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Leading Thermal Analysis

Evolved Gas Analysis Techniques for Battery Performance and Safety

Battery Power Show, Denver, CO, USA
Peter Ralbovsky, August 3, 2016

Evolved questions on Evolved Gas Analysis (EGA)

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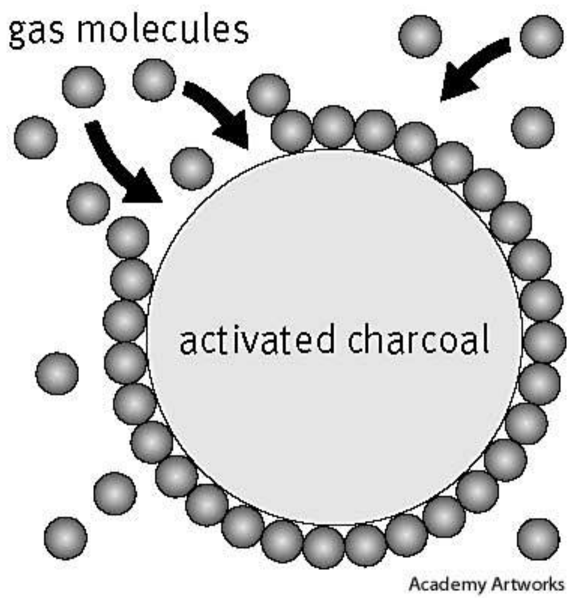
- How does EGA work? Why is it important?
- What techniques can be used for gas analysis?
- What are the advantages and disadvantages to the analysis techniques?
- How does EGA sampling work?
- What are the problems with sampling?
- What is different about the data analysis?

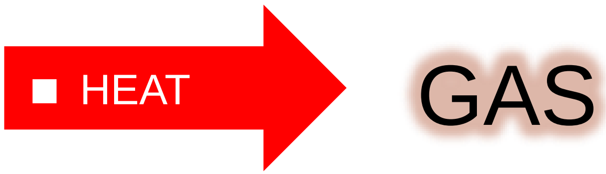
Evolved Gas Analysis (EGA)

- EGA is the analysis of gaseous products from
  - decomposition of materials

    A → B (solid) + C (gas)
  - from off-gassing
    - Vapor pressure
    - Bound or trapped gas
      - Physical/Chemical adsorption
      - Absorption



- Normally we apply heat to start or enhance the process of gas production (no matter what is the mechanism)
- Natural to link thermal analysis and EGA



http://img.tfd.com/hm/sci/JPG/ASadsorp.jpg

Thermal Analysis and Calorimetry for Materials, Components and Full Cells

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Battery Testing

Materials
(Anode/Cathode/
Electrolyte/Separator)

- **Single Materials**
  - DSC, STA, TGA, LFA, DIL
- **Components** (Behaour relative to each other)
  - No Pressure
    - STA (DTA -TG, TG)
  - Pressure
    - Adiabatic Scanning Calorimetry

Cells / Batteries

- **Small Cells**
  - Adiabatic & Scanning & Isothermal
- **Larges Cells and Packs**
  - Isothermal Calorimetry

In principal Evolved Gas Analysis can be applied to many of the techniques used

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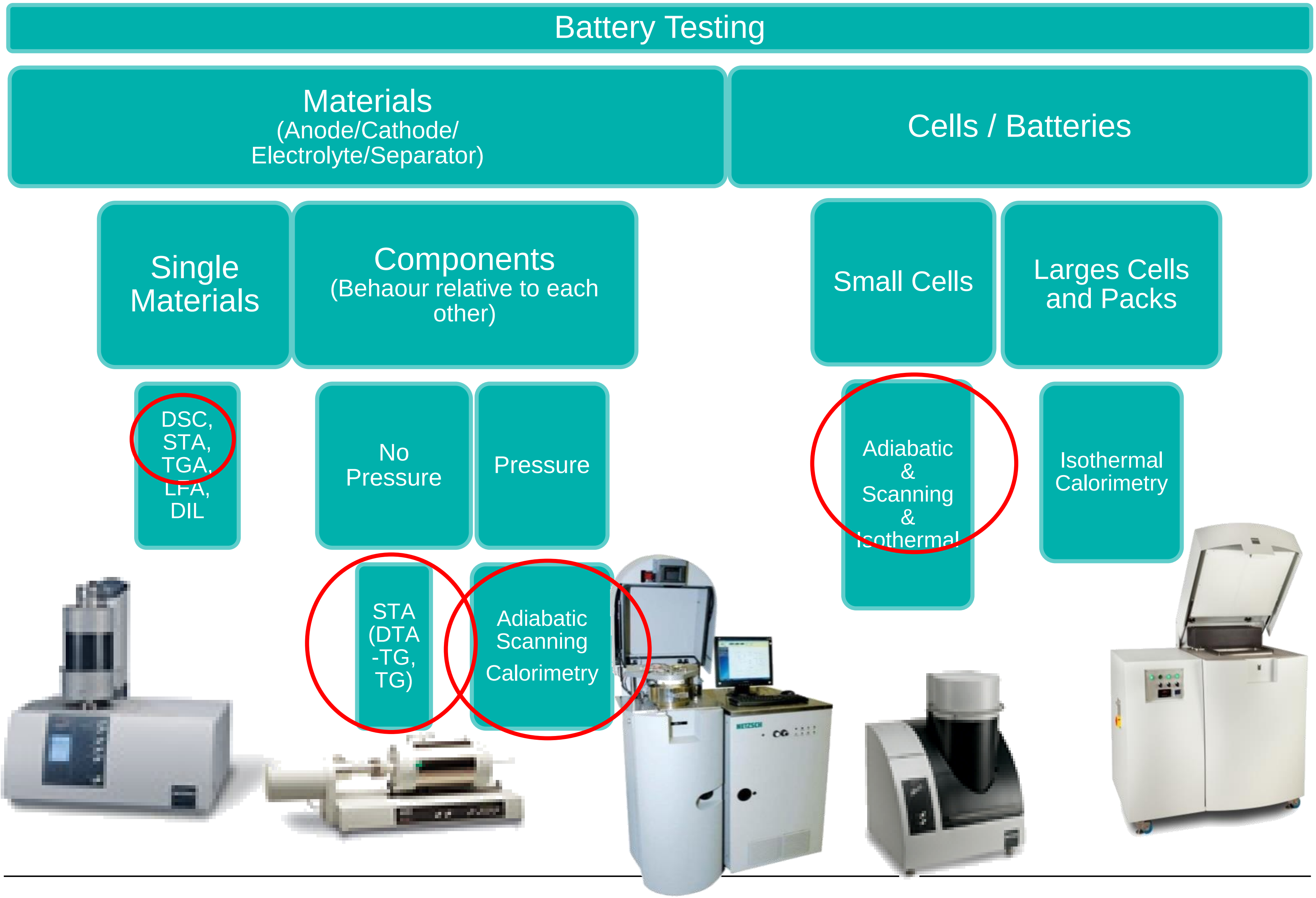

Evolved Gas Analysis (EGA) in Battery Area is Important

- EGA allows us to characterize materials more completely
  - R&D or in Quality Control
- EGA allows us to more completely understand a decomposition so it can be prevented or delayed
- EGA allows us to identify gaseous products that are created during catastrophic failures for safety considerations and emergency response
- EGA is a sensitive in perhaps one of the few ways to understand the source and impact of small gas production over repeated cycling.

Agenda

1. DSC, TGA, STA Overview
2. Calorimetry of Decomposition Reactions in Batteries and Battery Materials
3. EGA Analysis Techniques

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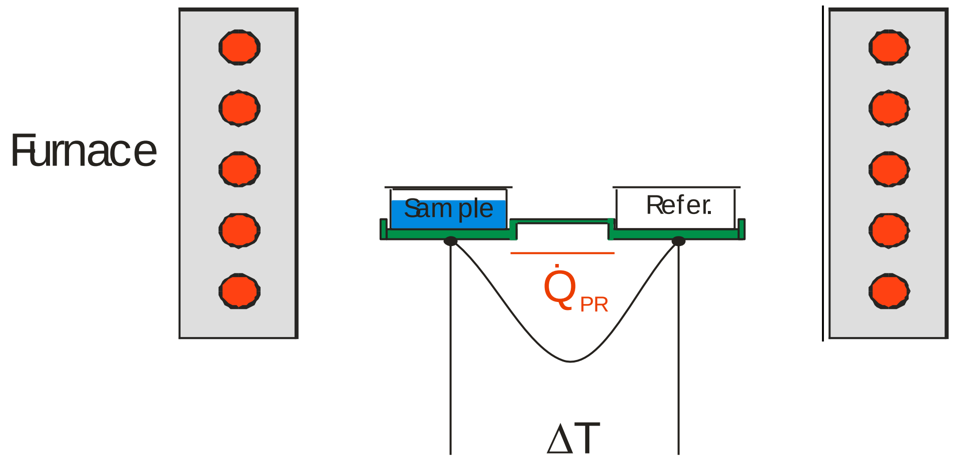
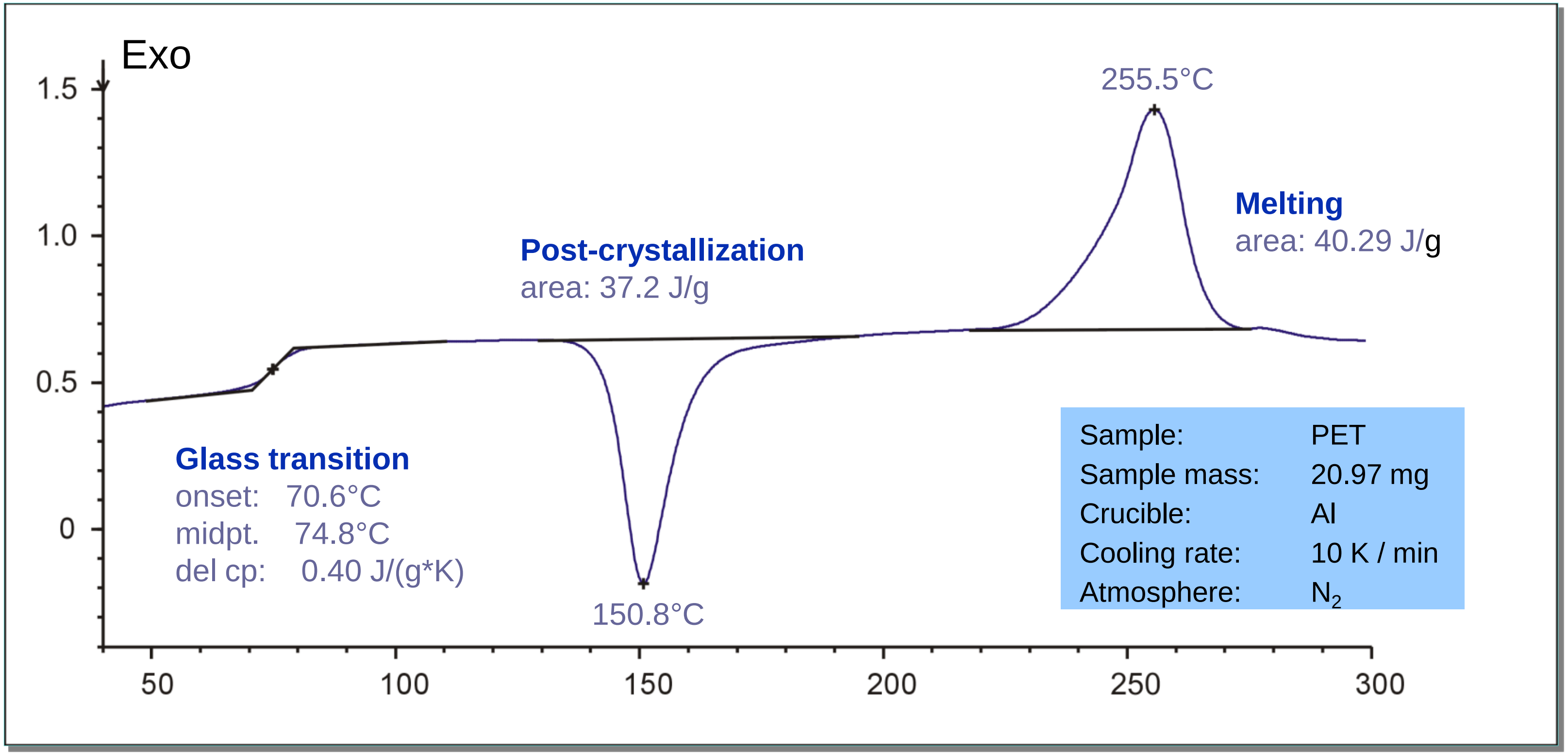
DSC Principle



Heat Flux DSC: sample and reference together in one furnace

During a phase transition a temperature difference (heat flux difference) between the sample and reference can be measured by means of a thermocouple.

