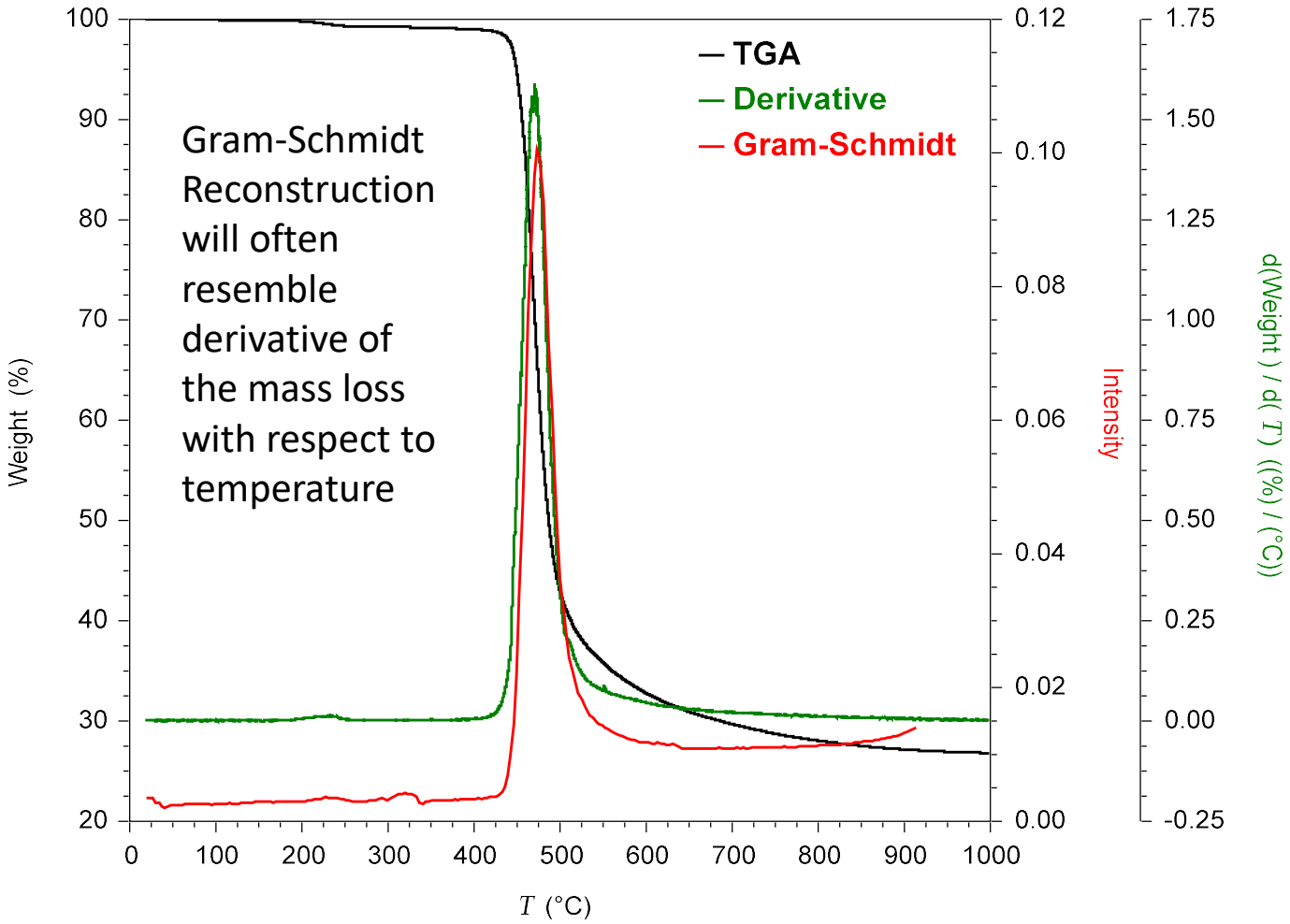
Engineering polymer

- -Heat resistant
- -Good tensile properties
- -High surface energy – paintable
- -Difficult to process

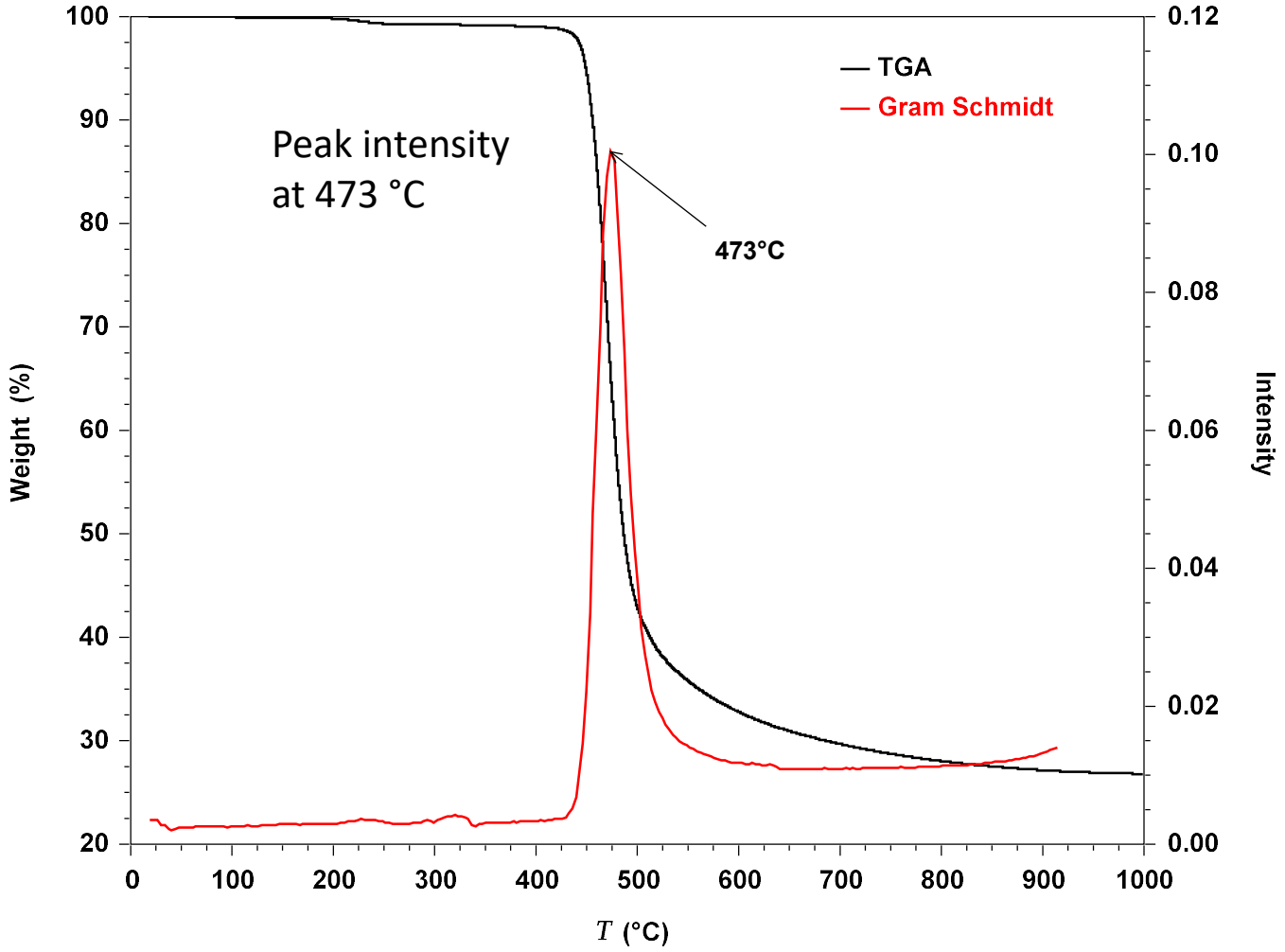




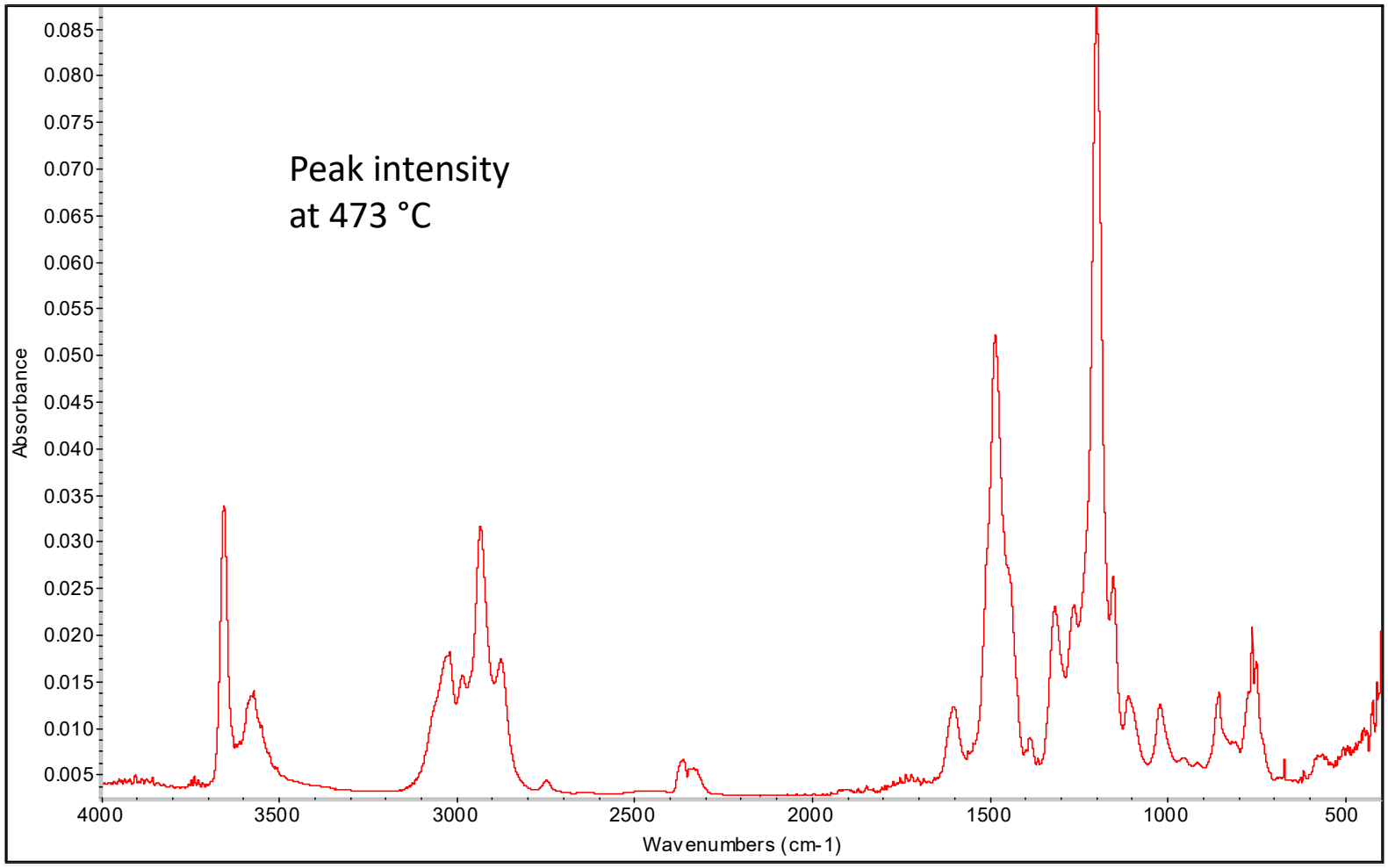
TGA-FTIR: Analysis of Polyphenylene Oxide



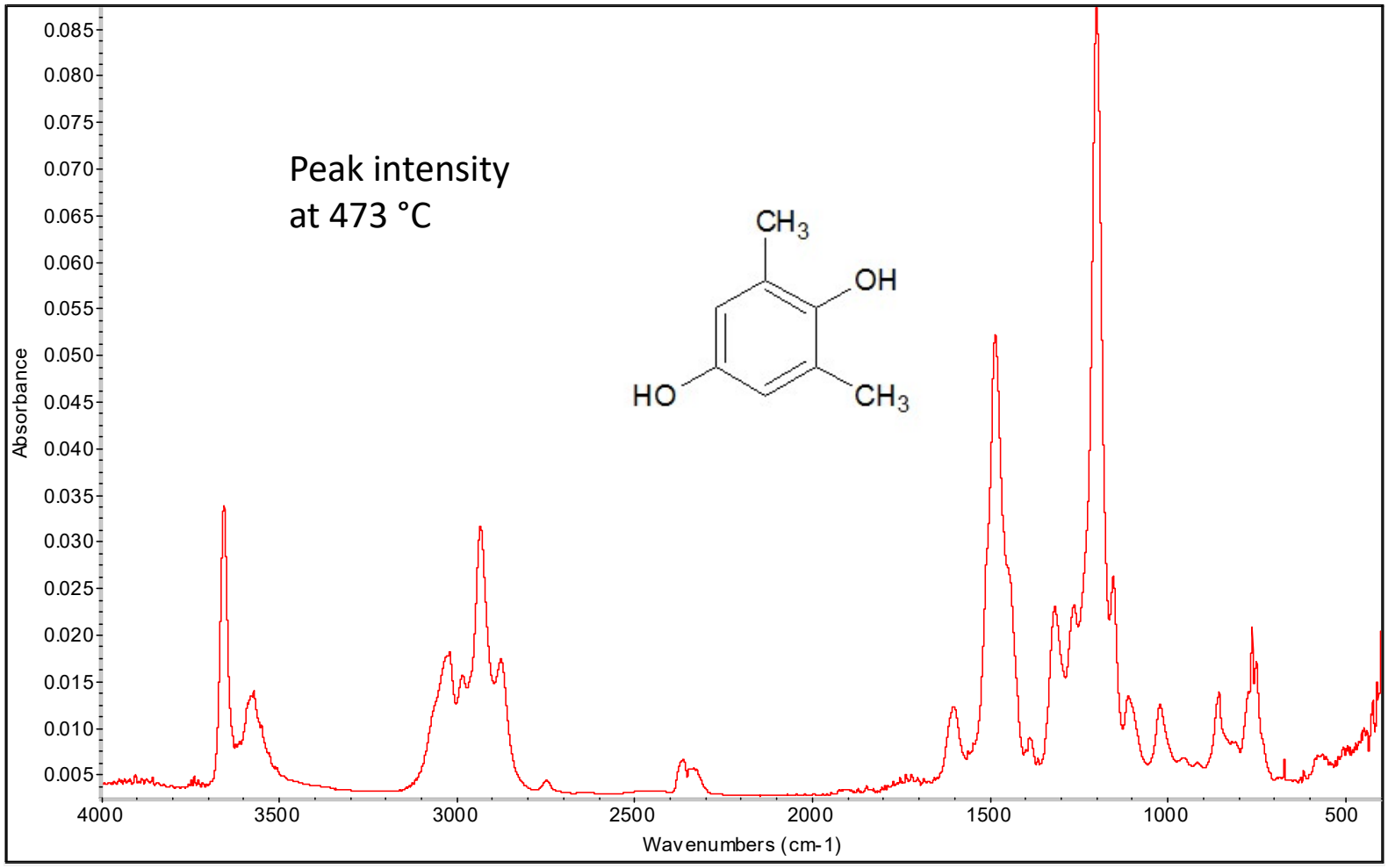
TGA-FTIR: Analysis of Polyphenylene Oxide



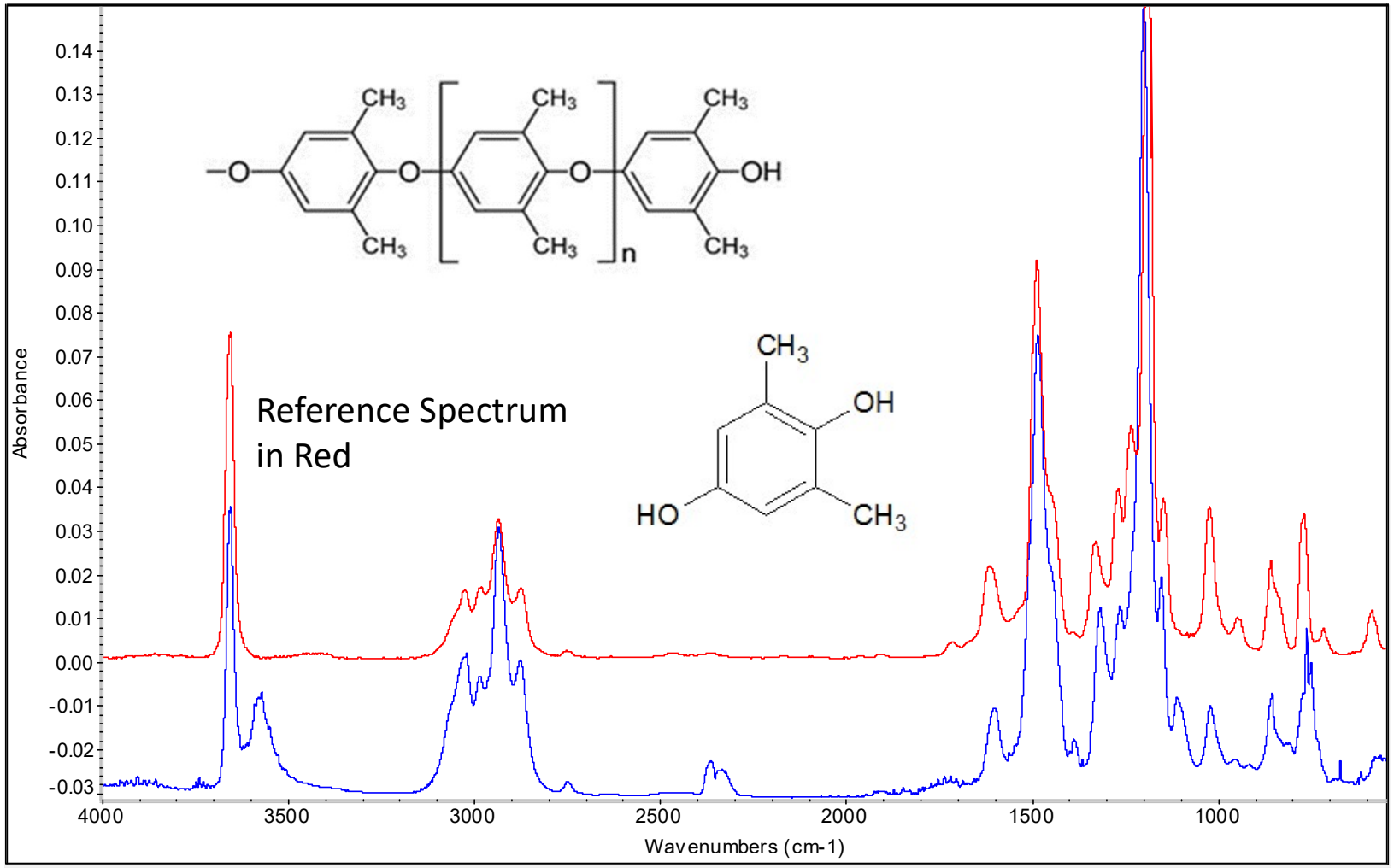
TGA-FTIR: Analysis of Polyphenylene Oxide



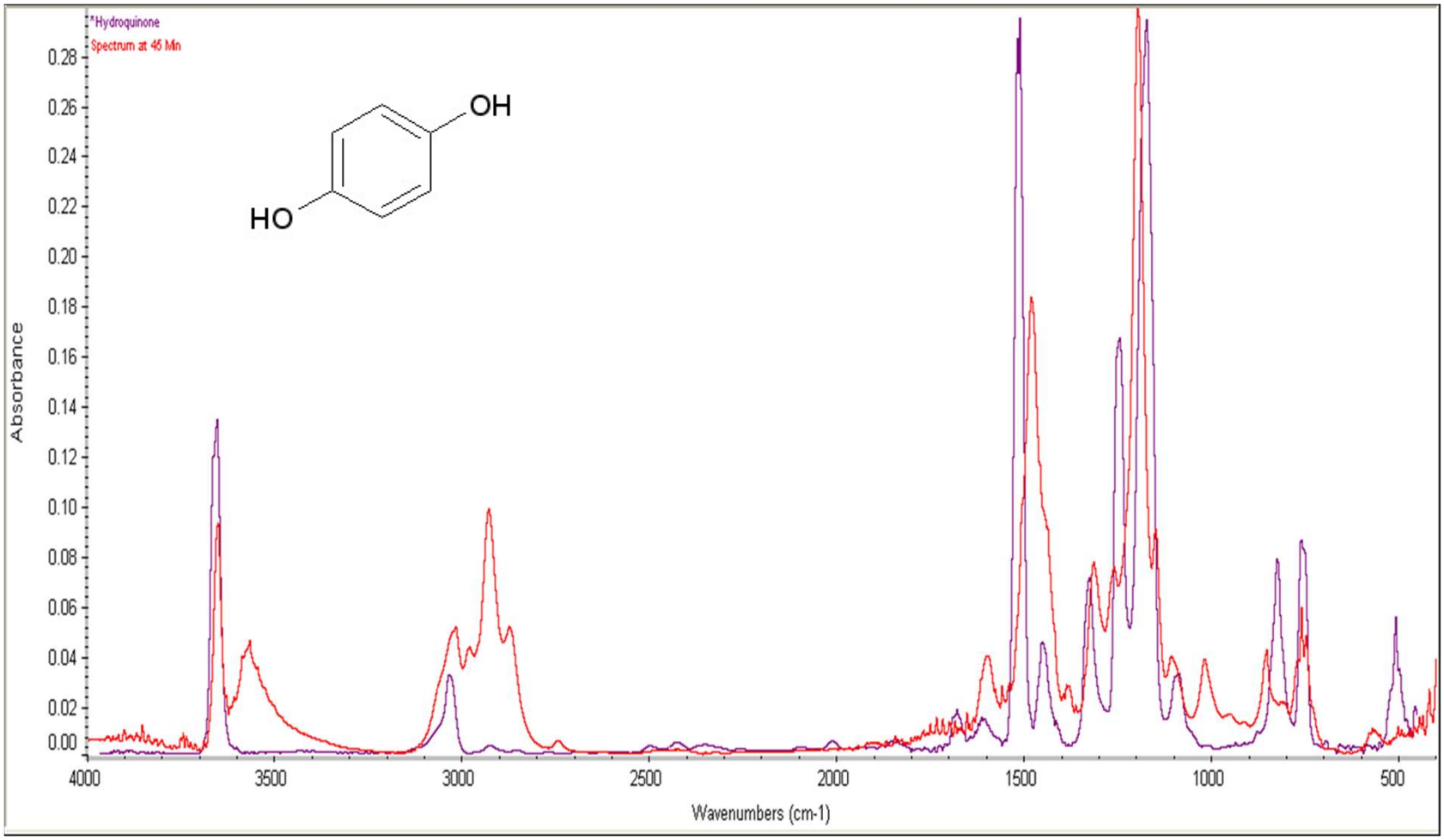
TGA-FTIR: Analysis of Polyphenylene Oxide



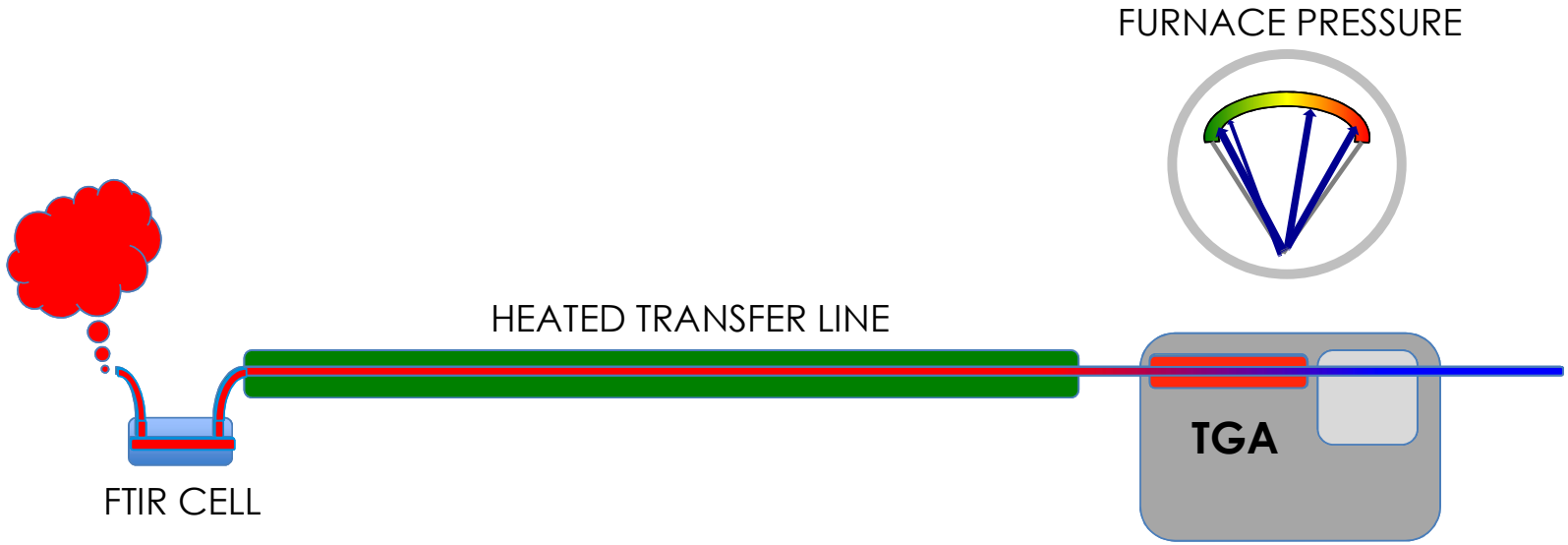
TGA-FTIR: Analysis of Polyphenylene Oxide



TGA-FTIR: Analysis of Polyphenylene Oxide
2 entities of at least 6 detected



Traditional TGA-IR Interface



Gases are "pushed" by the TGA purge gas pressure to a restricting point/capillary, the pressure increases in the TGA creating a stagnation of corrosive gas emitted by the sample and turbulence effects across the transfer line (TL).
The non-constant flow passes through the TL as well as the Evolved Gas to the detection cell.

REDshift

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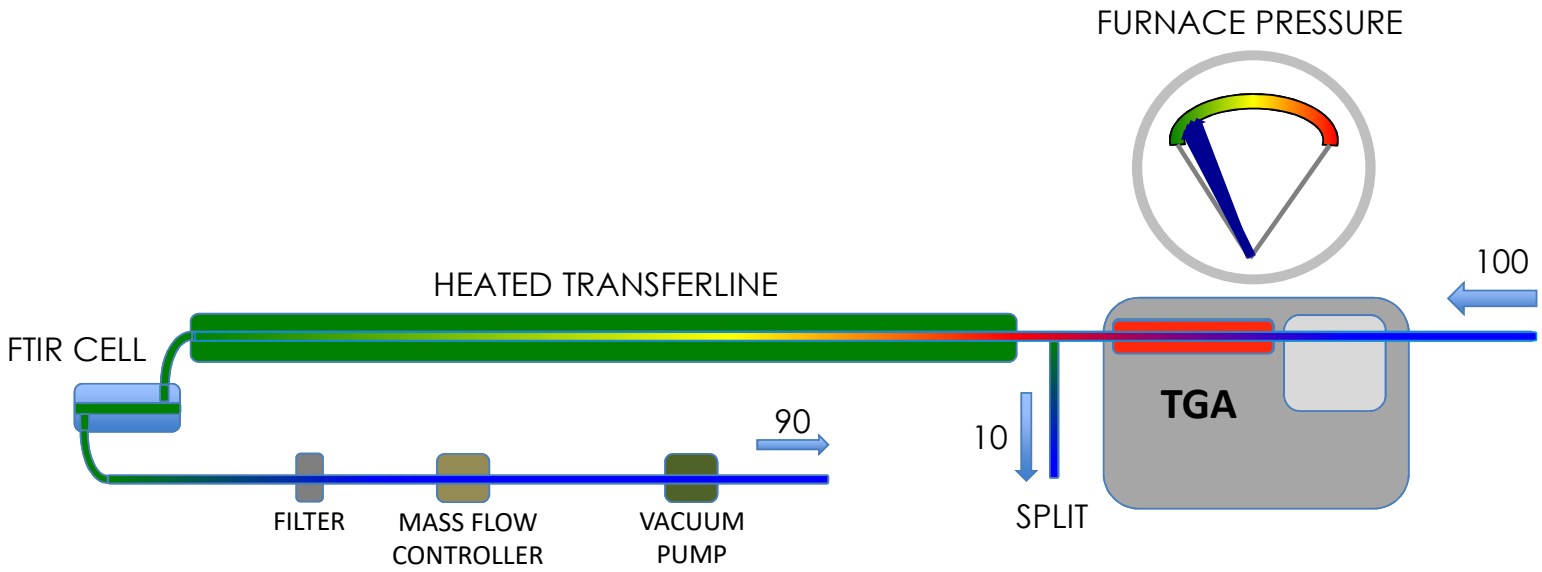
TGA Furnace Measuring System – TL8000



The flow is controlled instead of the pressure.

This is achieved through a mass flow controller after the detection cell and a splitting device just before the transfer line.

This system provides constant flow through the transfer line as well as temperature control of the Evolved Gas.
The TL is constantly heated up to max 350°C.

FURNACE TEMPERATURE

20 C 280 C 350 C 400 C 500 C

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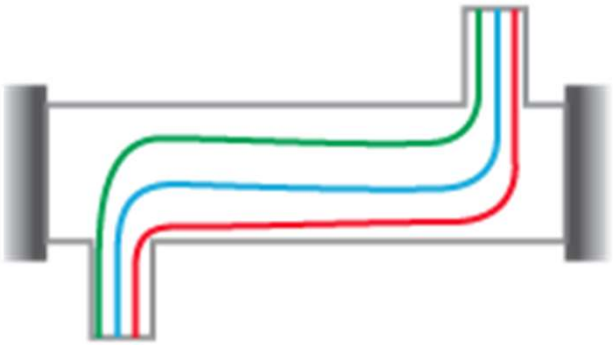
Technology of the FTIR Gas Cell

Zero-Gravity Cell (ZG-Cell) design allows heavy molecular weight components elimination providing the cell with little maintenance and more sensitive and accurate data.