DSC – Typical sample measurements



Amorphous part: glass transition and post-crystallization;
Crystalline part: melting peak

Crucibles for DSC measurements

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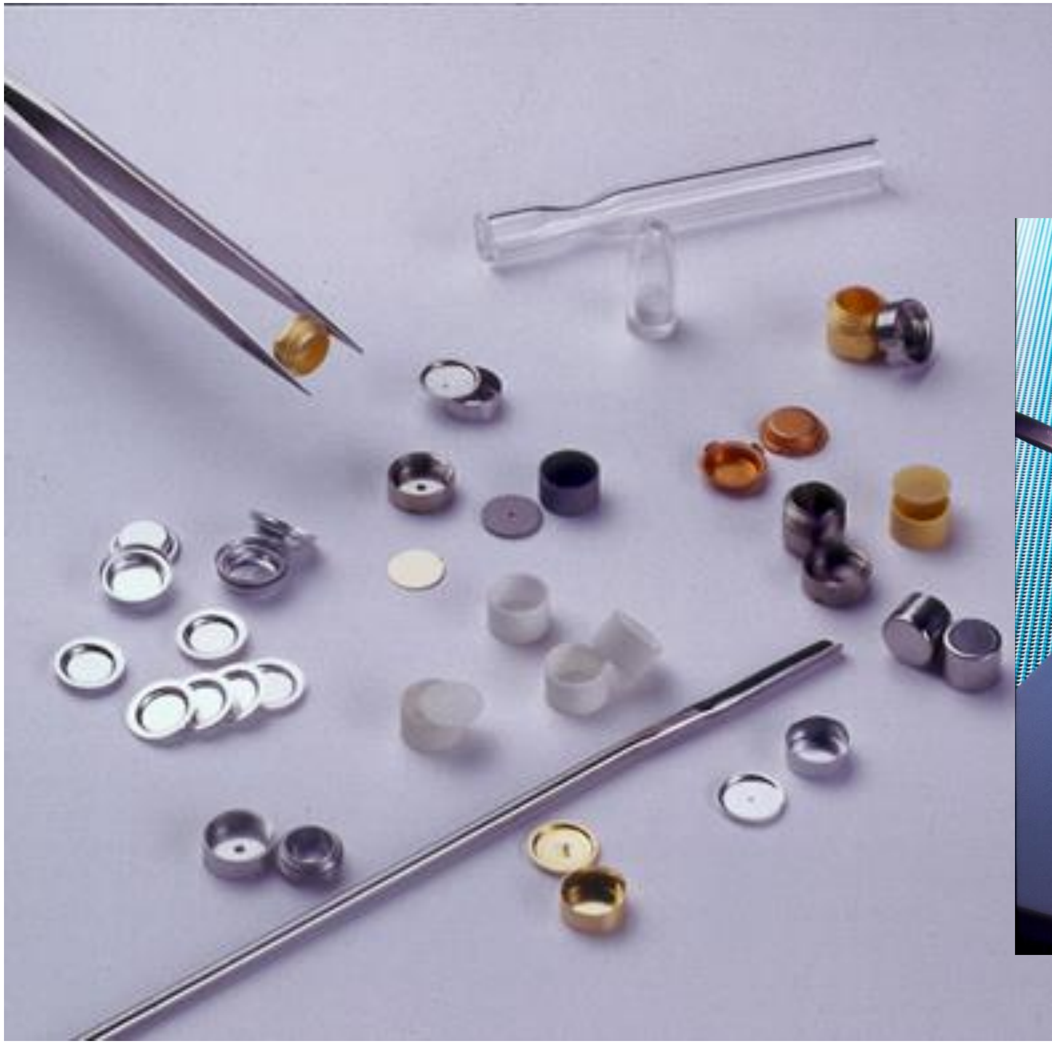
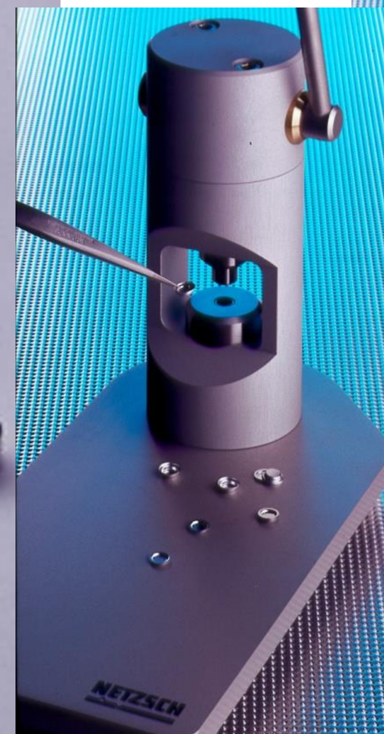
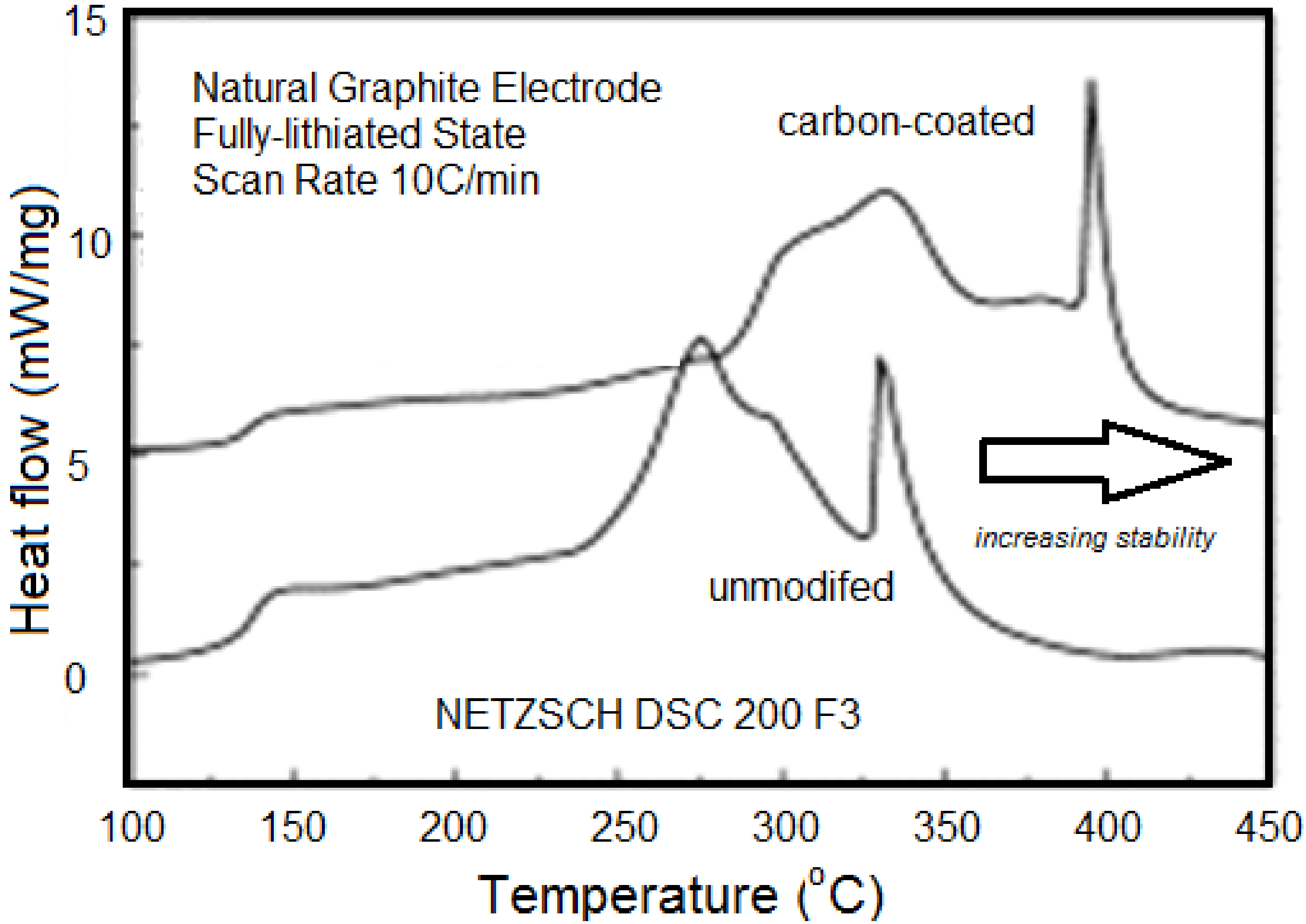




DSC Curves Showing Improved Anode Stability



[1]Effect of carbon coating on thermal stability of natural graphite spheres used as anode materials in lithium-ion batteries Journal of Power Sources, vol 190, Issue 2, 15 May 2009, Pages 553–557

Unraveling the DSC of Lithiated Graphite Anode

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- Two Curves of anode with liquid electrolyte and one of an anode washed with DMC
- What does it mean?
  - Older example but typical of complicated DSC traces
  - Step through the method used by the researcher
  - Same methods and analysis can apply
- First hypothesis is that DMC removed the SEI layer
  - Soluble in DMC
  - Lead to self discharge if DMC is in the electrolyte

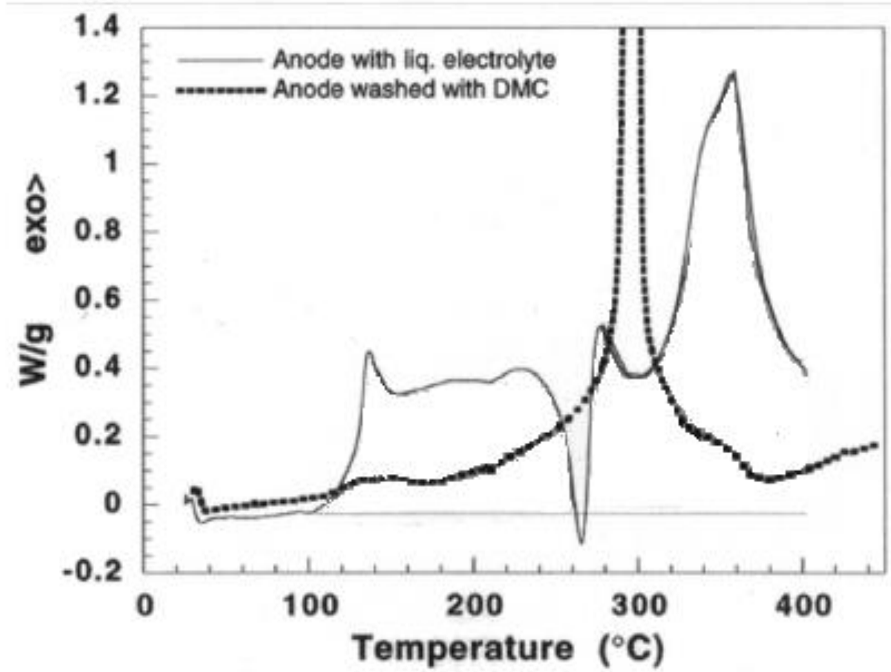

Fig. 1. DSC trace of the reactions occurring in a fully lithiatedMCMB 25-28 graphite plastic anode containing electrolyte or not.

Differential Scanning Calorimetry Study of the Reactivity of Carbon Anodes in Plastic Li-ion Batteries
J. Electrochem . Soc 1998, Volume 145, Issue 2,pages 472-477

Determining SEI Formation using DSC

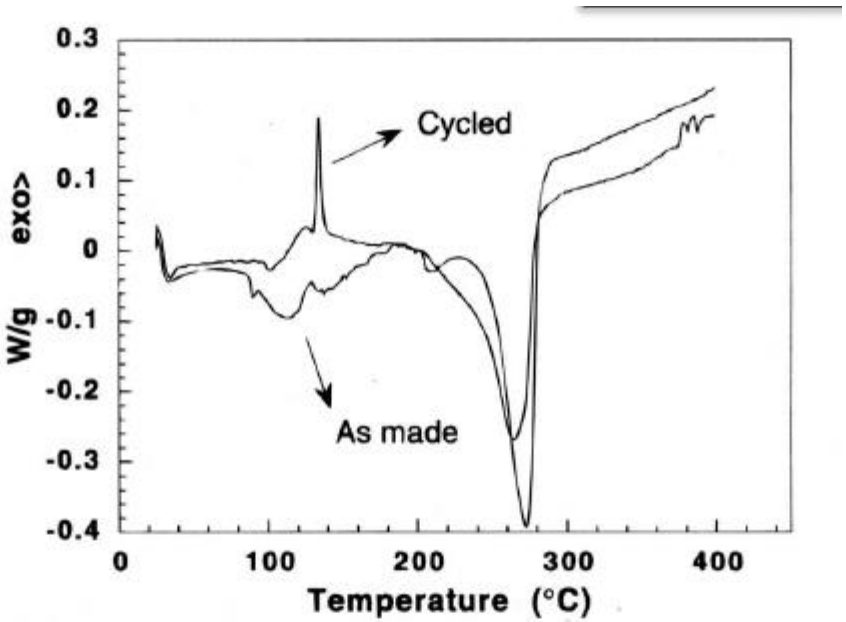

Fig. 2. DSC trace of the delithiated MCMB 25-28 graphite plastic anodes before and after formation of the passivation layer.