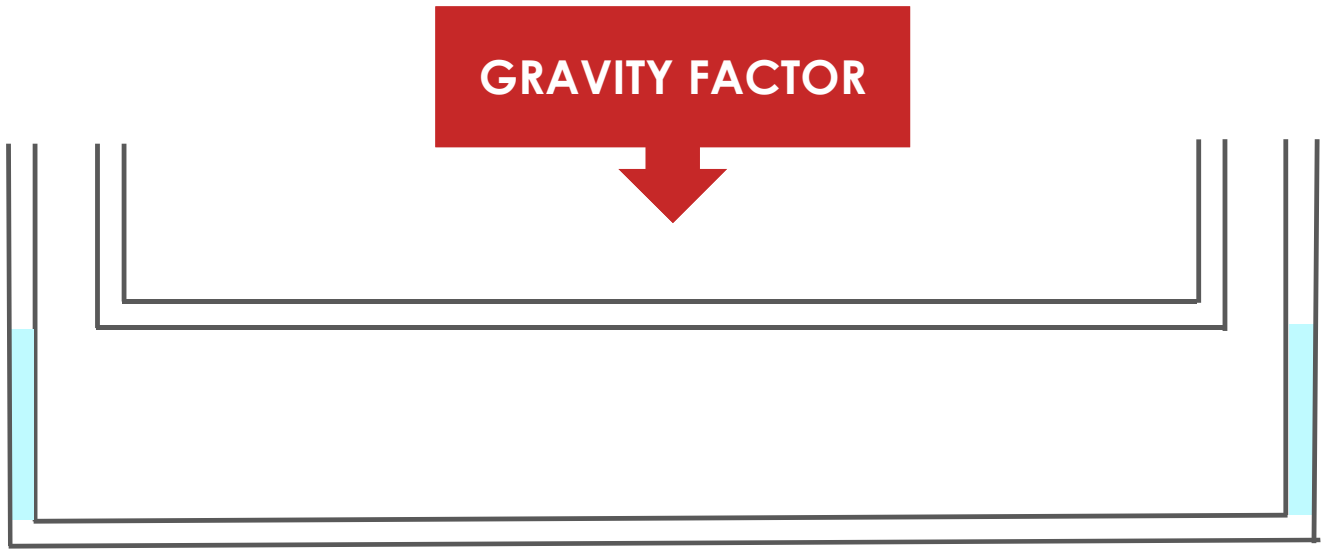
ZG-Cell is provided with an automatic accessory identification, low volume and efficient sample area purging.

TL8000



Conventional

Conventional FTIR Gas Cell



MOLECULAR WEIGHT

- LOW
- MEDIUM
- HIGH

REDshift

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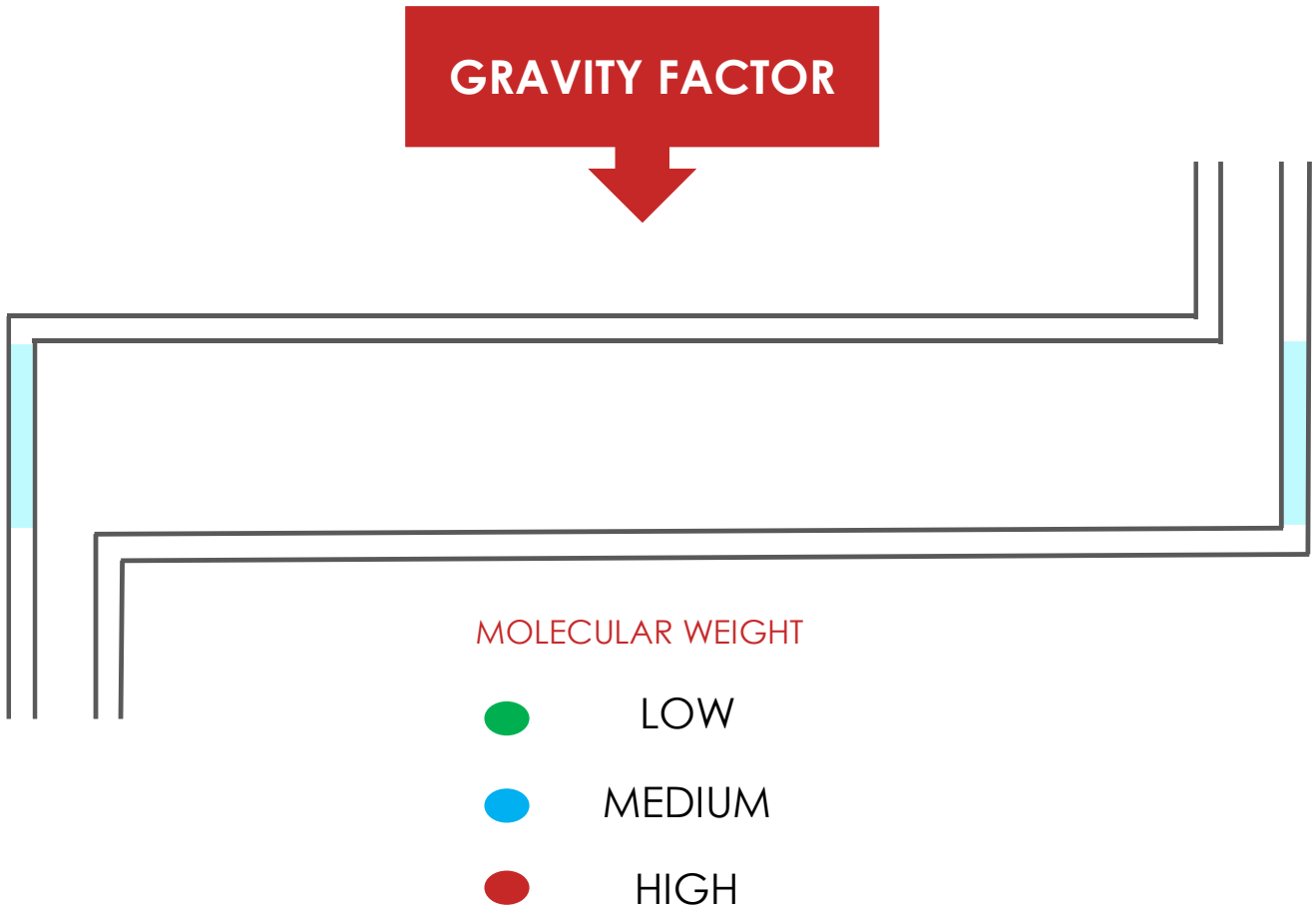
Zero Gravity FTIR Gas Cell - REDshift



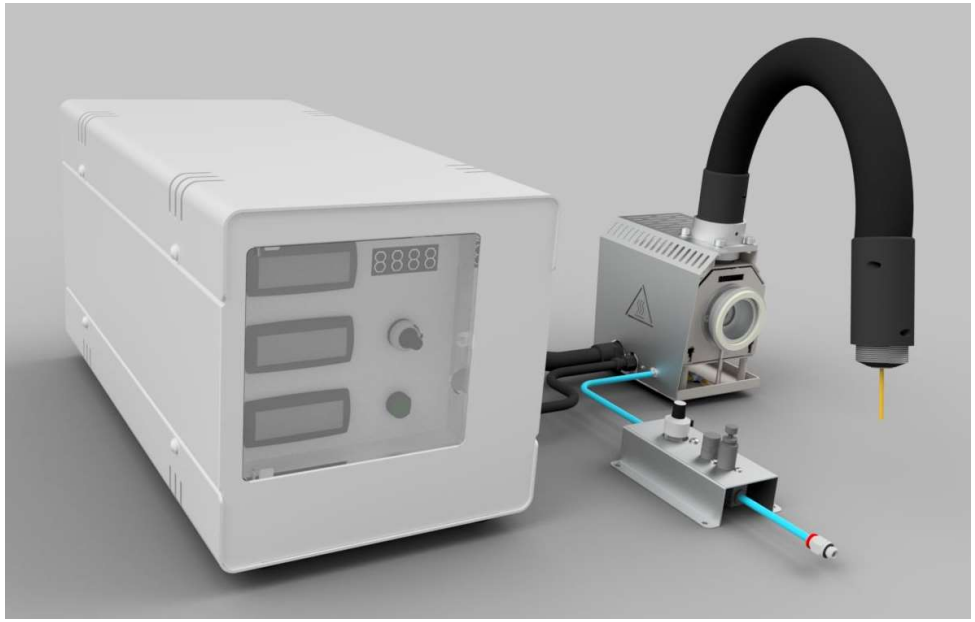
REDshift

TA

TGA-IR Highlights - REDshift

ADVANTAGES:

- Functional group analysis
- Real time analysis
- Quantitative and qualitative results
- Difficulties in mixture analysis can be swapped by H_2O and/or CO_2
- Non-destructive on vapor
- Easy to clean with no condensation and dirty gas deposit
- Low cost option



The Discovery Mass Spectrometer (DMS)

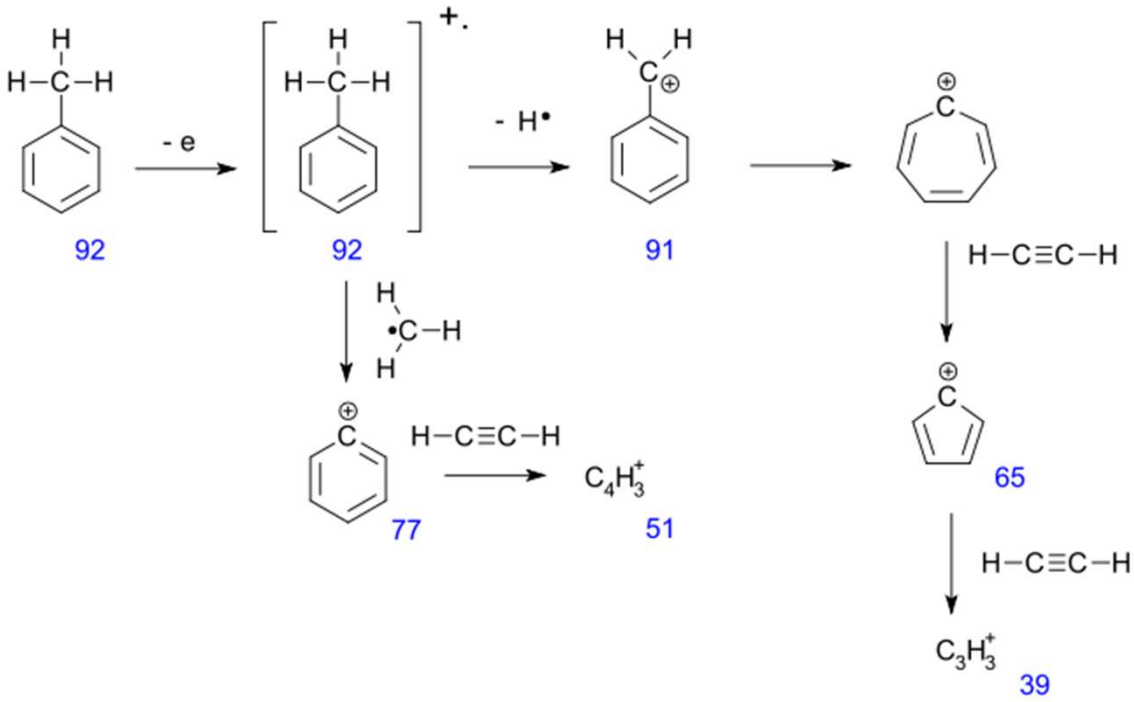
- Benchtop, unit resolution quadrupole mass spec designed and optimized for evolved gas analysis (EGA)

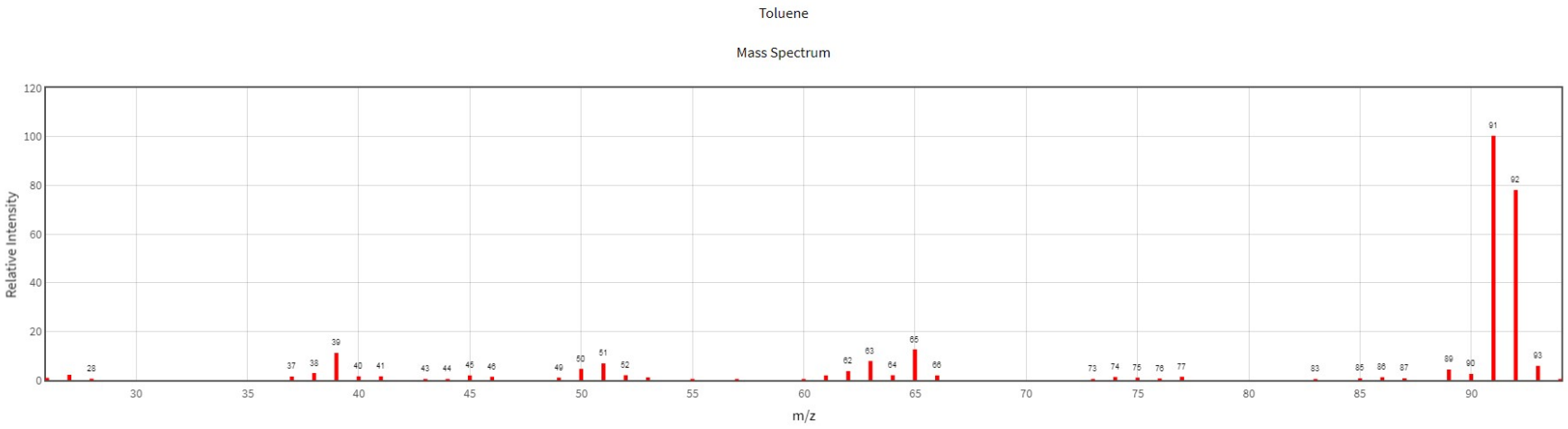
- Quadrupole detection system includes…
  - a closed ion source
  - a quadrupole mass filter assembly
  - 1-300 amu range
  - dual detector system (Faraday and Secondary Electron Multiplier)

  …ensuring excellent sensitivity from ppb to percent concentrations

TGA/MS: Experiments

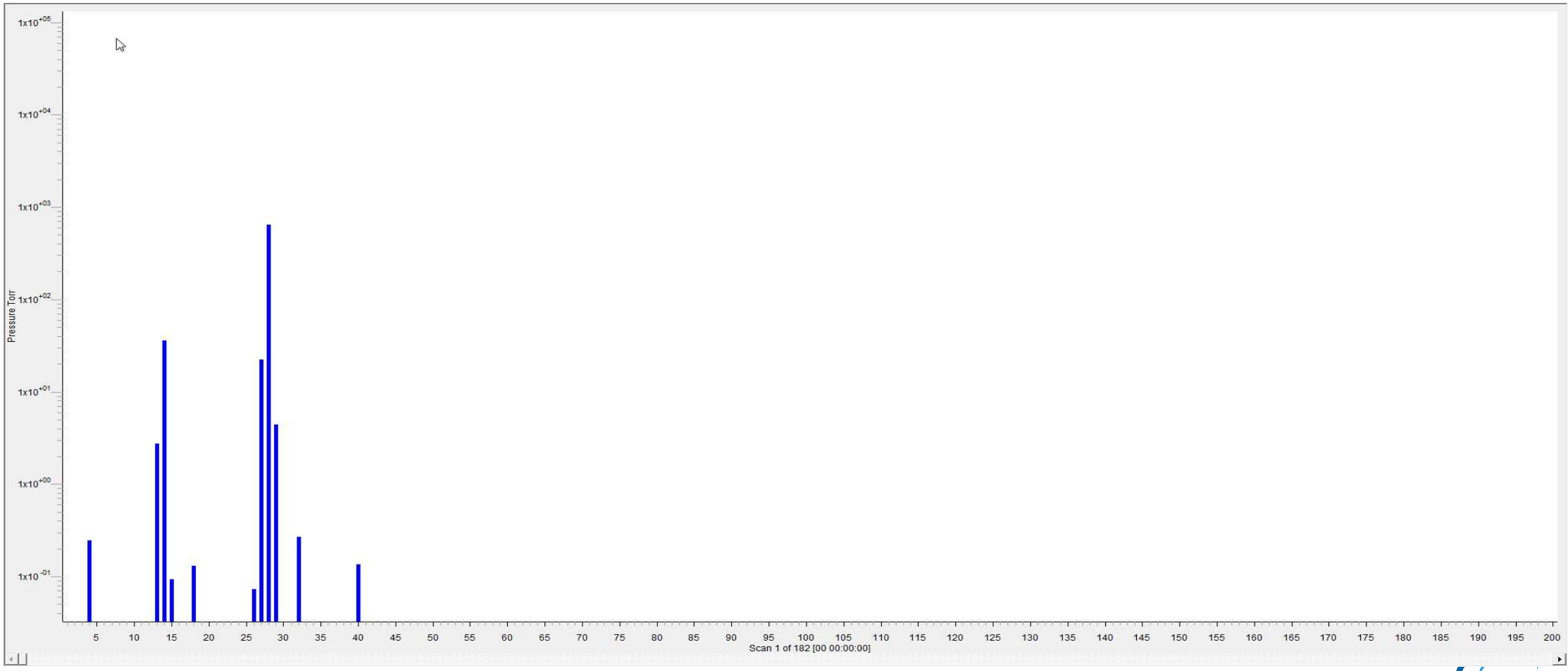
- Barchart
  - Scan across specified ion range - m/z 1 to m/z 300
  - Typically used as first approach for an unknown compound
- Peak Jump
  - Scan specific ions
  - Example, scan m/z 91, 65, 51, 39 if you are looking for residual toluene