- In this same study they tested fully lithiated MCMB 25-28 graphite plastic anodes under various conditions:
  - (a) immediately after intercalation in a pan sealed under Ar;
  - (b) after 65 h relaxation, in a pan sealed under Ar.
- They found that there is a shift in this peak
  - Self-discharging
  - Formation of CO2 from decomposition of Li-akyl carbonates

Differential Scanning Calorimetry Study of the Reactivity of Carbon Anodes in Plastic Li-ion Batteries
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Thermogravimetry Analysis (TGA)

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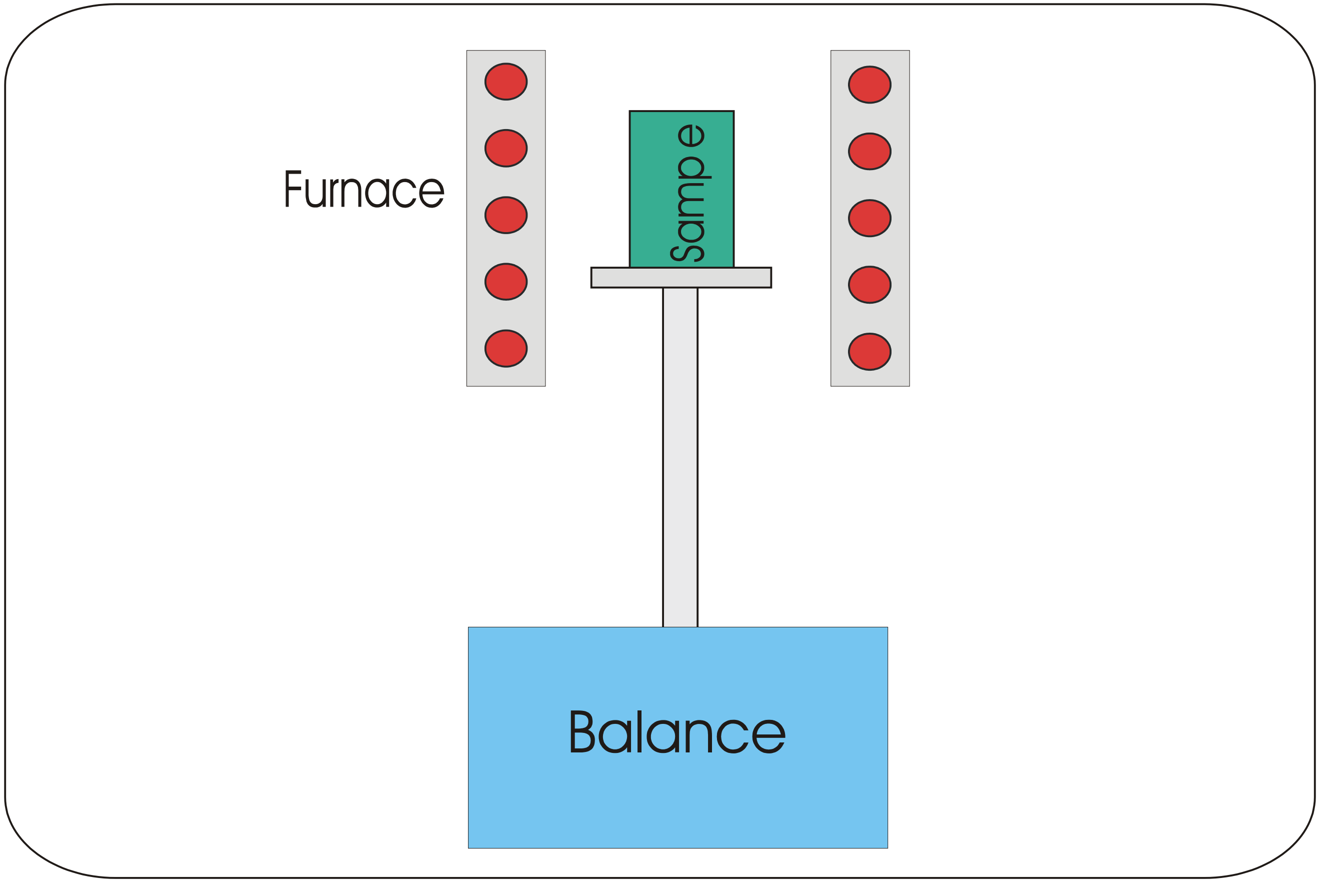
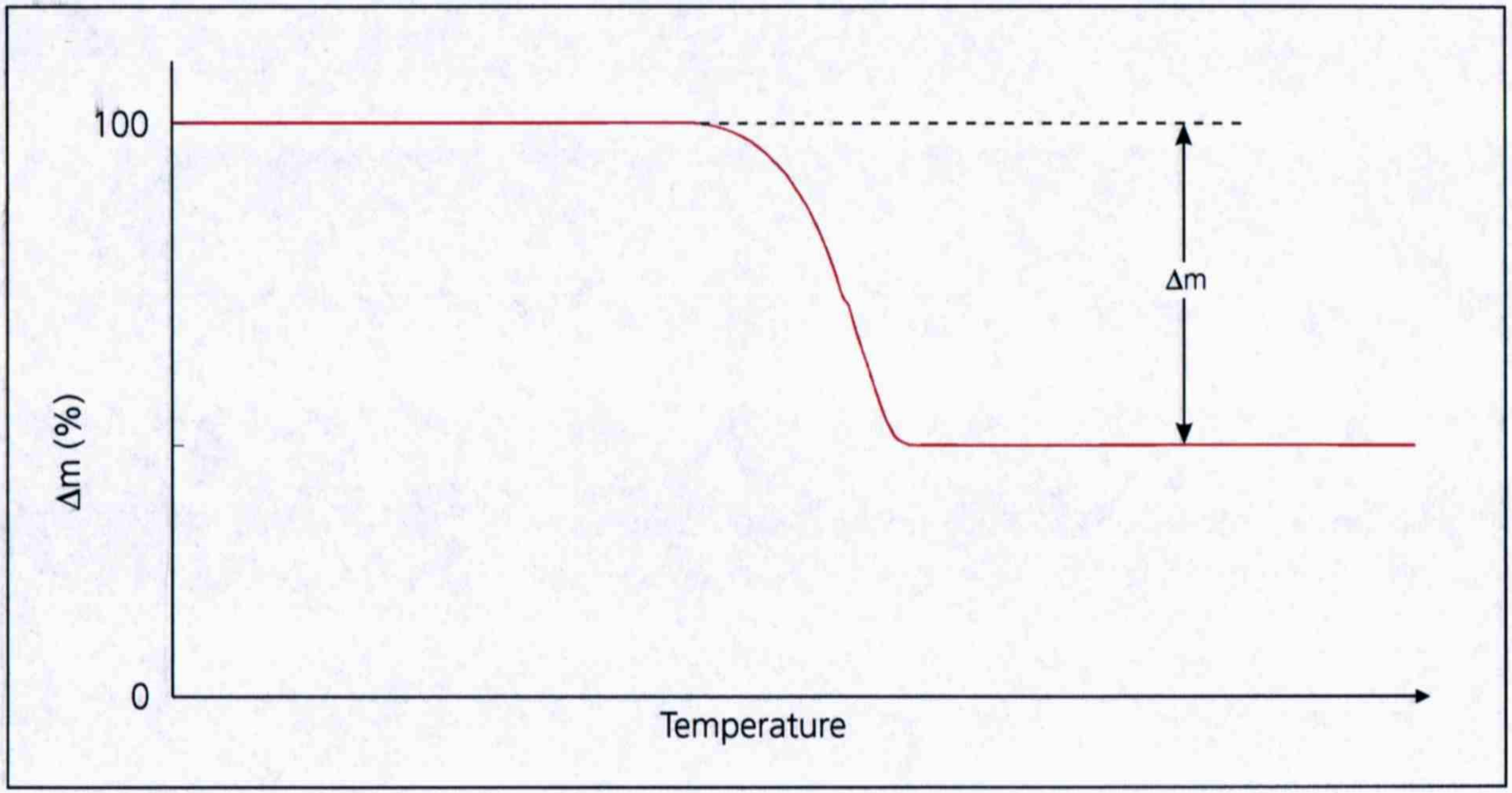
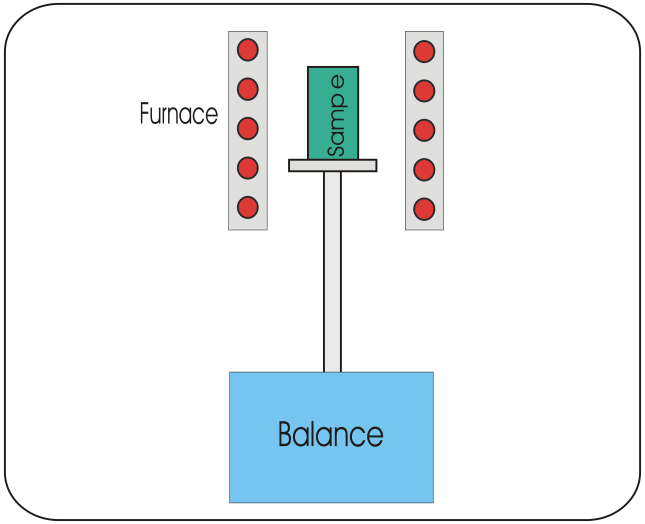


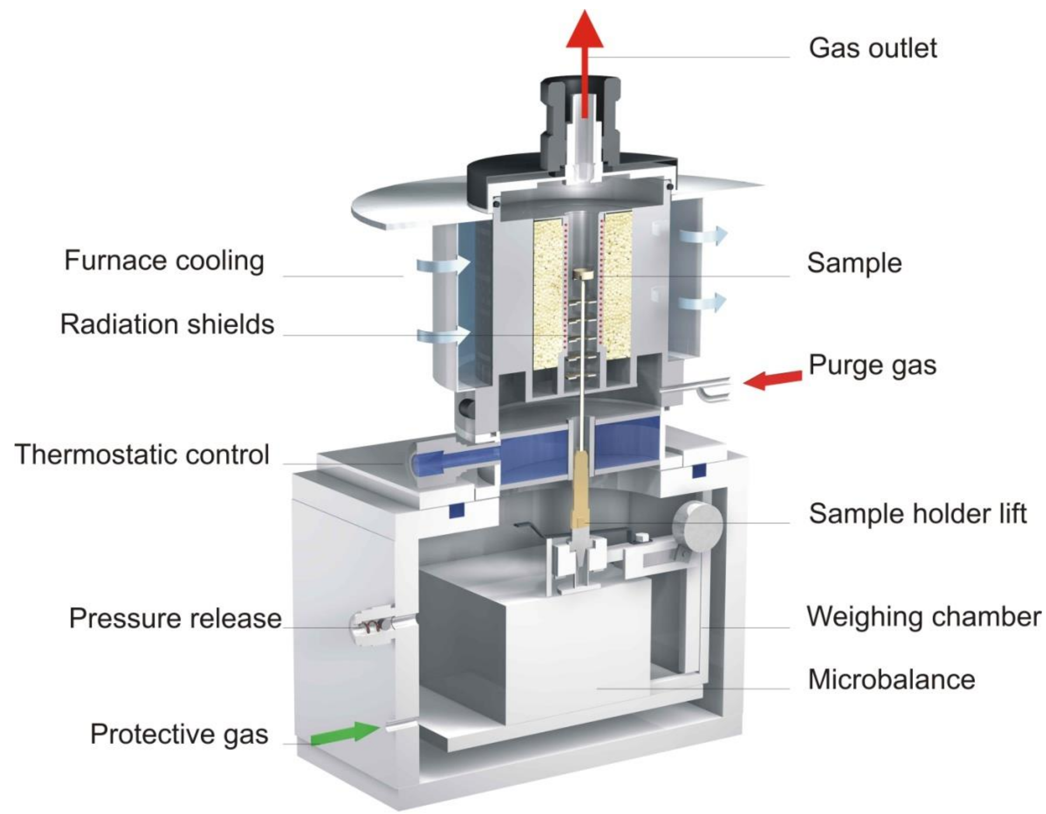
TG curve



Thermogravimetric Analysis (TGA)

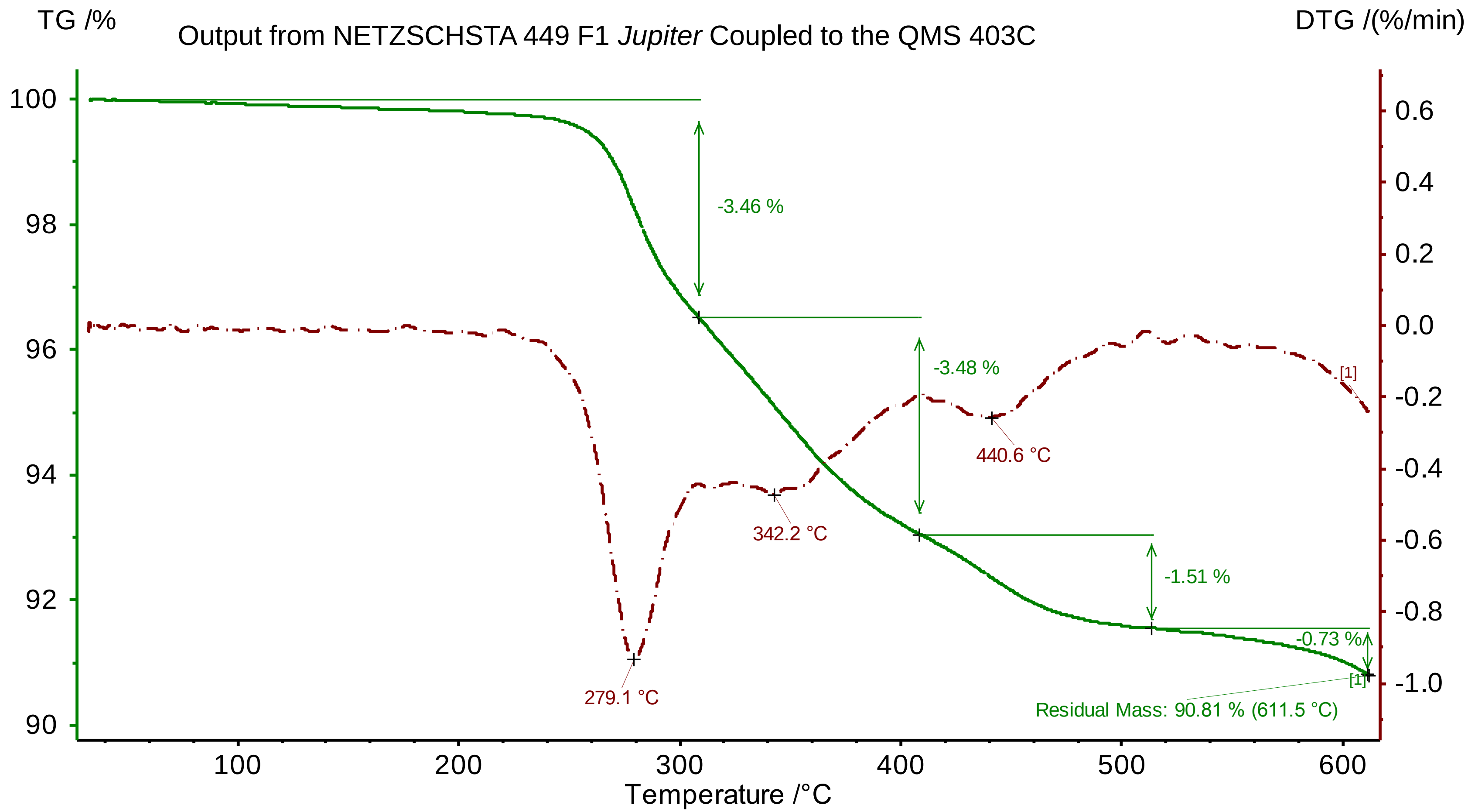


Top-Loading Design

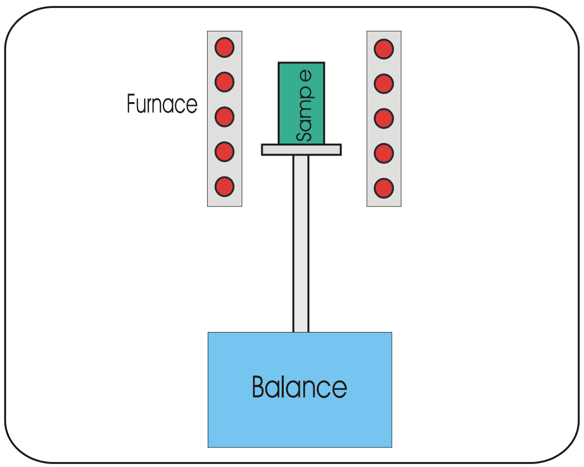


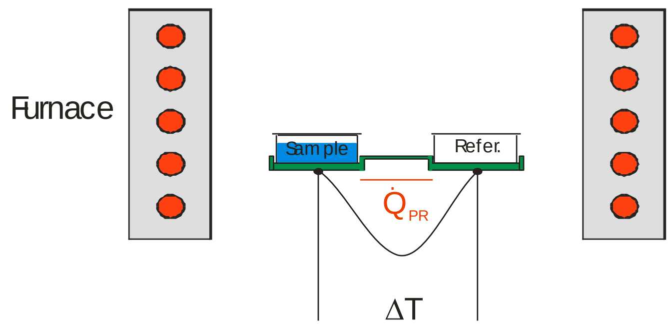
TG 209 F3

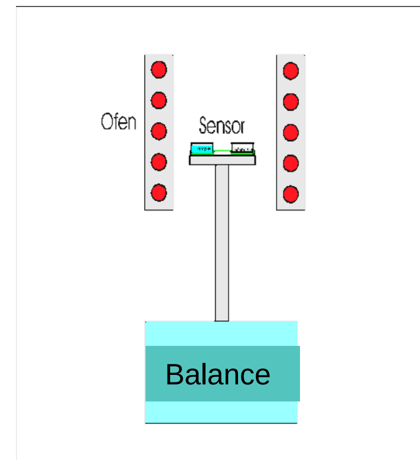
TG and DTG curves for the delithiated LiCoO2 cathode material with 10 K/min heating rate



Simultaneous Thermal Analysis implies the application of two or more thermoanalytical techniques (usually TG and DTA/DSC) on one sample.







TGA + **DSC** = **STA**

Thermogravimetry

Differential Scanning Calorimtery

Advantages of STA

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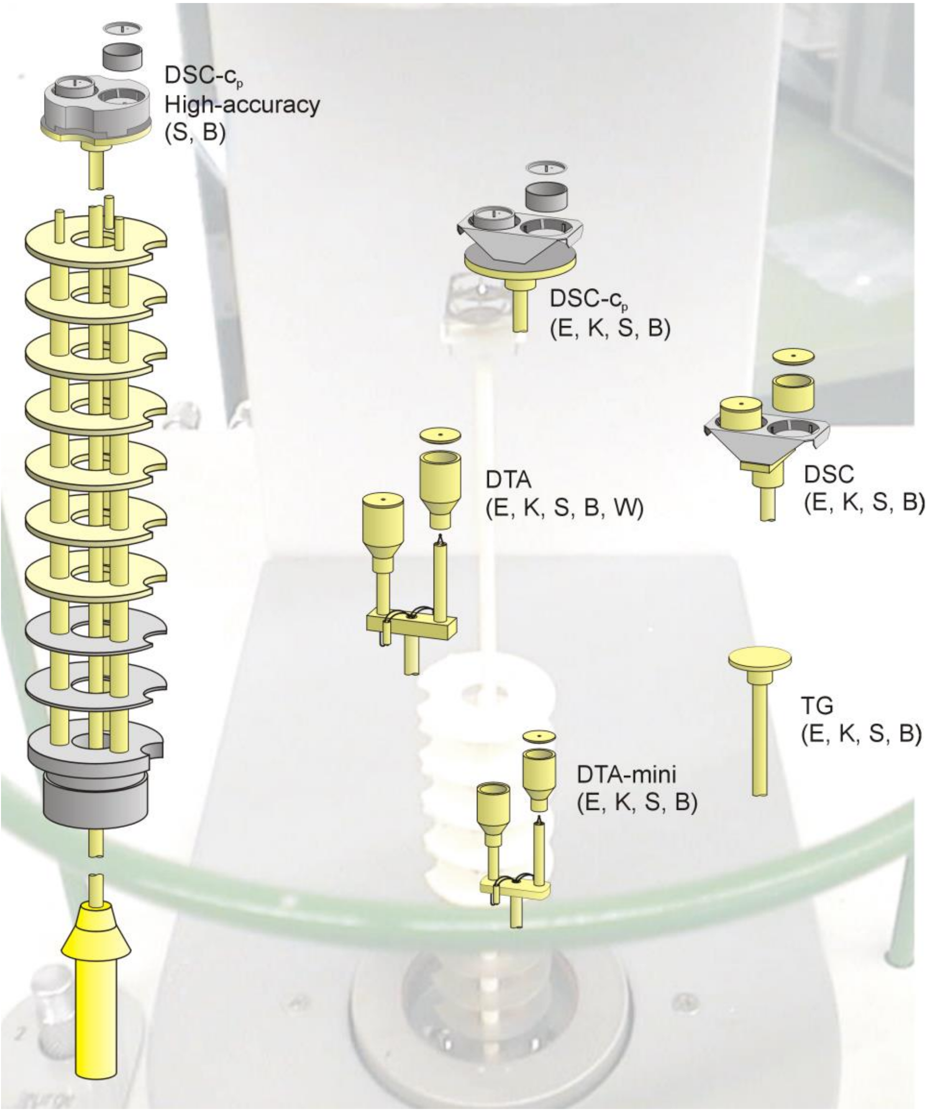
TGA and DSC are applied simultaneously to the same sample!

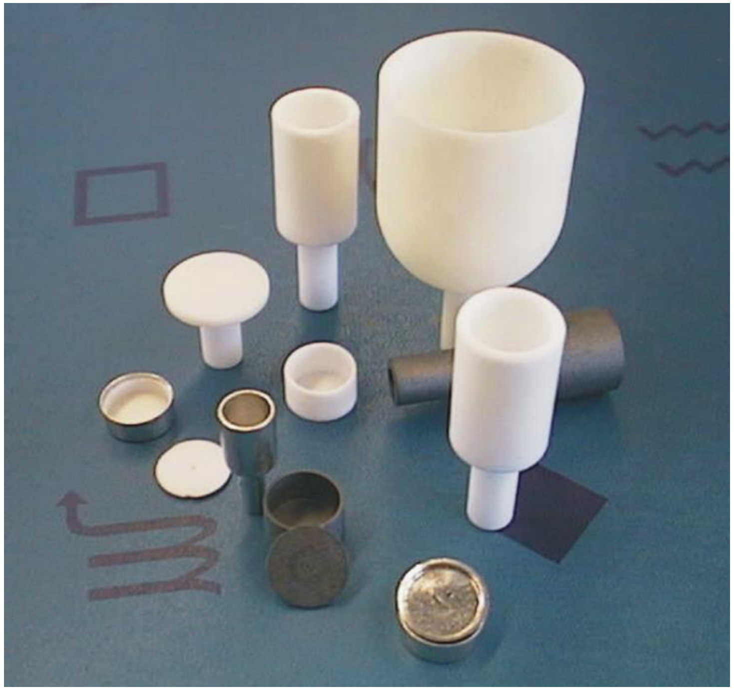
→ Time effective! Also (expensive) sample material can be saved.