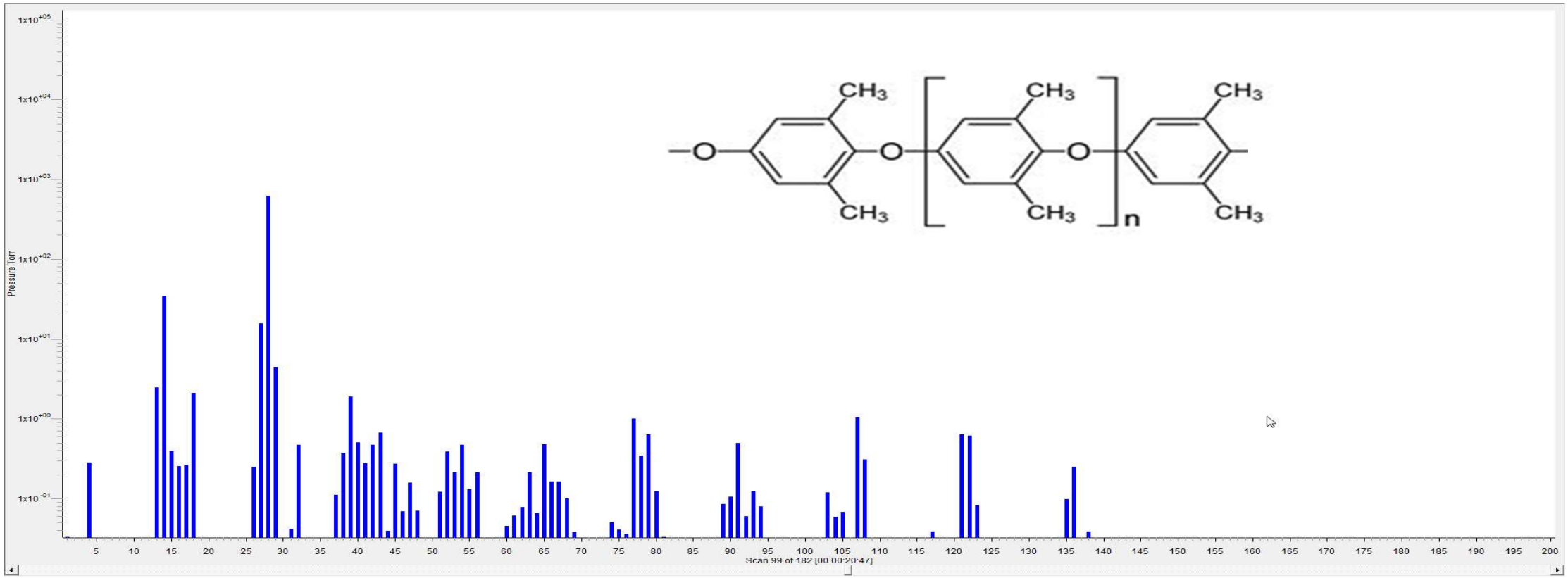


Reference: NIST MS Library

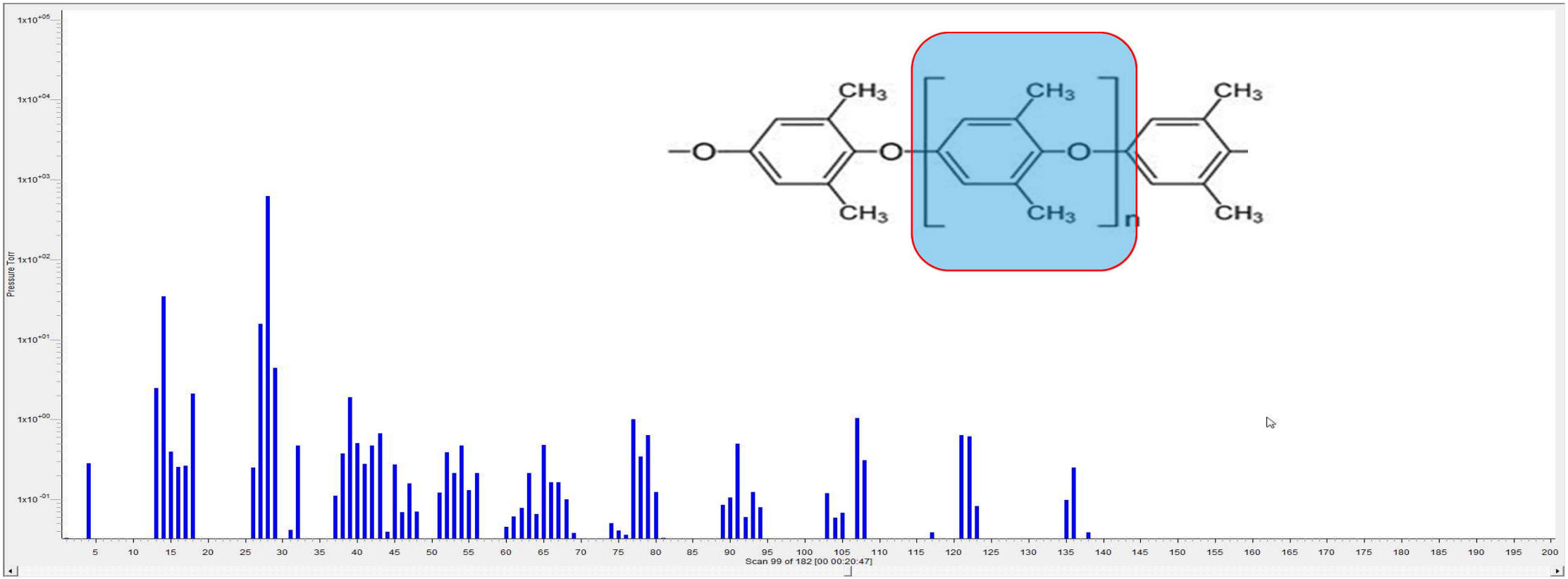
Simplified Bar Chart Display: N2 Background for Polyphenylene Oxide at Start of Experiment



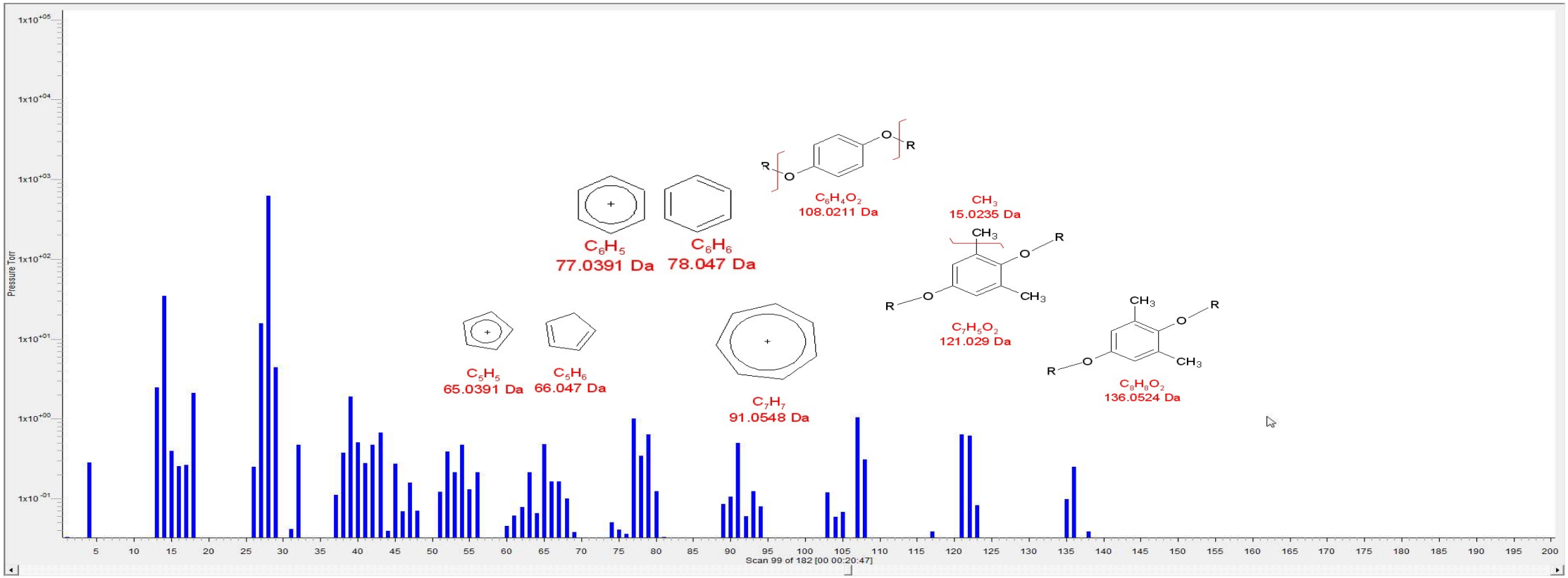
TGA-MS: Polyphenylene Oxide (PPO)



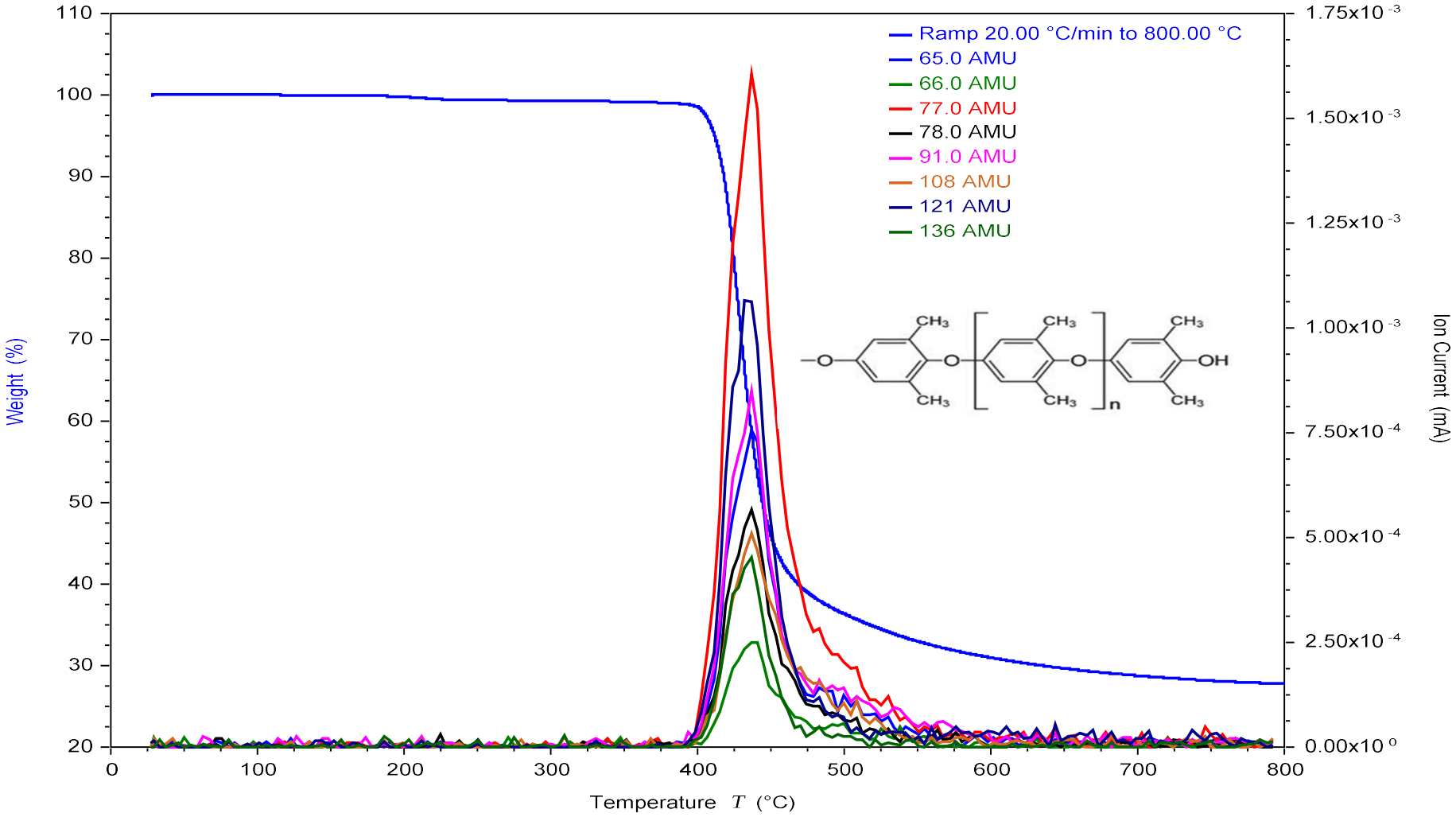
TGA MS: Polyphenylene Oxide (PPO)



TGA-MS: Polyphenylene Oxide (PPO)



TGA-MS: Polyphenylene Oxide (PPO)



Simple Quantitative Analysis by TGA / MS

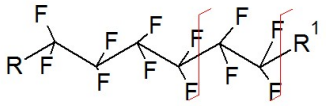
Advantages

- Minimal Sample Preparation
- No Solvents
- Good sensitivity
- Potential alternative for difficult samples
- Relatively fast analysis
- Excellent scouting technique for GC/MS
- Simple - Quantification by TGA/MS differs little from spectroscopic methods. Detector response is simply plotted as a function of concentration of a known standard.