→ Direct comparison of TGA and DSC possible (same measurement conditions on exactly the same sample)

→ Exact determination of enthalpy changes (sample mass continuously monitored, enthalpy recalculated)

DSC/DTA Sample Carriers





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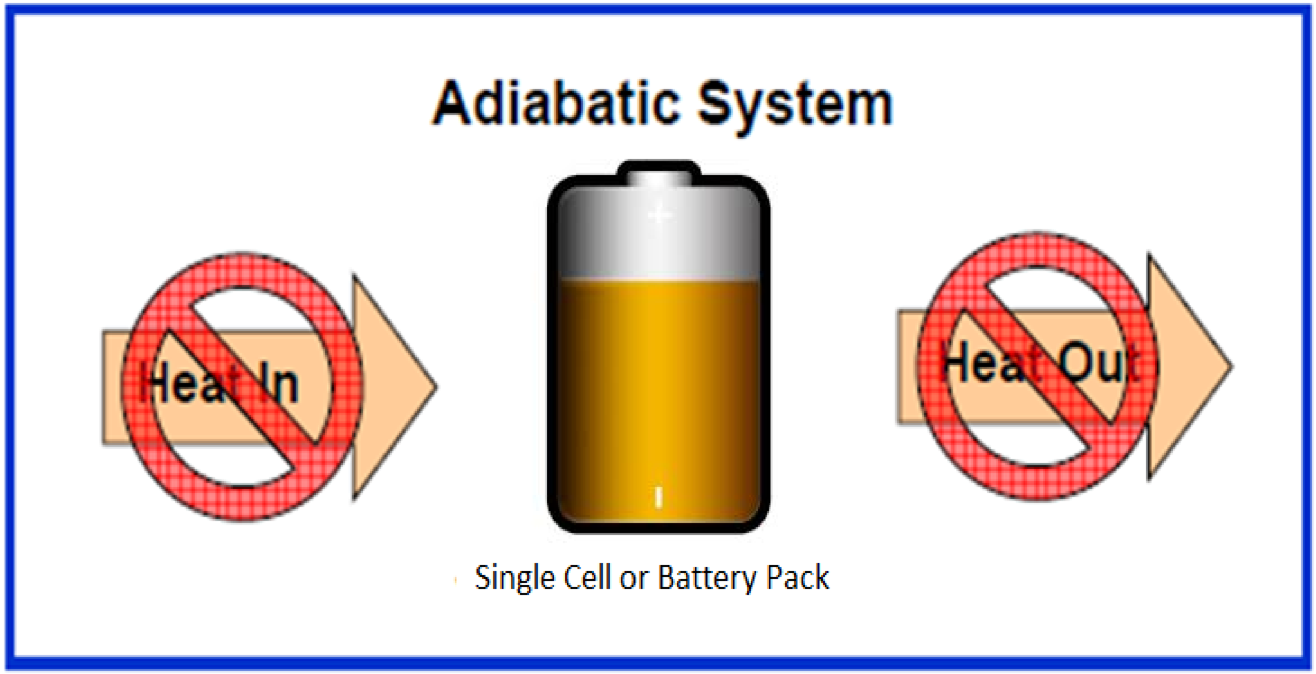
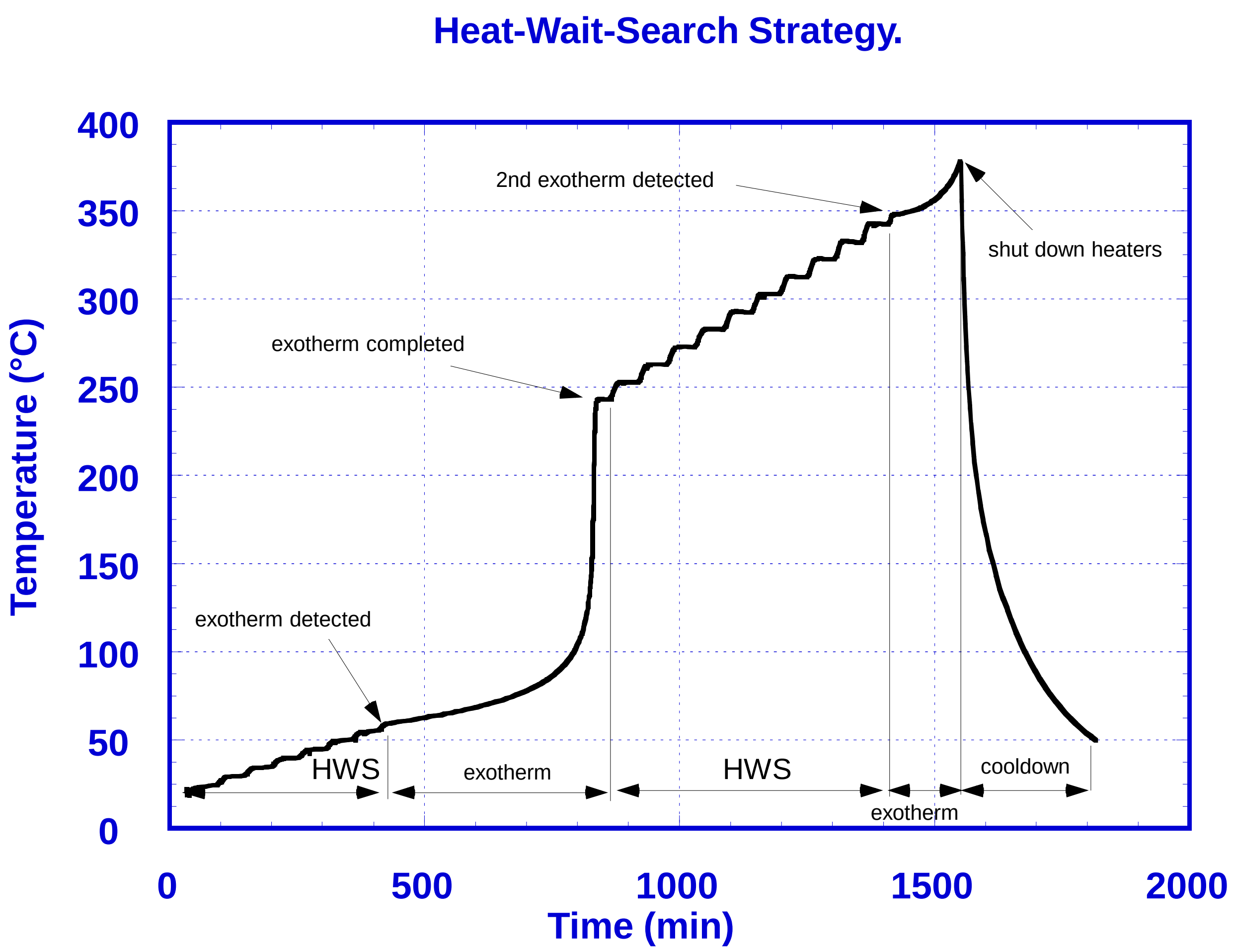
Adiabatic Calorimetry



The use of adiabatic systems has the advantage that no heat loss is allowed from the sample and therefore, the behavior in real large scale chemical reactors can be simulated (worst case scenario).

The ARC & APTAC Operational Modes



Plotting Self-Heat Rate and Pressure Rate Kinetic Analysis can be done

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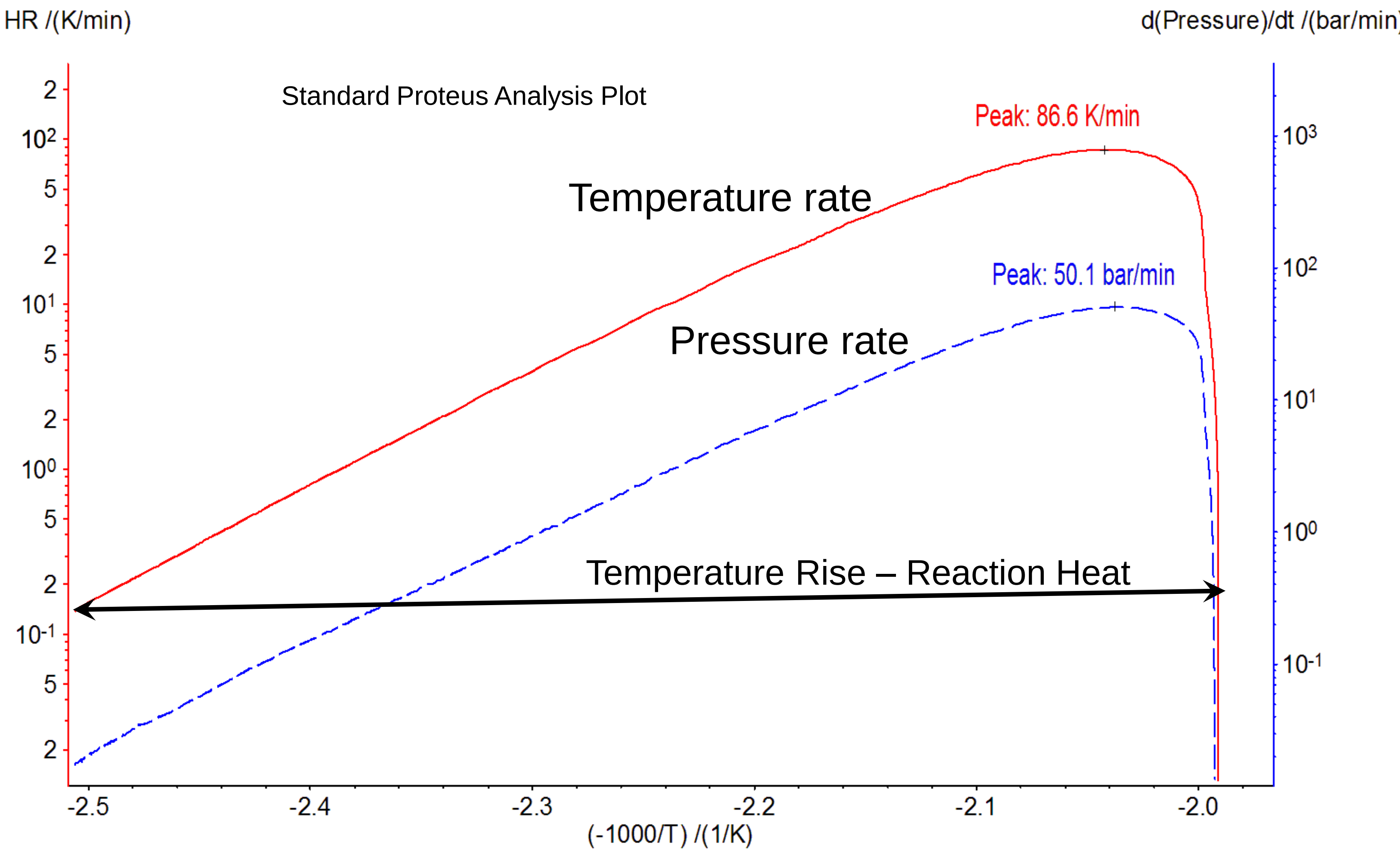
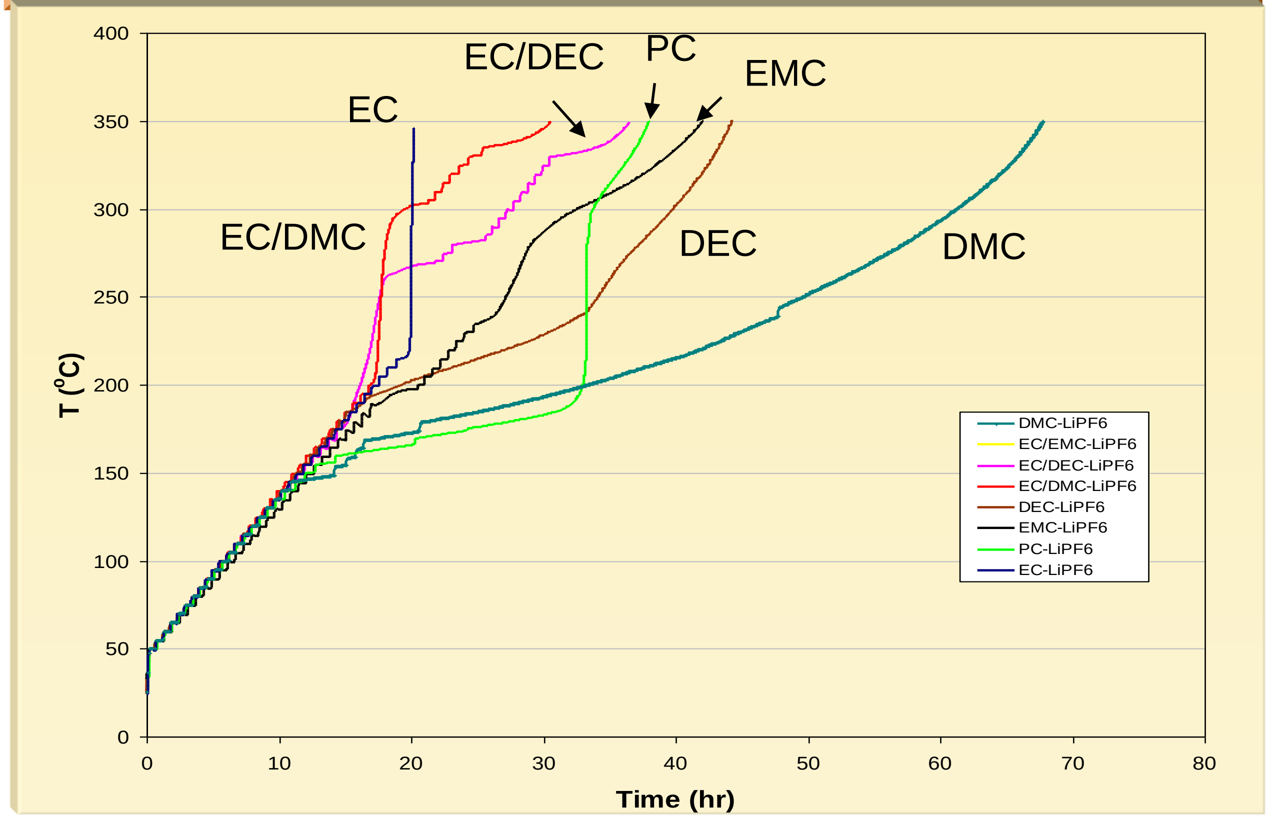


Battery Safety

Compatibility Study with Anode and Different Electrolytes

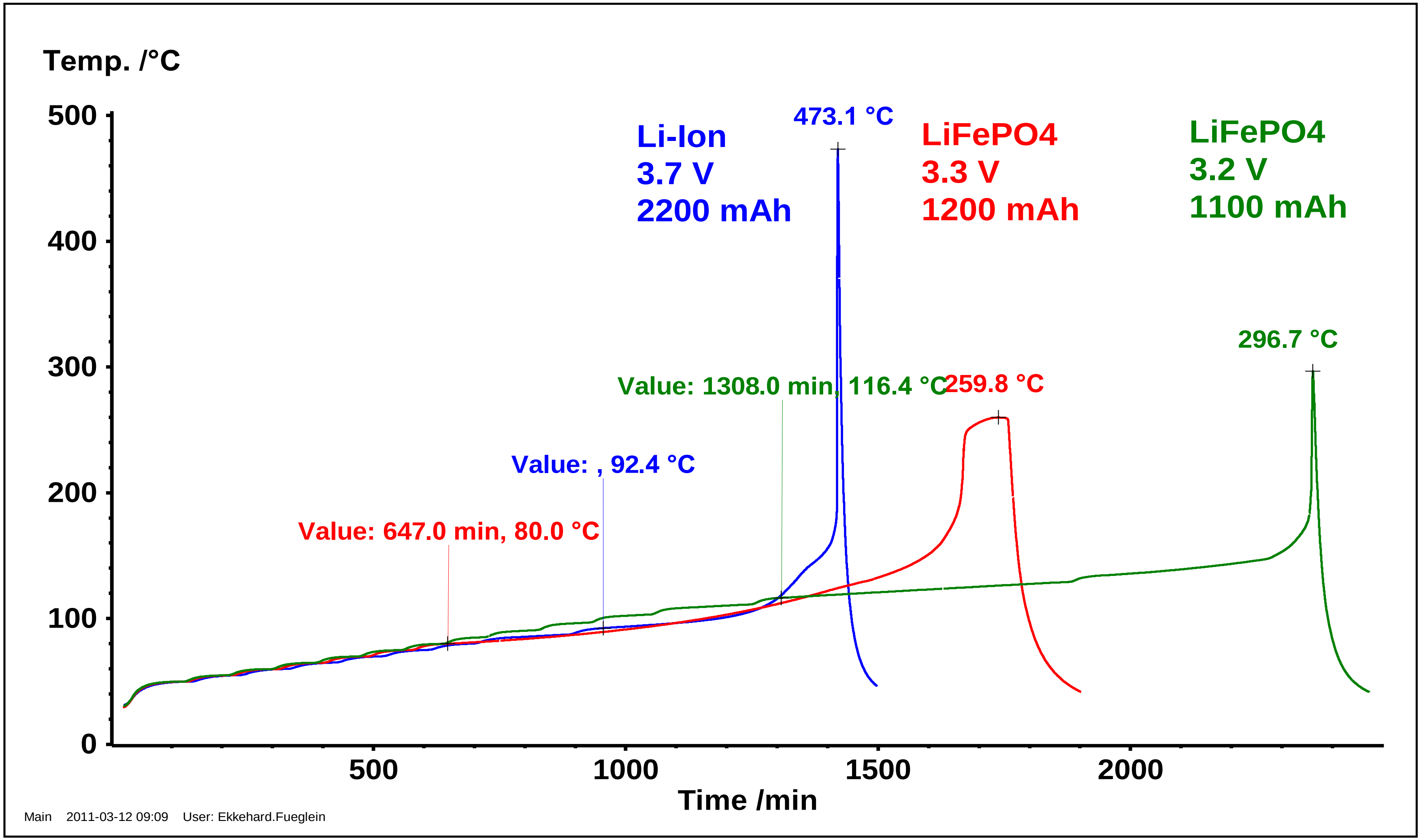
ARC Testing of Graphite Anode with Different Solvents + $LiPF_6$



Measuring a solid anode and a liquid electrolyte solution is often times easier to do in a larger calorimeter like the MMC or ARC. This is a series of standard HWS steps to took at the compatibility of battery materials

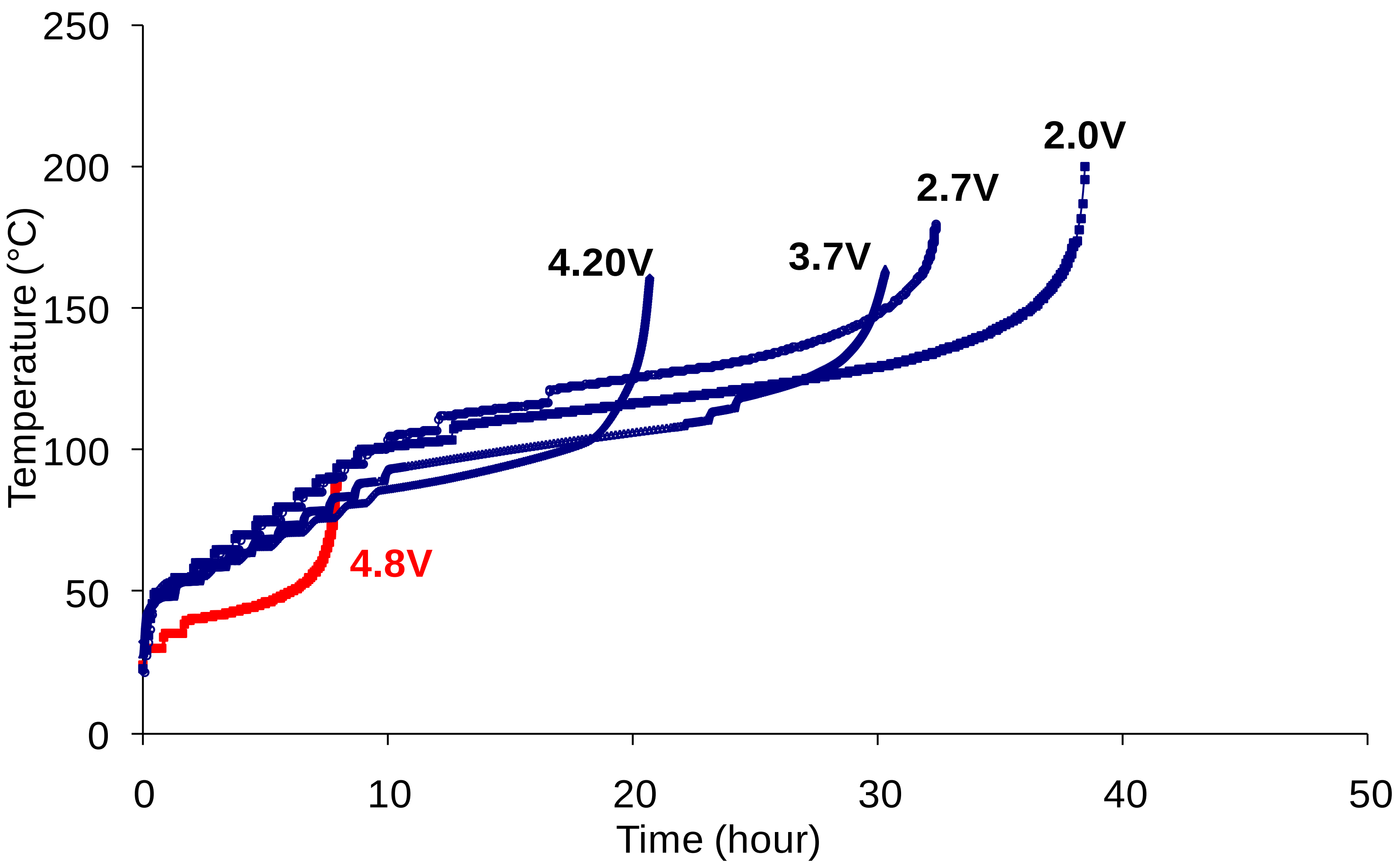
Source: ADL CSI ARC

Comparison of Three Lithium Ion Batteries for Thermal Runaway



Source: NETZSCH ARC 254

Battery Safety – Thermal Stability dependence of SOC (State-of-Charge) and Overcharging



Source: ADL CSI ARC

Pouch Cell
Closed System for Gas collection

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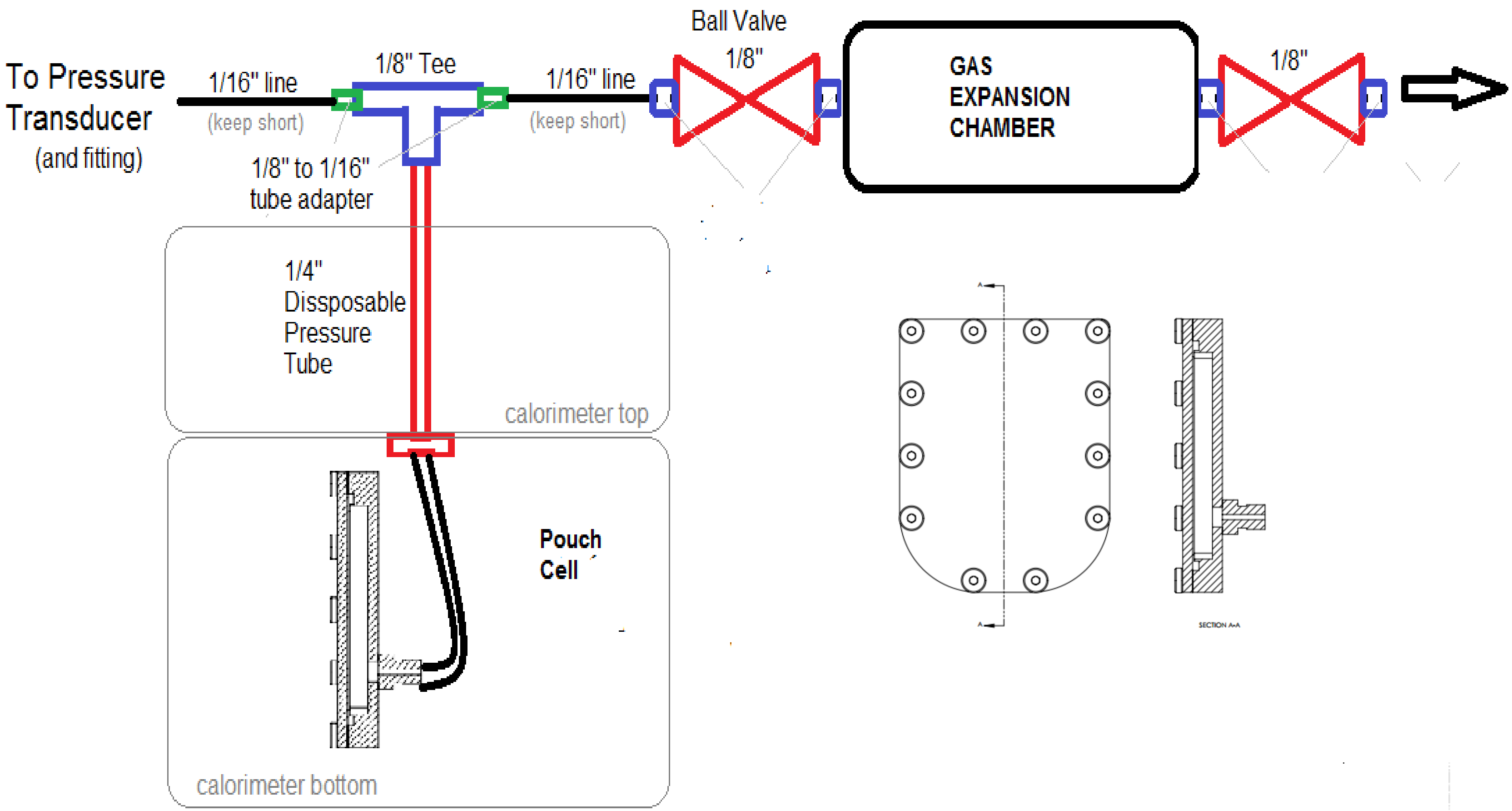

Configure Cell holder types and plumbing to meet testing requirements

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Evolved Gas Analysis in Thermal Analysis

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In Thermogravimetry (TG) or Simultaneous Thermal Analysis (STA), the mass change (and transformation energetics) of a sample is measured versus temperature or time.