Challenges

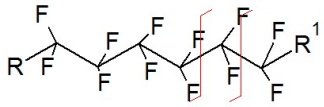
- Separation based only on kinetic stability
  - May be improved using typical TGA experimental variations
- Need to verify ion specificity
- Analysis of decomposition products in many cases – reference mass spectra may not be relevant
- Interference from any diluents used
- Limited utility – ‘right tool for the job’

Quantifying PTFE in a Polymer Blend
Ion Fragments for PTFE

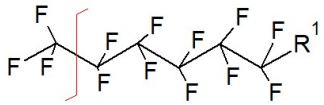


C_2F_4 99.9936 Da

CF 31.009 Da



CF_2 49.9968 Da



CF_3 68.9952 Da

TABLE I

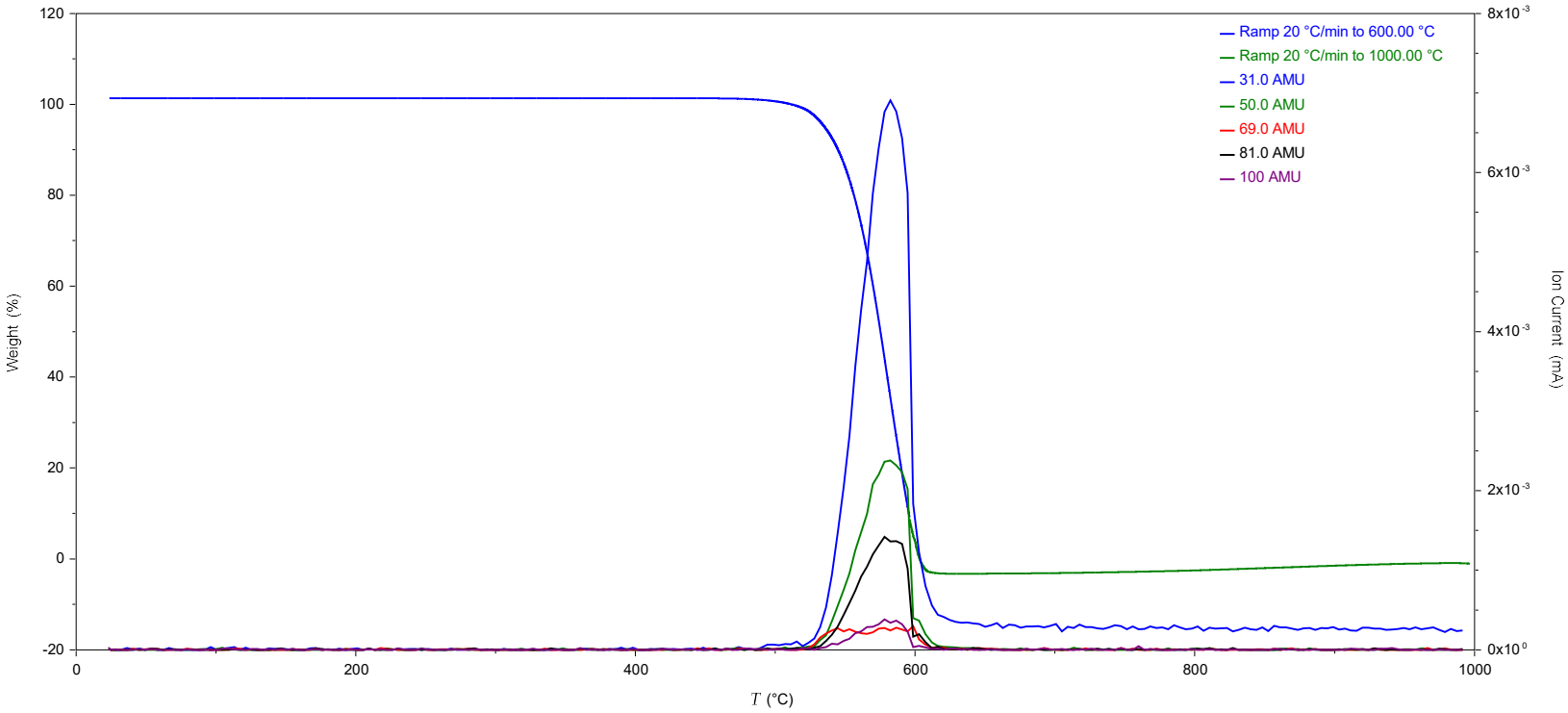
THE MASS SPECTRUM OF TETRAFLUOROETHYLENE

		Normalized ion intensities, %			
		High pressure,[a]	Zero	Low pressure	
m/e	Assignment	0.06 torr	pressure[a]	M.S.D.[b]	L. and L.[c]
12	C^+	0.33	2.6	2.9	..
19	F^+	0.15	0.8	0.55	..
24	C_2^+	0.10	1.35	0.93	..
31	CF^+	31.4	38.0	37.8	28.6
43	C_2F^+	0.06	0.9	0.52	..
50	CF_2^+	1.44	14.0	11.7	10.6
62	$C_2F_2^+$	0.08	0.65	0.37	0.3
69	CF_3^+	7.4	1.10	1.35	1.3
81	$C_2F_3^+$	13.0	28.0	27.6	37.3
100	$C_2F_4^+$	39.8	13.0	16.25	20.4
55	C_3F^+	0.01			
74	$C_3F_2^+$	0.01			
93	$C_3F_3^+$	0.16			
112	$C_3F_4^+$	0.05			
119	$C_2F_5^+$	0.03			
124	$C_4F_4^+$	0.01			
131	$C_3F_5^+$	6.0			
162	$C_4F_6^+$	0.2			
169	$C_3F_7^+$	0.05			
181	$C_4F_7^+$	0.02			

[a] 80-v. electron beam energy and 12.5-v. cm.$^{-1}$ repeller field. [b] "Mass Spectral Data," American Petroleum Institute Research Project 44 (70-v. electron beam energy). [c] See ref. 8 (75-v. electron beam energy).

Mass Spectrometric Study of Ion-Molecule Reactions in Tetrafluroethylene;
Derwish, Galli, Giardini-Guidoni, Volpi*; Laboratorio de Chimica Delle Radiazione e Chimica Nucleare del CNEN, Istituto de Chimica Generale ed Inorganica, Universita de Roma 1964*

TGA/MS of PTFE Reference

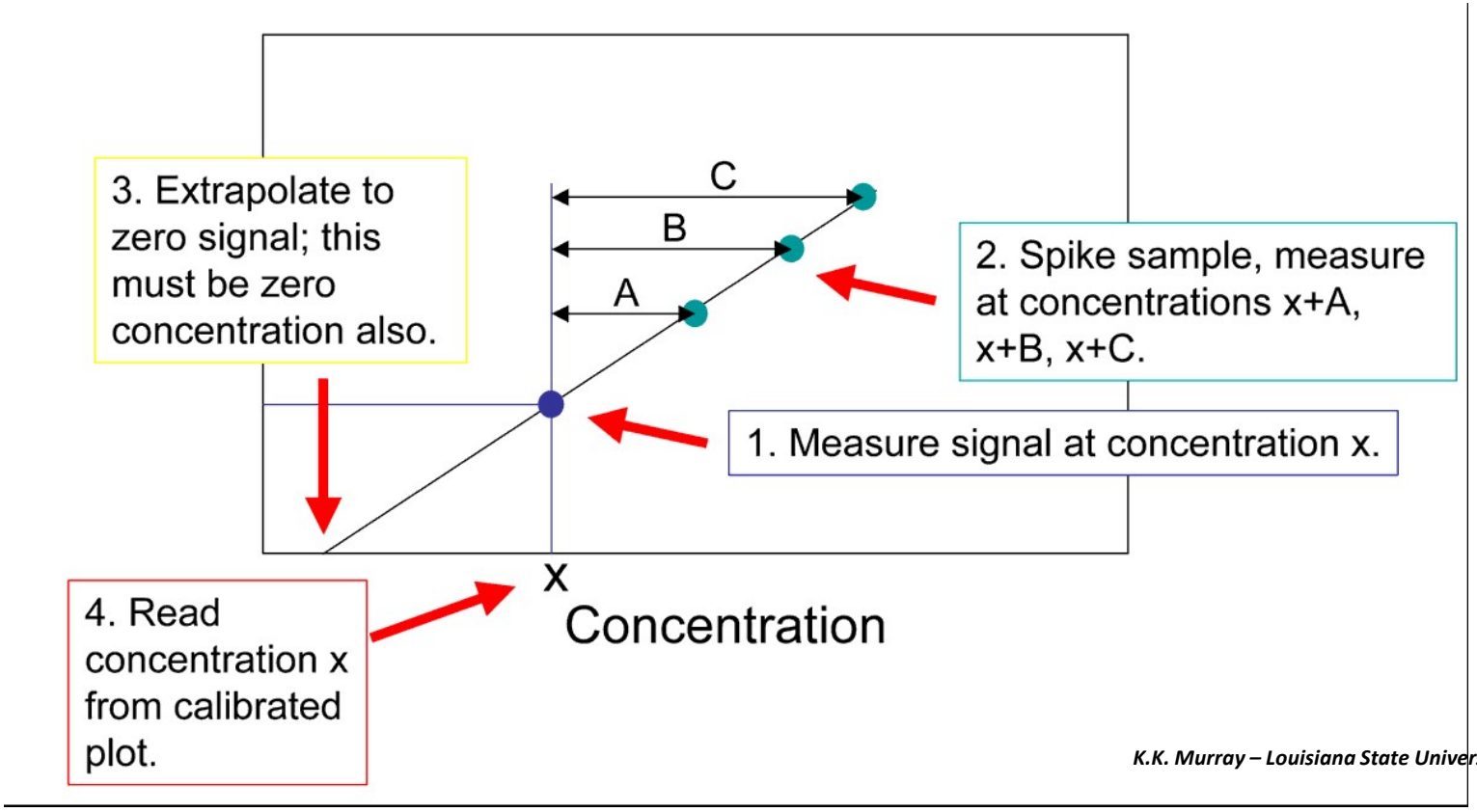


The detector response of m/z 31 will be plotted as a function of added mass fraction of the PTFE.

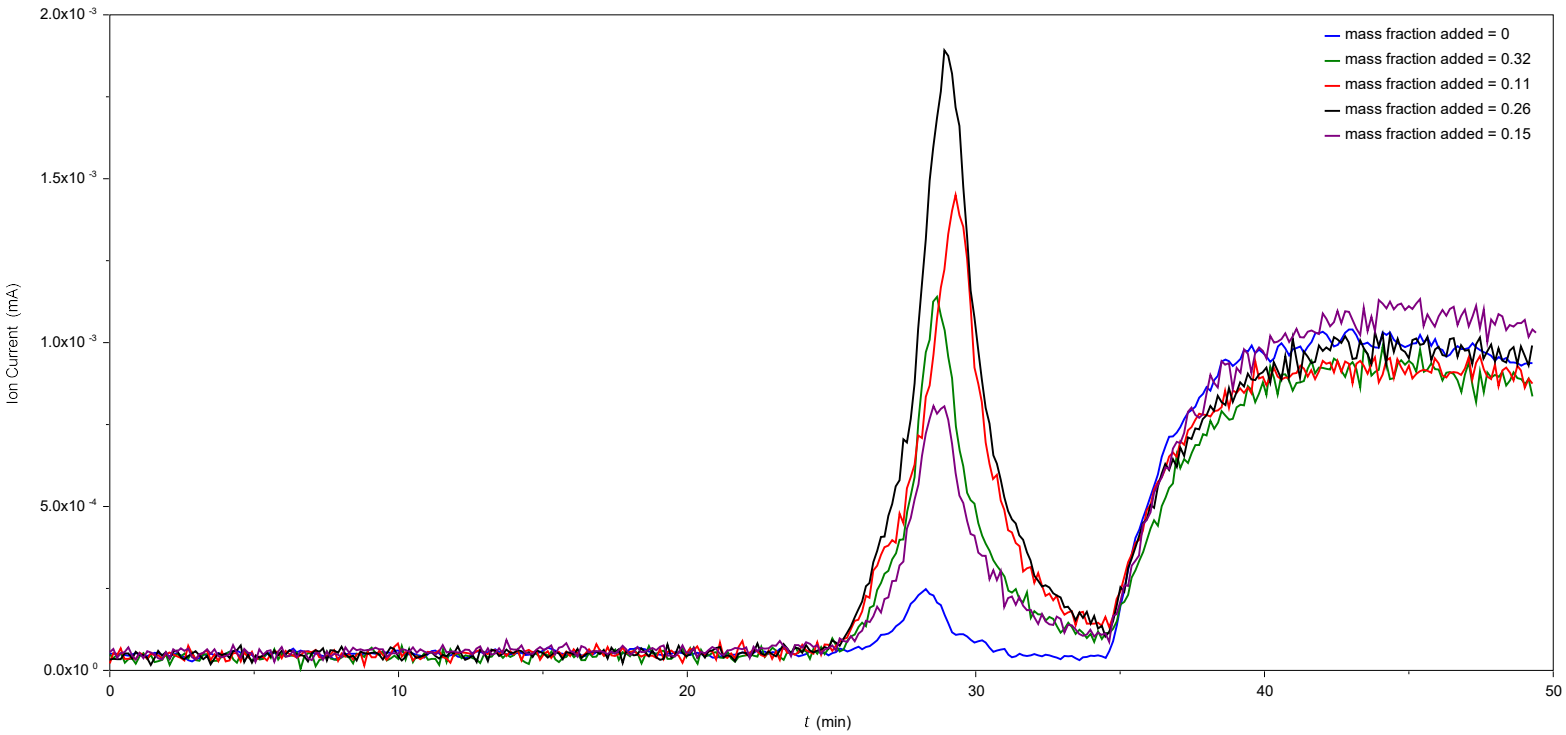
Quantification – Method of Standard Additions

- For the samples, a method similar to the familiar standard additions method employed in GC and HPLC methods can be used. It can be shown that the concentration of an analyte can be calculated by adding known concentrations of the same analyte, plotting the detector response as function of added analyte, and solving for the negative concentration which is the x-intercept. (See next slide for diagram).
- Neat sample with analyte of interest added in varying concentrations are prepared and analyzed. Ideally analyte of interest should be compounded into the polymer matrix in the form of a concentrate, and an internal standard identified to account for any matrix effects, but this is not always practical and probably not necessary to obtain an approximate concentration.

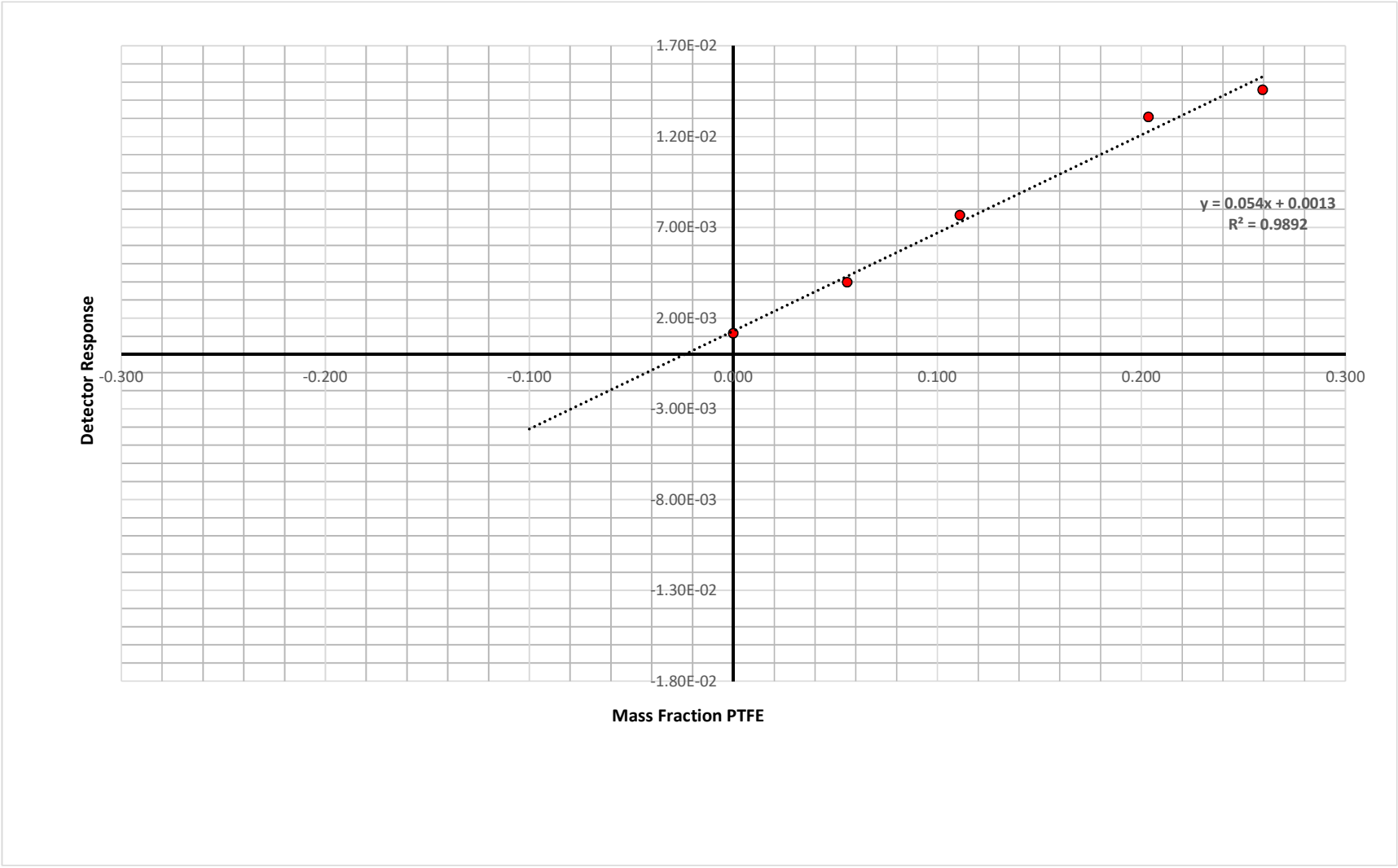
Quantification – Method of Standard Additions