Evolved Gas Analysis yields additional information regarding the nature (composition) of the gases evolved during a mass-loss step.

In most cases, a **Quadrupole Mass Spectrometer (QMS)** and/or an **Fourier Transform Infrared Spectrometer (FT-IR)** system are coupled to a TG/STA system for evolved gas analysis.

Possibilities:

- TG/STA-FT-IR coupling (transfer line)
- TG/STA-MS coupling (capillary coupling)
- STA-MS coupling (SKIMMER®)

Different Coupling Techniques Available

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STA/TG-MS Coupling: yields information on the composition (mass numbers of elements and molecules) of the evolved gases.

⇒ High sensitivity

⇒ Fast and easy interpretation of atomic/inorganic vapors and standard gases (H_2, H_2O, CO_2, ...)

⇒ Fragmentation, interpretation of organic molecules is sometimes difficult

STA/TG-FTIR Coupling: yields information on the composition (absorption bands) of the evolved gases (bonding conditions).

⇒ Easy interpretation (spectra data bases) of organic vapors without fragmentation

⇒ Symmetric molecules cannot be detected

.

TGA/STA- FTIR Coupling

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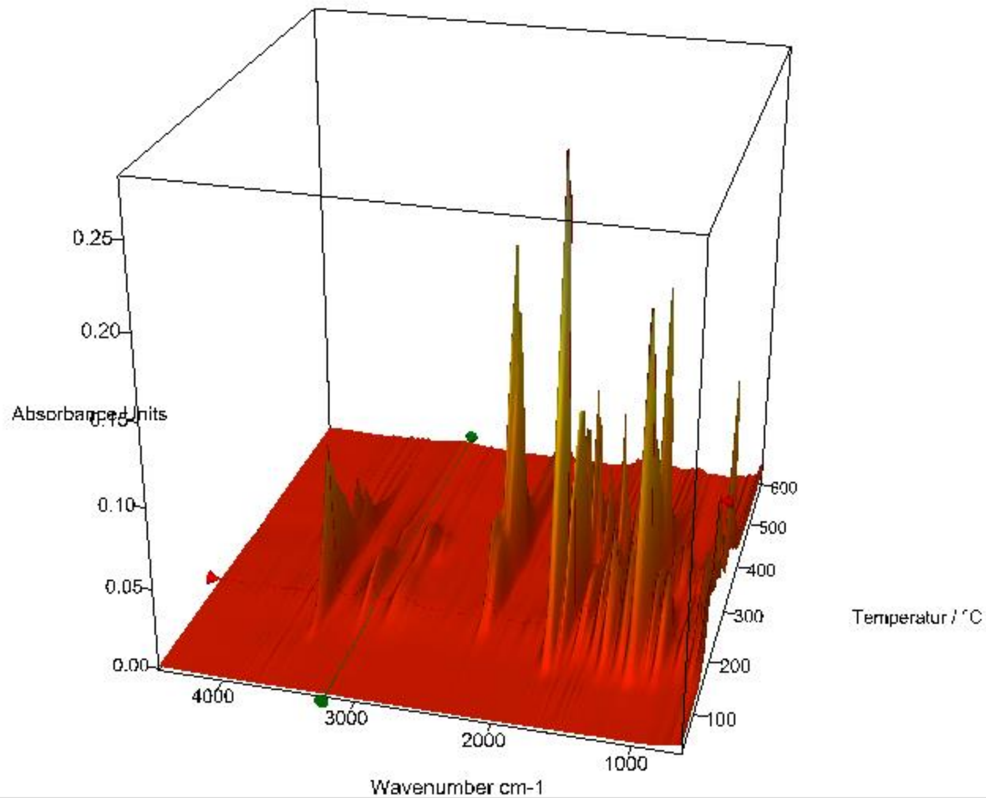
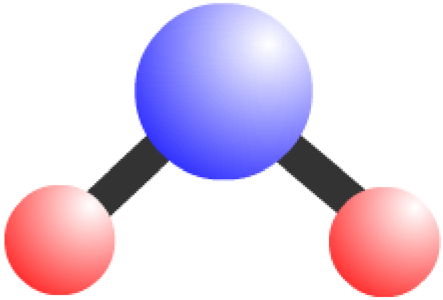
Gases, leaving the outlet of a TG/STA, are lead into a gas measuring cell of an FT-IR via a transfer line.

By means of measurement of the absorption spectra, the nature of the evolved gases can be analyzed.



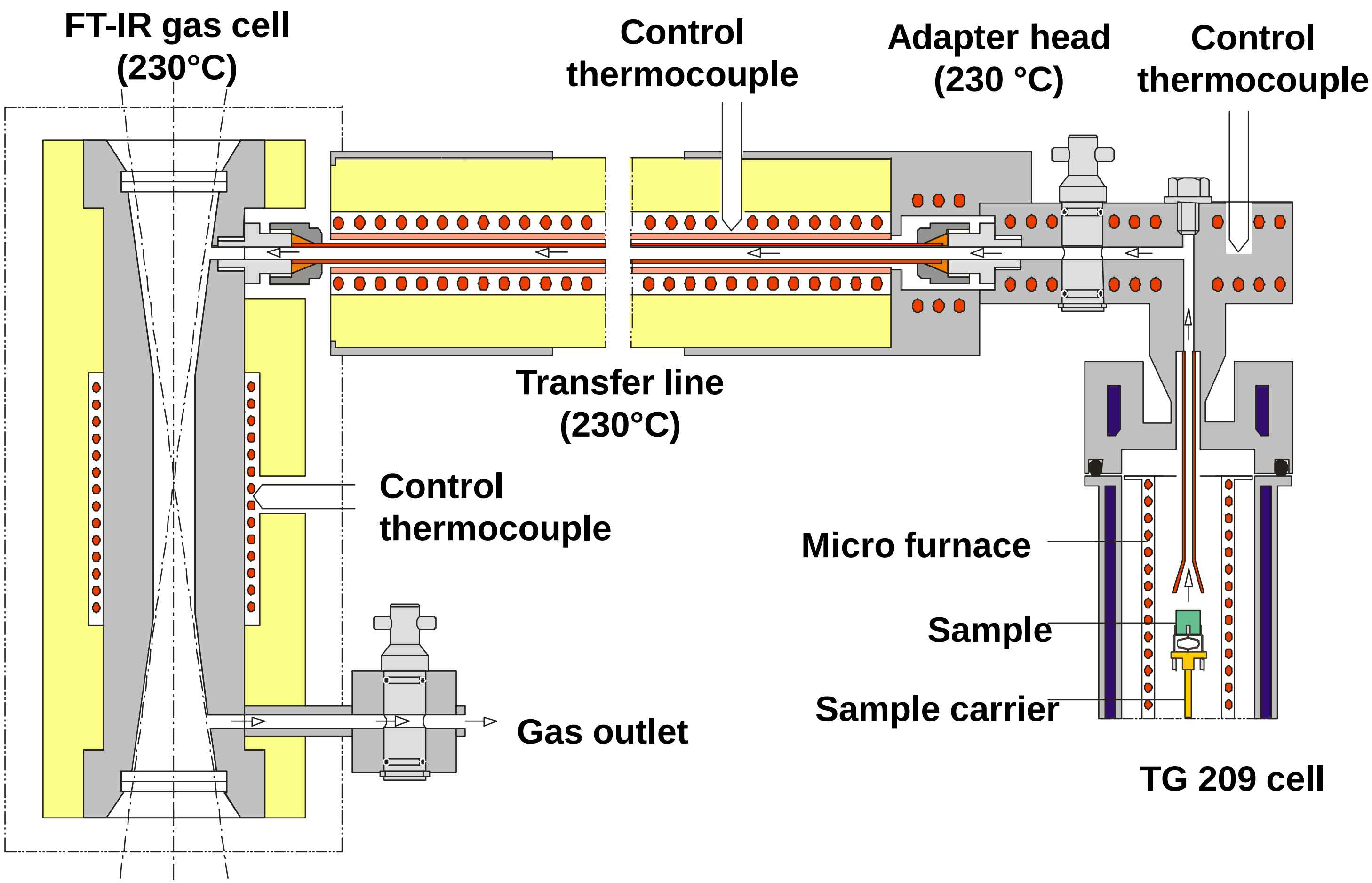
Example: Low level detection of water in battery materials

Interaction of Infrared Radiation with Molecules



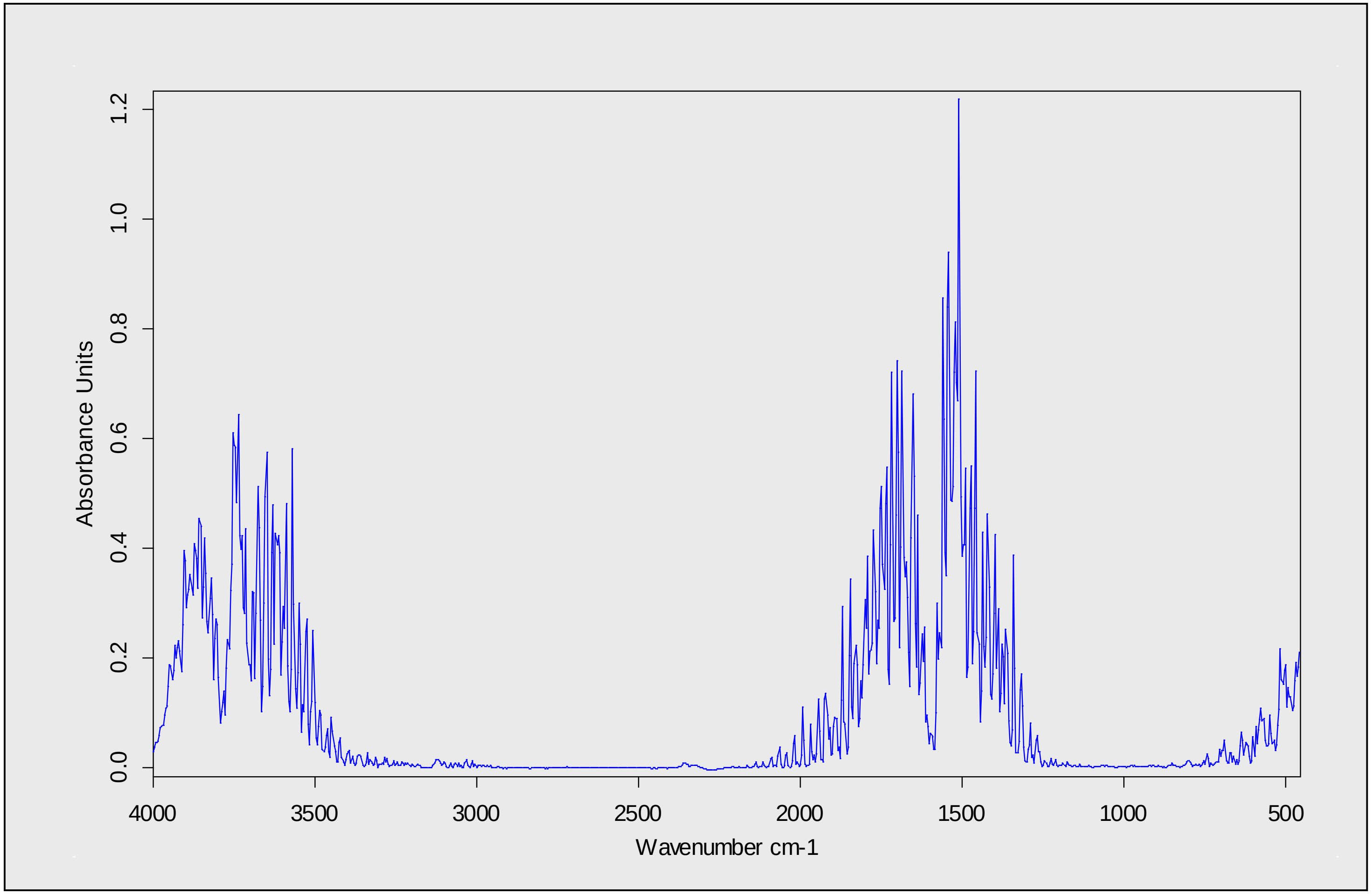
Vibration Excitation

TG-FT-IR Coupling – Realization



FTIR identification of water for QC on battery materials

- FTIR is good technique for water identification as the resulting spectrum is strong and easily identifiable