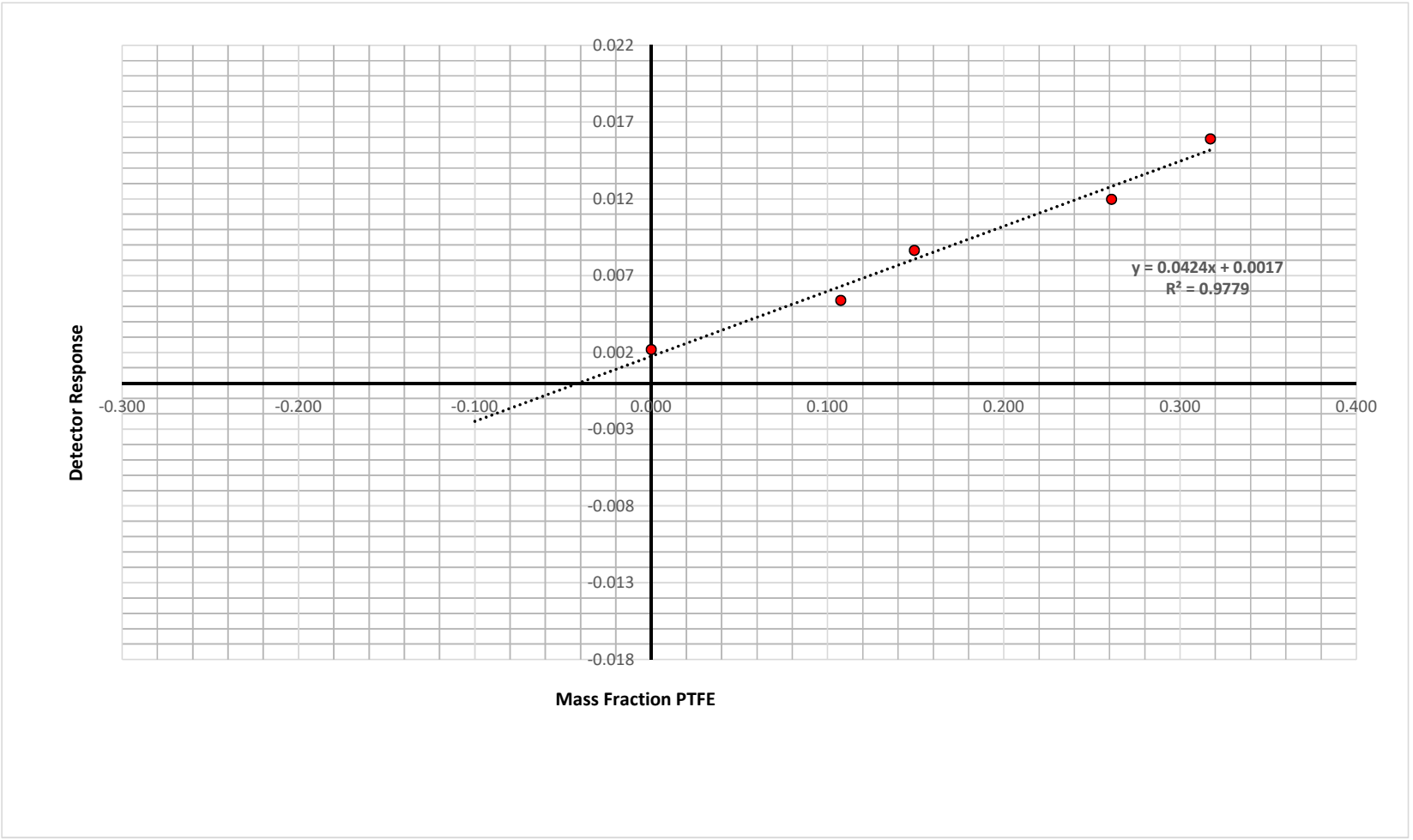
Experimental Results: Sample 1; PTFE – Ion Current m/z 31



Sample 1; PTFE 2.35%



Sample 2: PTFE 3.86%



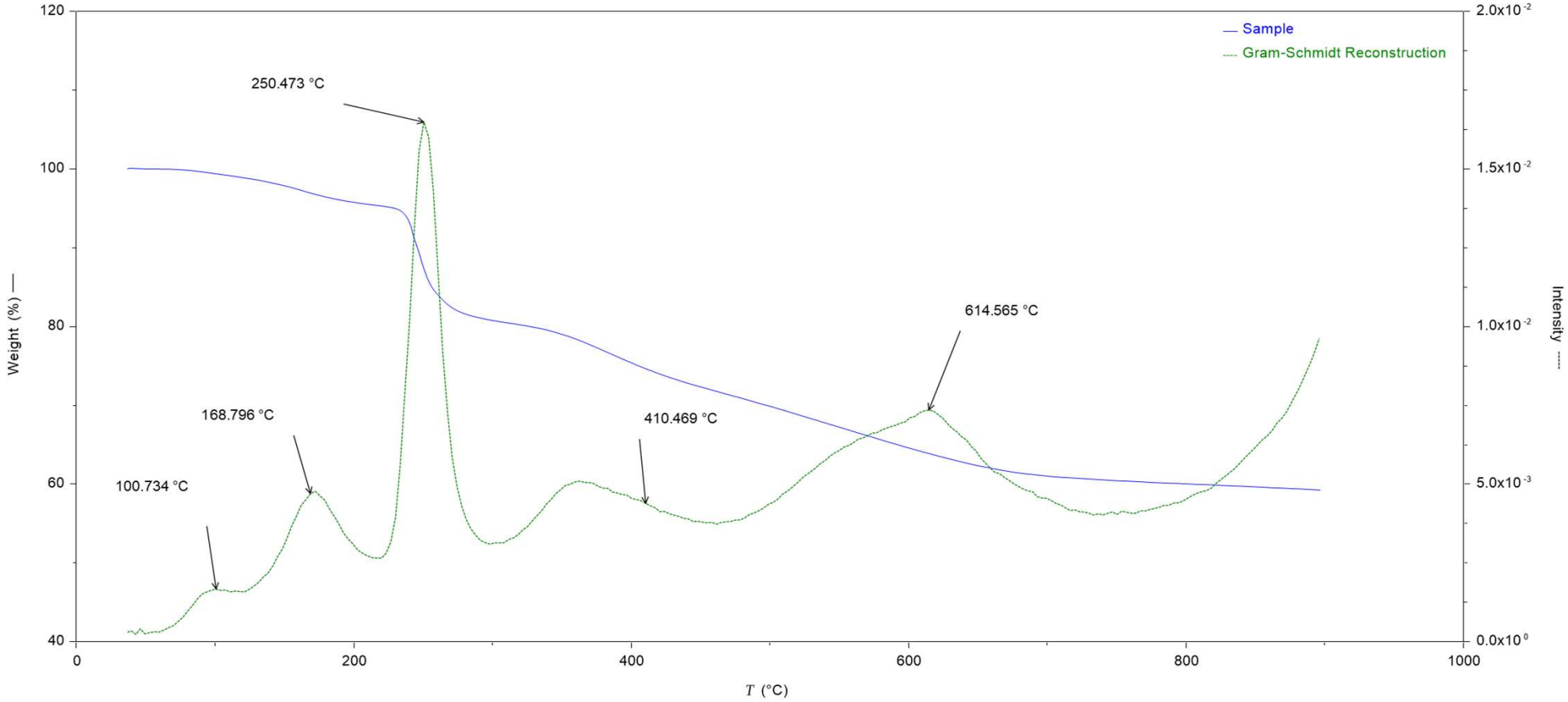
Quantification via TGA-MS

1. Quantification using TGA/MS presents a viable alternative for analysis of some samples where analysis by more common methods is not practical including:
    a. Samples not easily prepared for GC or HPLC
    b. Polymer blends
    c. Residual Solvent
    d. Oils and Grease
    e. Biomass
2. Setup and experiment are very simple
3. Data reduction is straightforward.

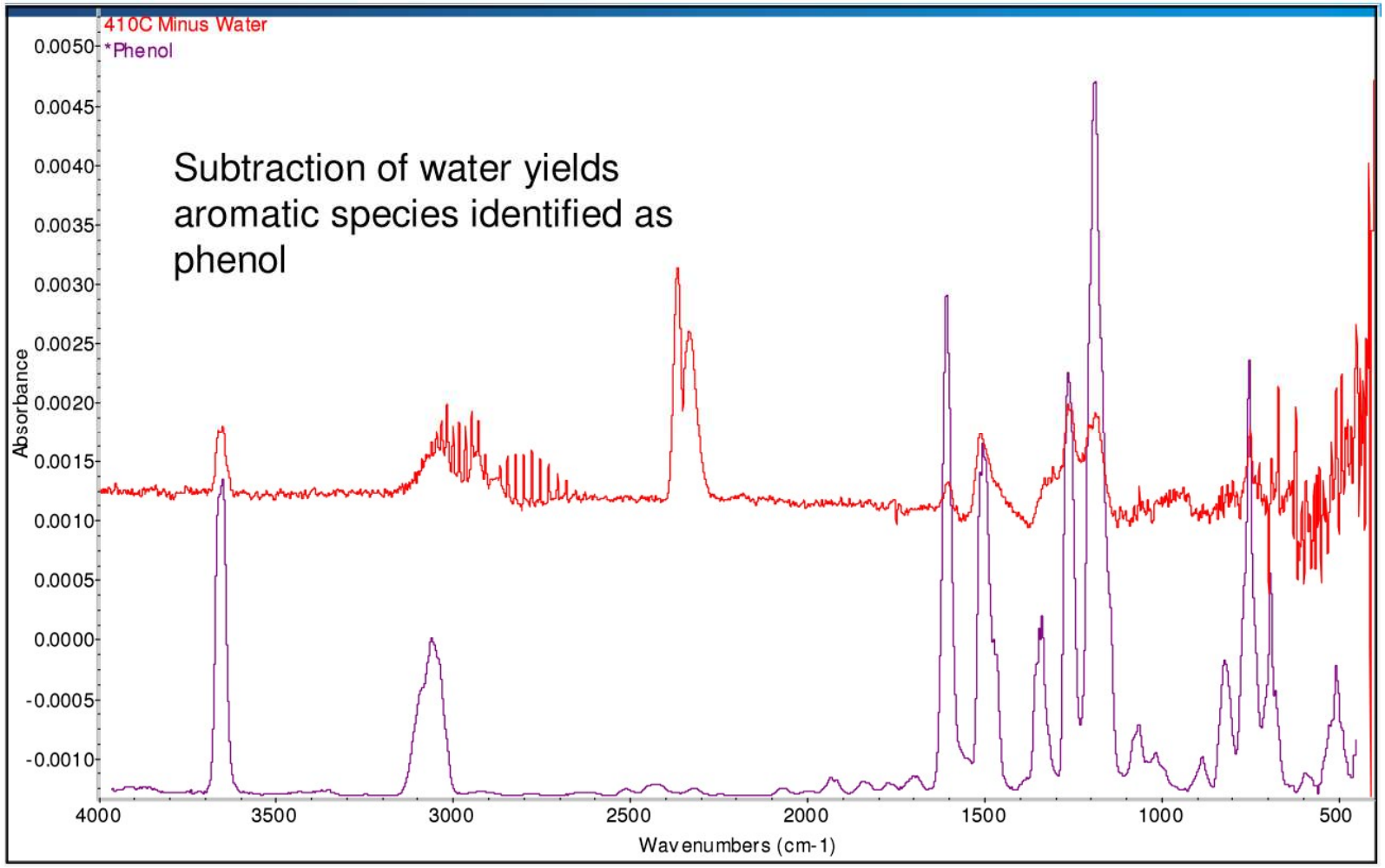
Evolve Gas Analysis – TGA Hyphenation

REDshift

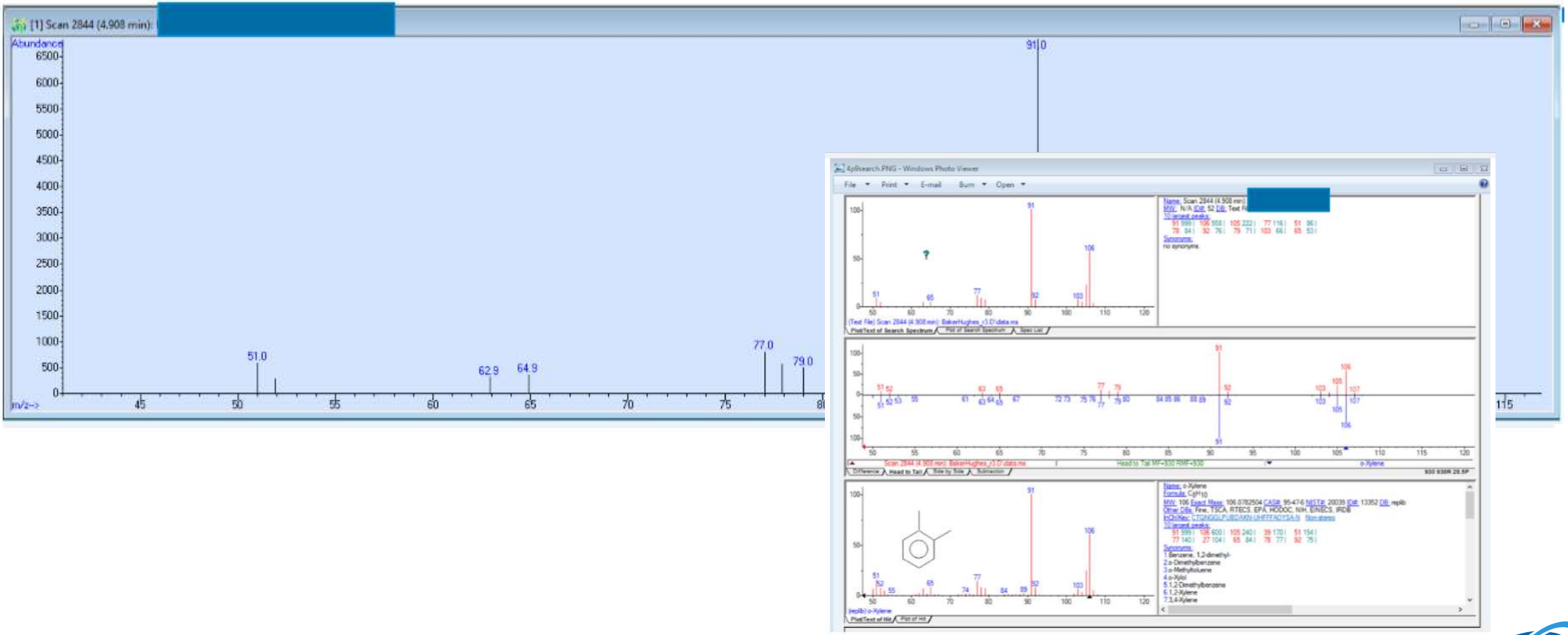
TGA/FTIR: TGA Weight Loss and Gram Schmidt Reconstruction of a Phenolic Adhesive



TGA/FTIR: FTIR Spectrum of Phenolic Adhesive at 410°C



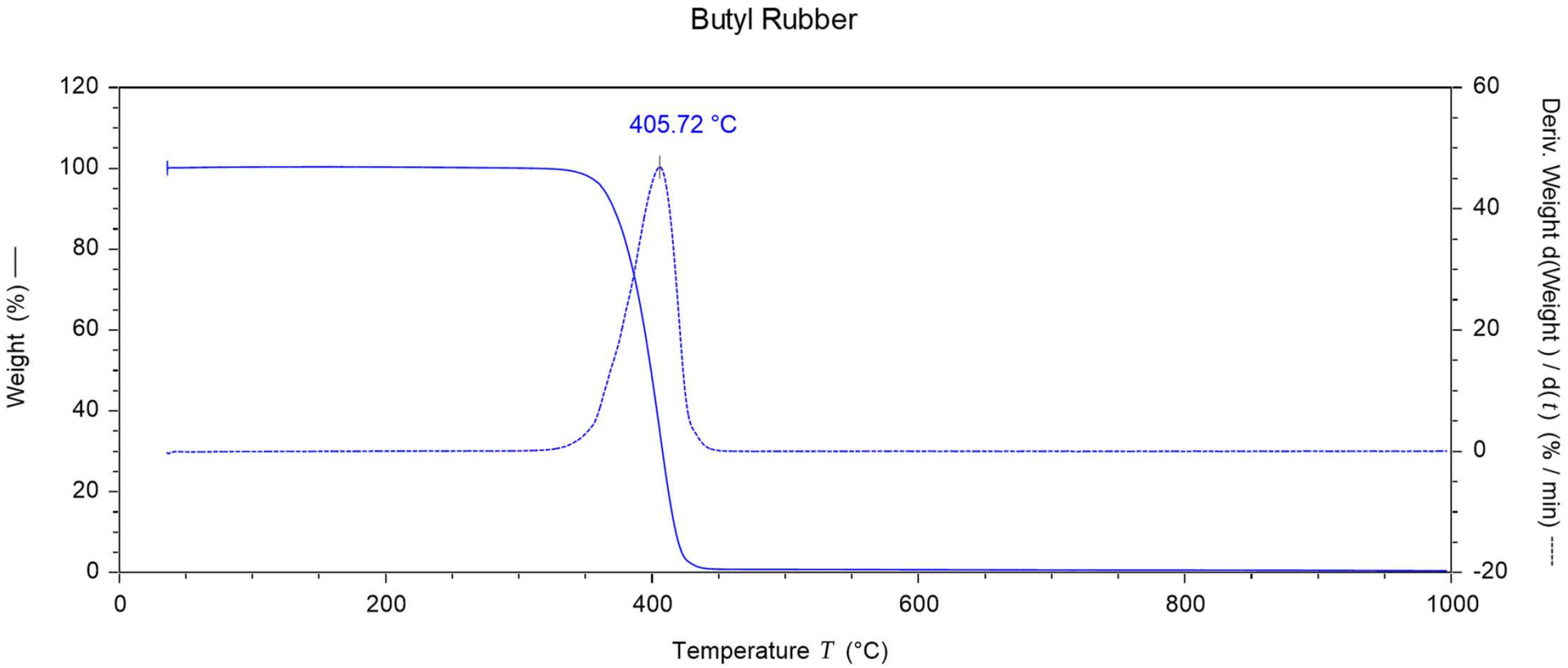
Evolve Gas Analysis – TGA GC MS at 410°C



Summary of TGA/GC/MS Data During Evolution of Phenol at 410°C

Peak	Retention Time	Species
1	2.00	Benzene
2	2.80	Benzene
3	3.50	Toluene
4	4.60	*p*-xylene
5	4.90	*o*-xylene
6	5.99	phenol
7	6.30	1,3,5 –trimethyl benzene
8	7.05	2-methyl phenol (*o*-cresol)
9	7.34	4-methyl phenol (*p*-cresol)
10	7.90	2,6-dimethyl Phenol
11	8.50	2,4-dimethyl phenol
12	9.32	2,4,6-trimethyl phenol

TGA of a Butyl Rubber



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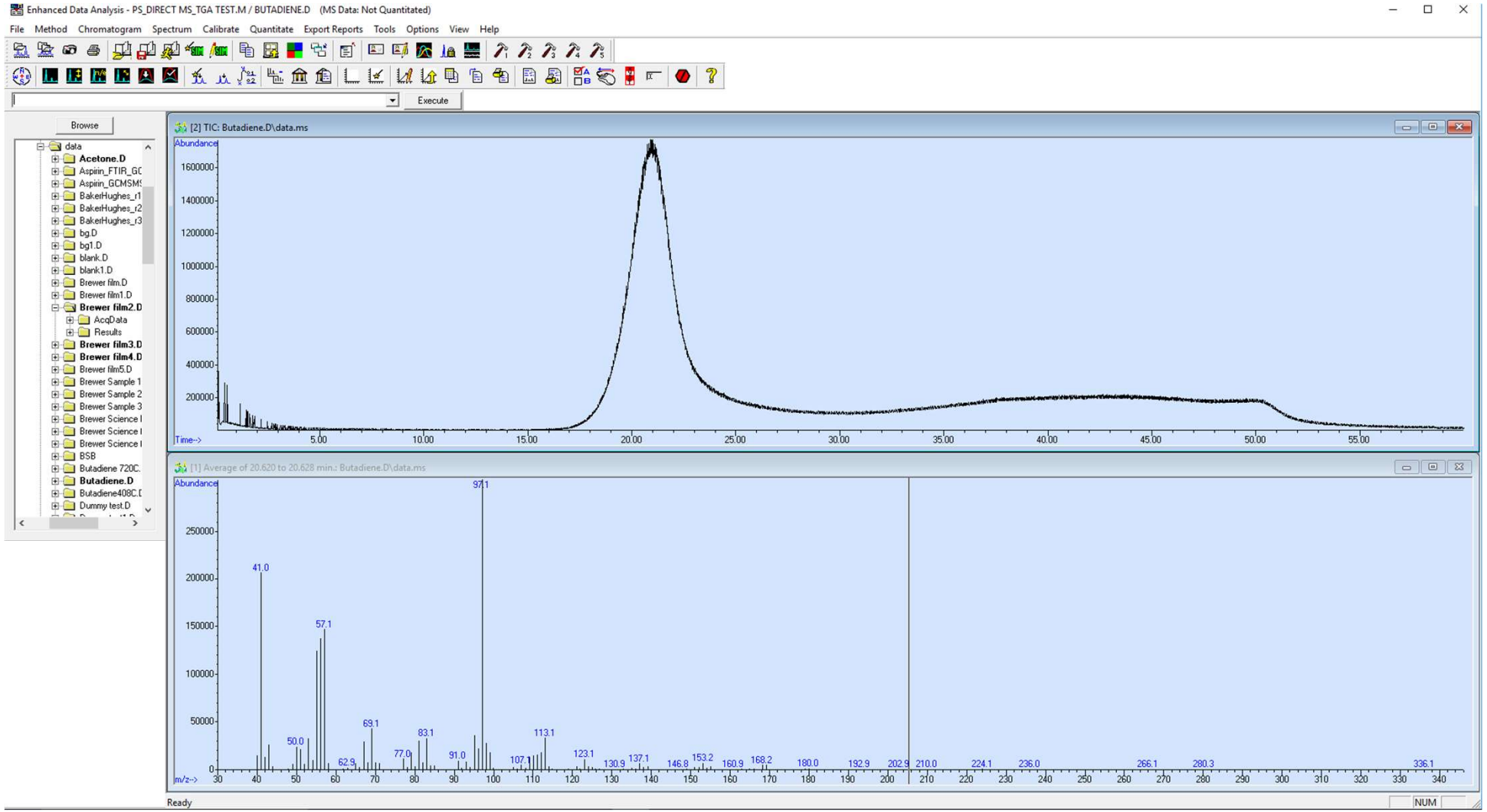

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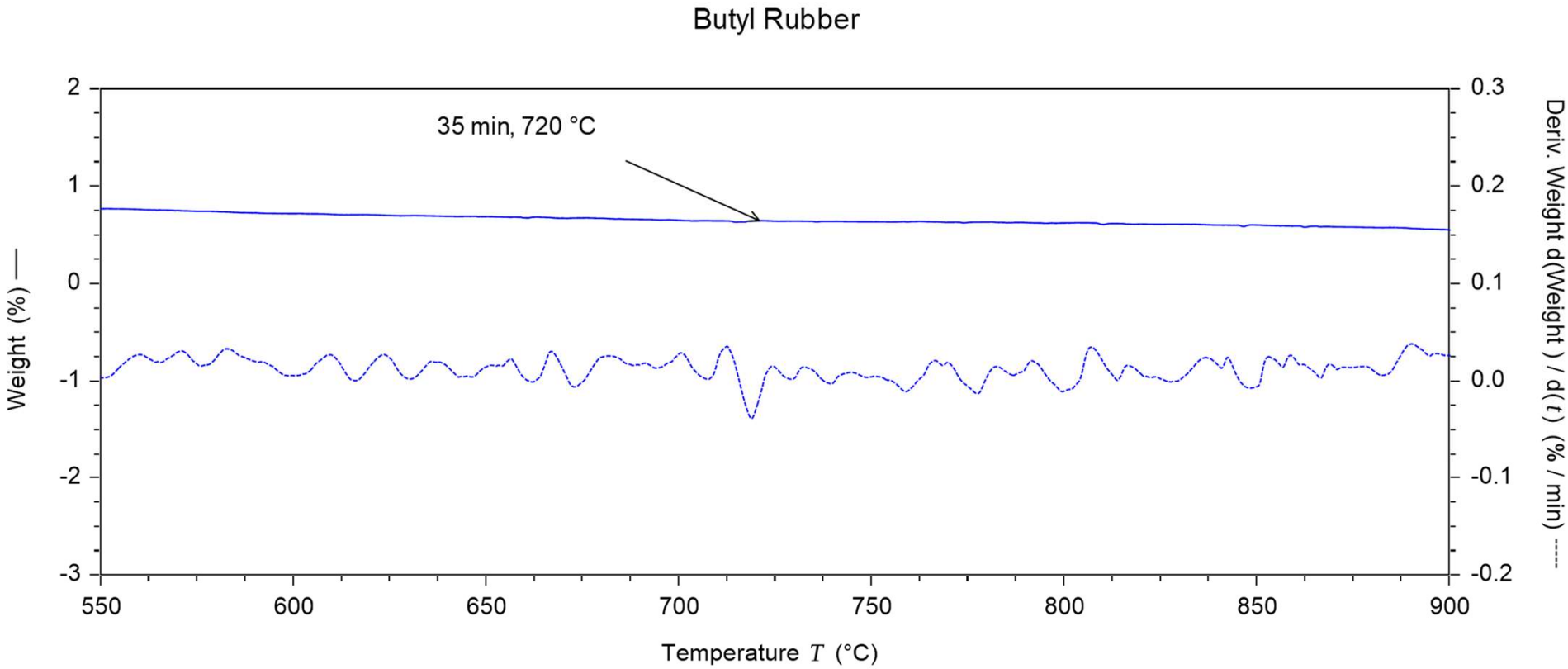
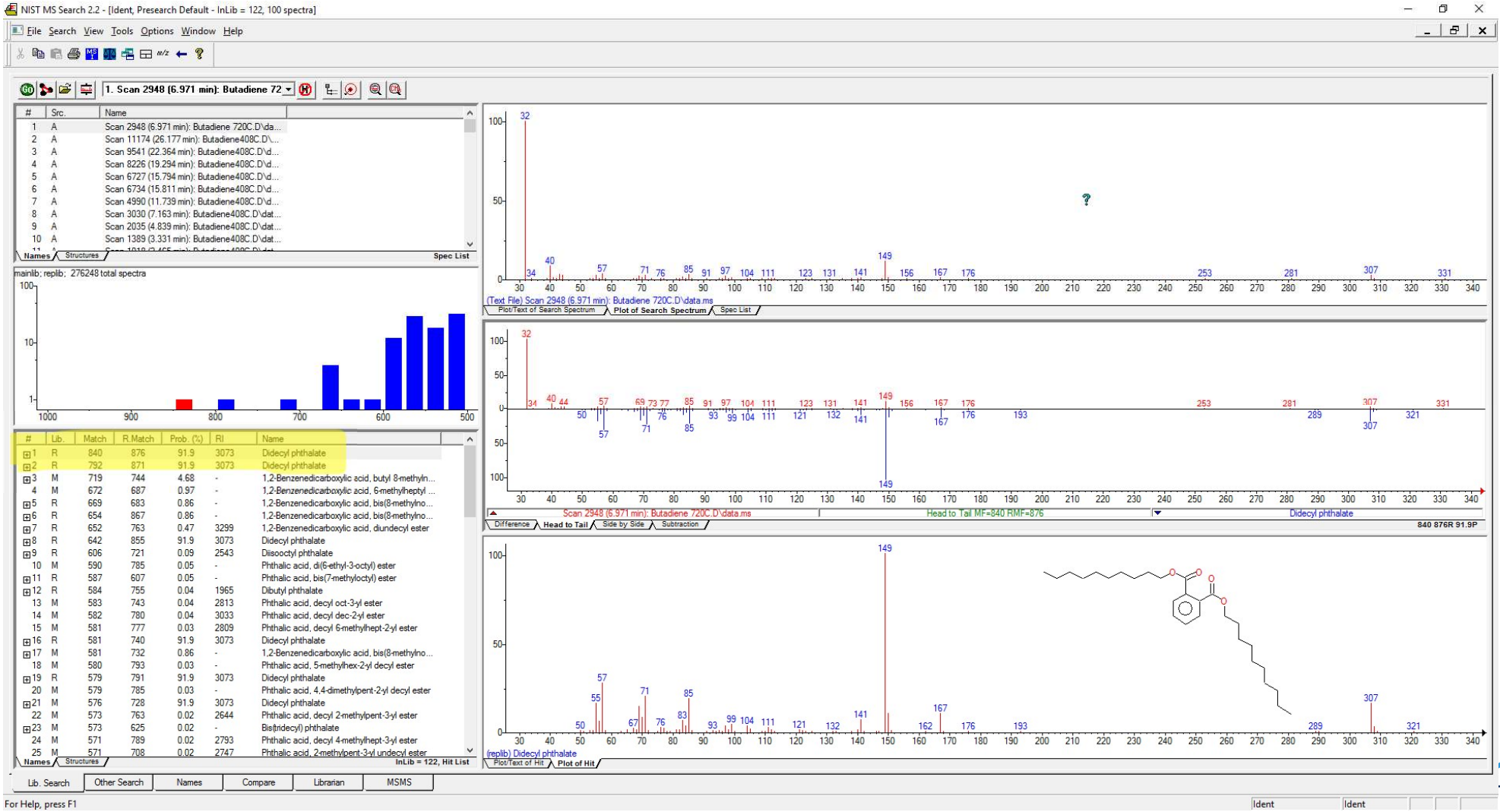


TGA-GC-MS of Butyl Rubber at 720°C



Evolve Gas Analysis – TGA Hyphenation

Three techniques traditionally used for hyphenation

Traditionally there are three techniques for transferring the gases developed in a TGA into an FTIR, GCMS or standalone MS:

1. The sample gas is “pushed” from the TGA using the purge gas pressure to force sample gas into the FTIR/GCMS/MS system.
2. The sample gas is “pulled” from the TGA using a vacuum to a gas sampling valve which switches to the FTIR/GCMS/MS system.
3. The sample gas is “pulled” from the TGA using the internal vacuum pressure of the MS detector.

These techniques typically experience sampling inaccuracy, increasing carry over and/or poor reproducibility. These techniques may also increase system maintenance requirements.

REDshift BALANCED FLOW TECHNOLOGY

Unique Features

▪ Balanced Flow MFC	→ Universal connectivity, constant gas, linear speed, thermal stability.
▪ 24 V High temperature TL	→ Up to 350°C, determination of high boiling point, long-term maintenance-free and safety.
▪ Low volume Zero Gravity IR cell	→ 11 ml cell volume, residence time: v = 100 ml/min τ = 6,6 seconds.
▪ Heated injector block with two independent gas circuit and King Cross gas connector	→ GSV long-term maintenance-free, high temperature up to 350°C, reduced GC contamination, TG-IR gas circuit separation.
▪ Two motorized gas sampling valves electronic controlled	→ TG-IR-GCMS and TG-IR-MS capability software controlled, reduced O2 contamination.

Thank You!

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1 – "SAMPLE PUSHED"

In the case of the gases being "pushed" by the TGA purge gas pressure, the gas is pushed through a flow restrictor. The restriction increases the pressure in the TGA and may create:

- A stagnation of corrosive gas emitted by a sample (increasing instrument maintenance),
- Create gas turbulence effects which can reduce the accuracy and reproducibility of the TGA data,
- Potentially compromise the physical integrity of the furnace (increased maintenance).

2 – VACUUM PUMP AND GAS SAMPLING VALVE

In the case of a vacuum pump and gas sampling valve; a capillary is introduced directly into the furnace of the TGA. These systems often experience:

- Frequent capillary clogging,

- In this system the sample gas runs continuously through the sampling valve contaminating the flow path with carry over, impacting accuracy and reproducibility.

3 – DIRECT MS CONNECTION

In cases where the TGA is connected directly to the MS vacuum, a capillary tube is inserted into the furnace of the TGA. Issues will again include:

- Frequent capillary clogging.

- MS is very sensitive to temperature and pressure fluctuations and because the gas emitted from a TGA varies dramatically in terms of temperature and pressure, during the sampling time, profiles and reproducibility of the sample can be very degraded.

Overview of the REDshift Switching Valves

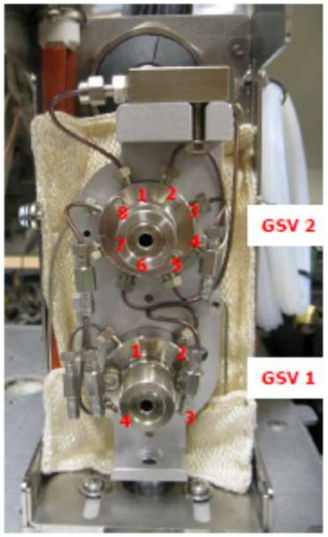


Figure 62 GSV with related port numbers

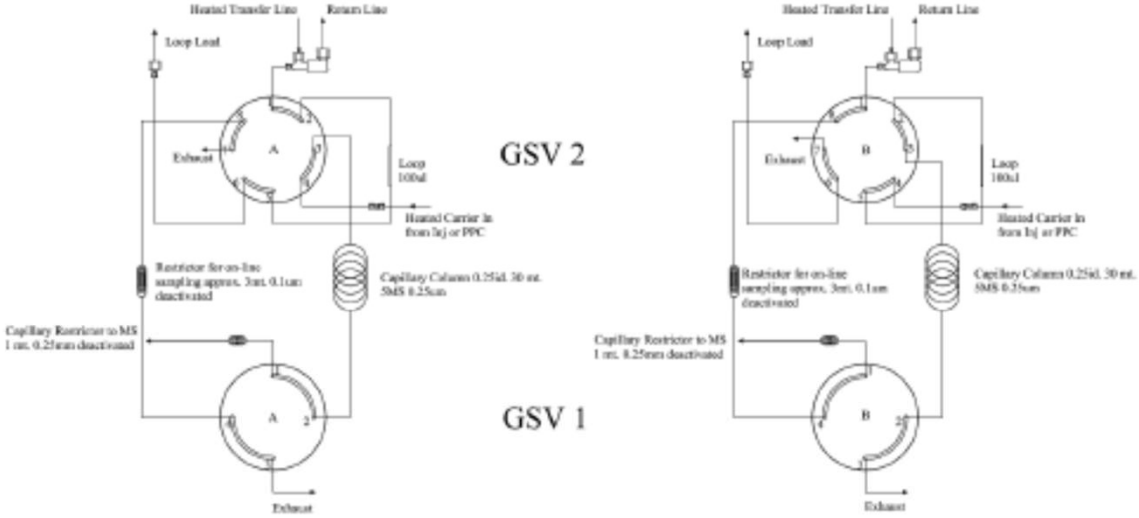
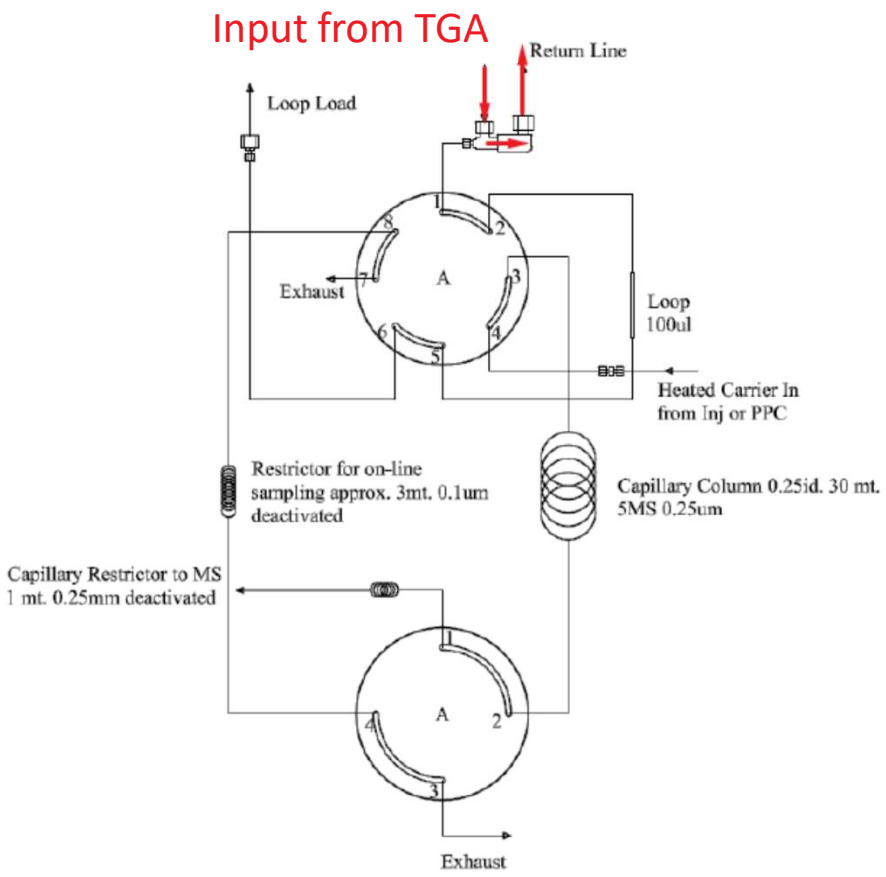


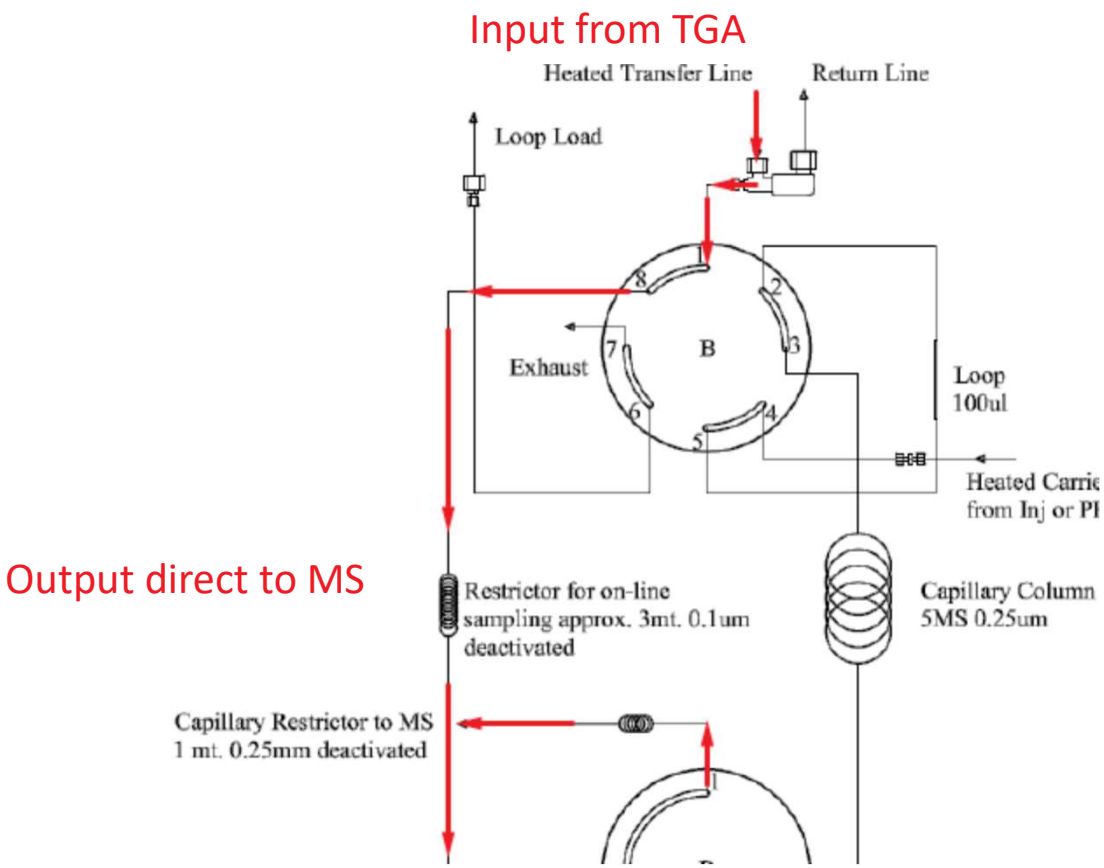
Figure 63 GSV port connection diagram, upper valve GSV2, bottom GSV1. Position A is the standby, position B valve has been activated.

Standby Flow Schematic of REDshift Valves



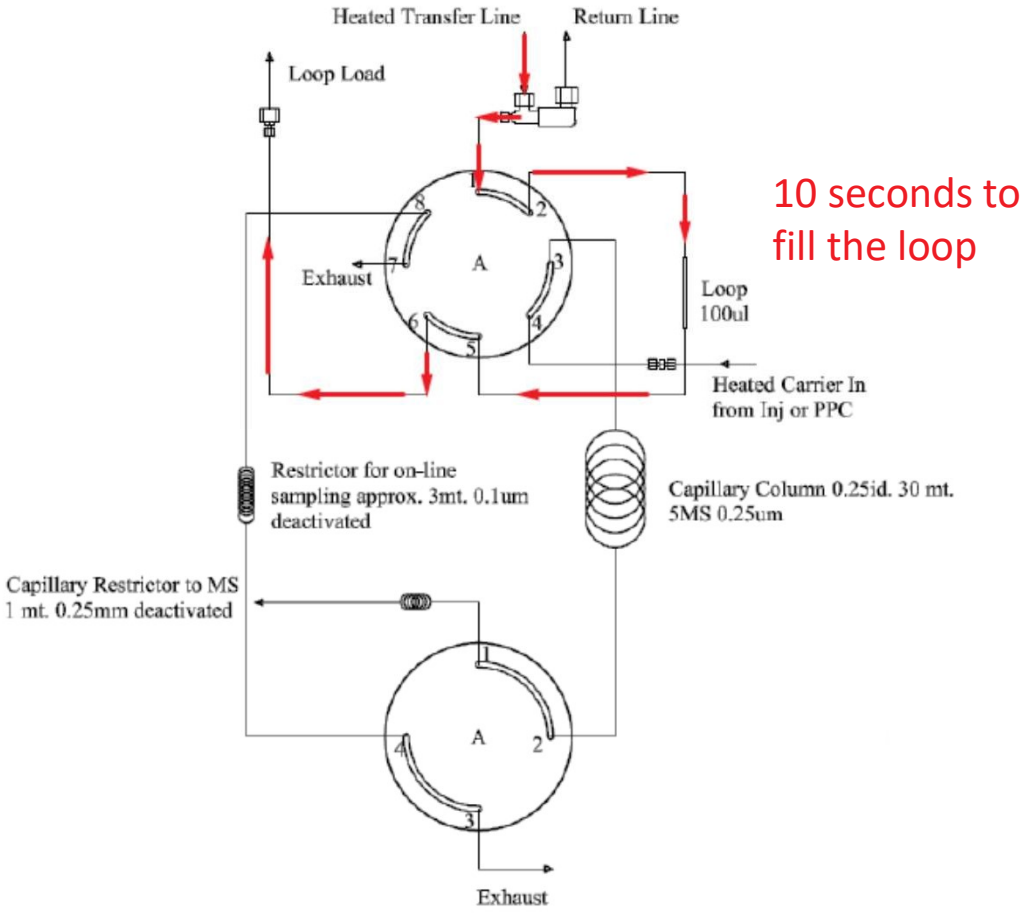
- When the REDshift system is idle, the gas flow from the TGA exits the REDshift valves immediately so that the off-gas does not contaminate the switching valves.

Flow Schematic for Direct MS from the TGA



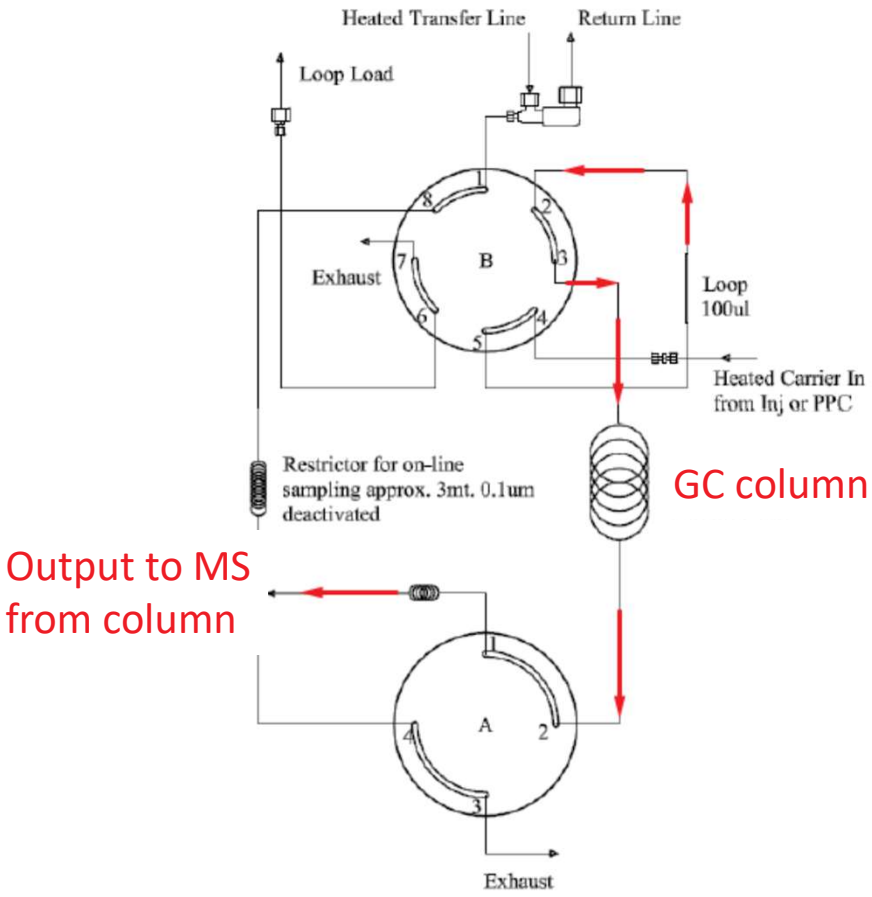
- The REDshift valves allow for a more direct path to the MS (bypassing the GC column) so that TGA and realtime MS can still be run without any hardware changes.
- In this case, both switching valves are in the “active” state
- The off-gas still travels through an inert capillary attached directly to the MS

Flow Schematic to Load the 100uL Loop for GC/MS



- For TGA-GC/MS tests, a 100uL sample of gas is all that is injected into the GC column
- When activated, the off-gas is diverted into the 100uL loop for 10 seconds before it is injected into the GC column
- Both REDshift valves are in the “deactivated” state for these 10 seconds

Flow Schematic to Unload the Loop into the GC/MS



- After the 10 second loop filling step, one of the REDshift switching valves is “activated” to send the 100uL sample of gas into the GC column
- Once injected into the column, the TGA off-gas is diverted away from the valves and the GC/MS experiment is started.