TG/STA –MS Coupling

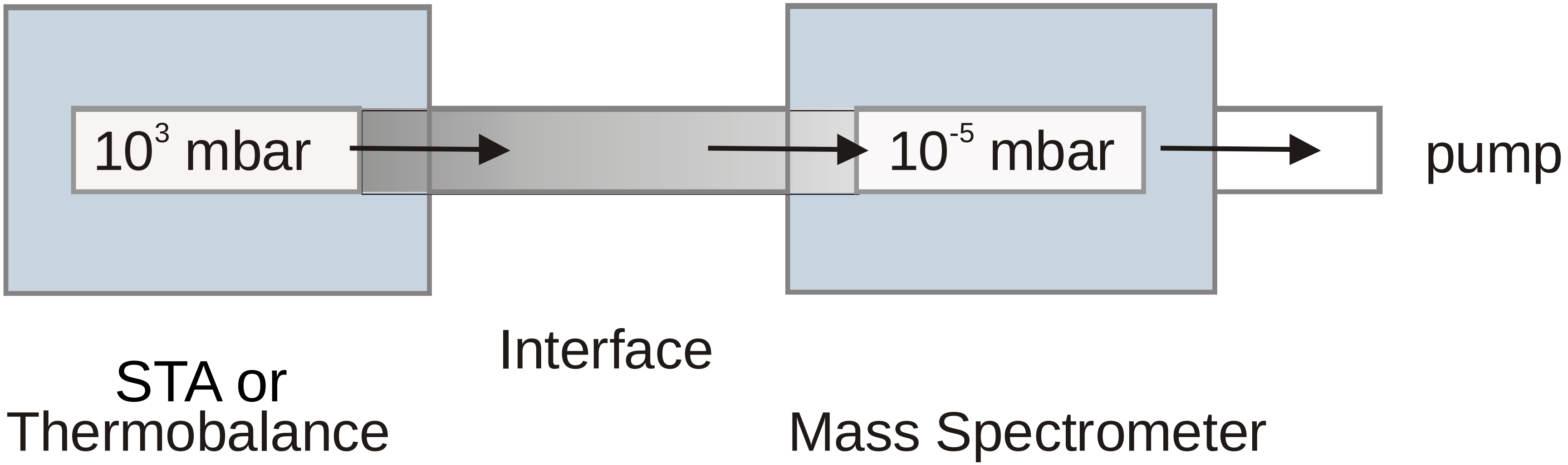
Gases, leaving the outlet of a TG/STA, are lead to a QMS system via a capillary (pressure reduction required).

By means of measurement of the mass numbers (m/z), conclusions on the composition of the evolved gases can be drawn.

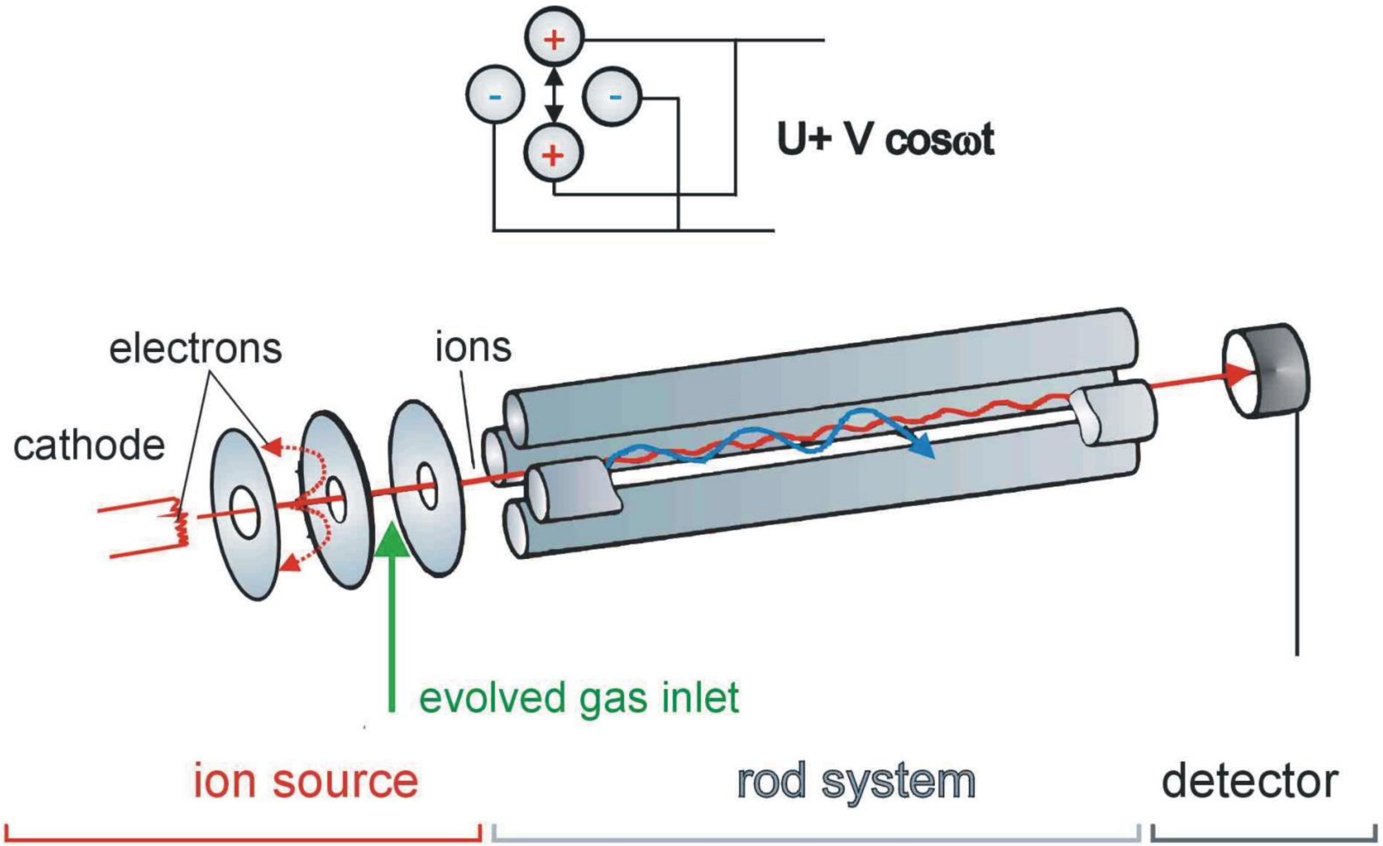
QMS systems are extremely sensitive. Interpretation of the MS spectra of inorganic materials can often easily be made.

Problems: Fragmentation, interpretation of spectra in organic compounds are difficult.

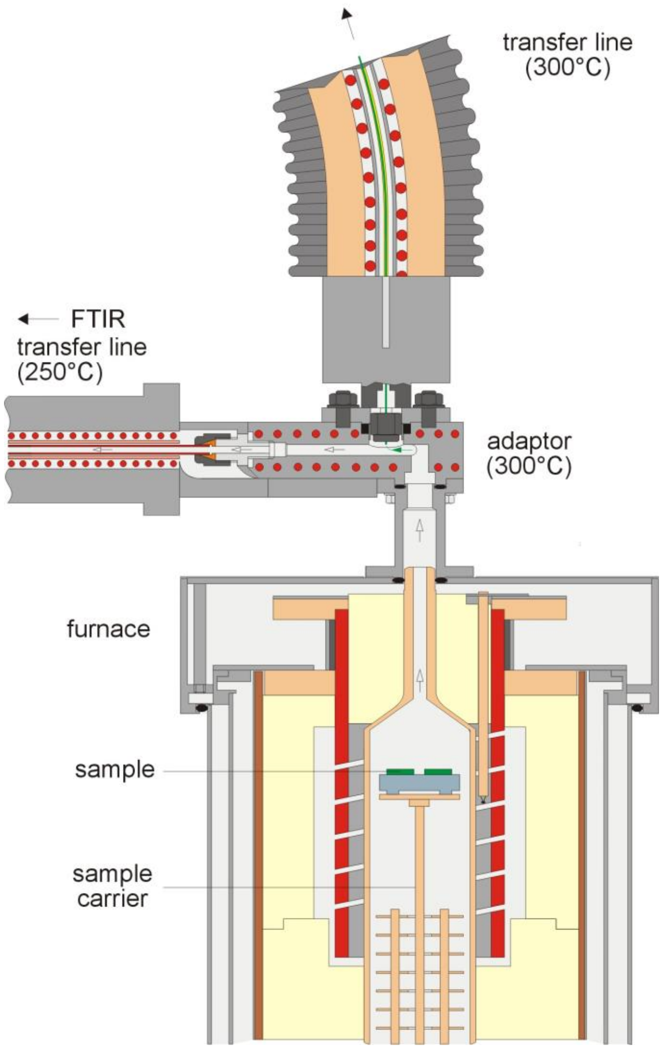
Quadruple Mass Spectrometry requires a reduction in the source pressure



Mass separation in a quadruple



The STA 449 *Aëolos*® Interface



Simultaneous measurement of STA, MS and FT-IR!

Entire coupling interface is heated up to 300°C (no cold spots)

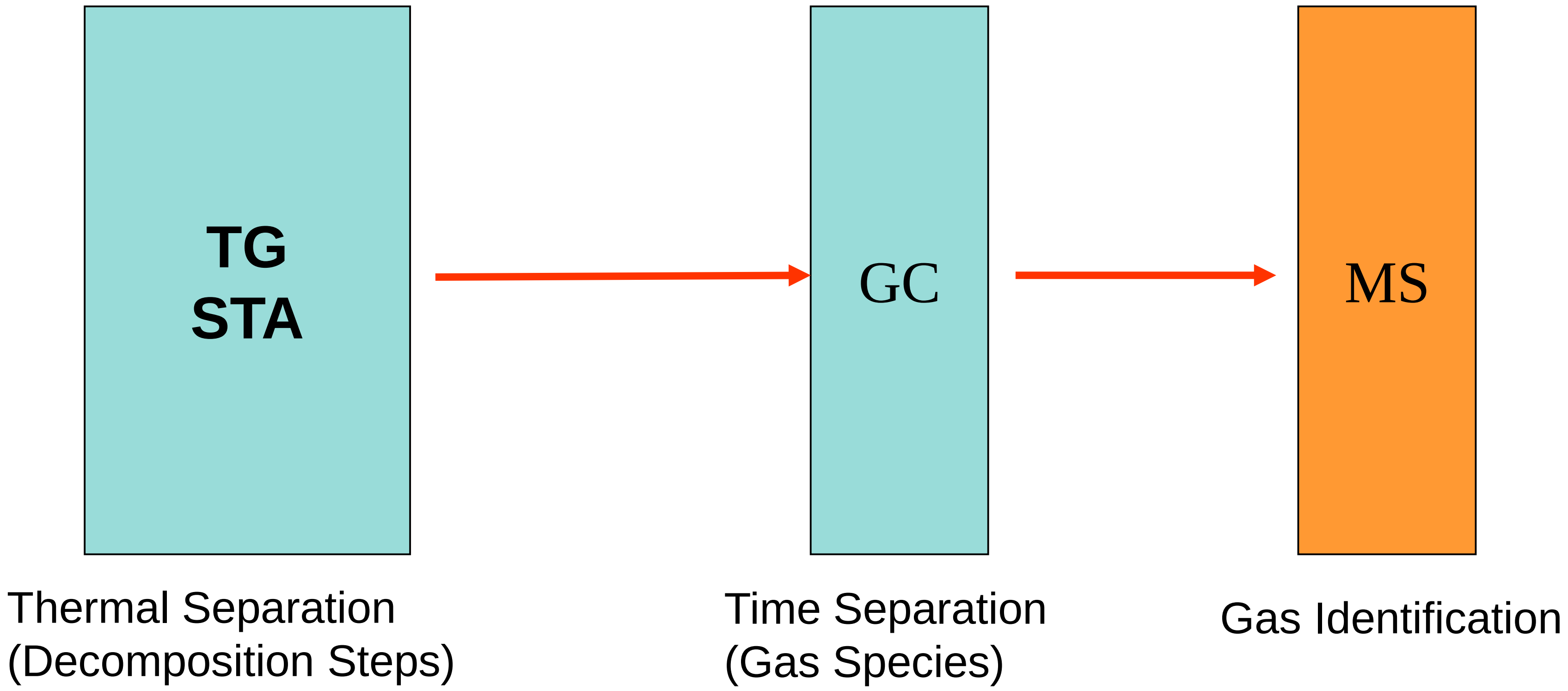
→ Prevention of condensation of evolved gases

→ Enhance the traceability of evolved gases

→ Minimize the risk of blocking of the coupling capillary

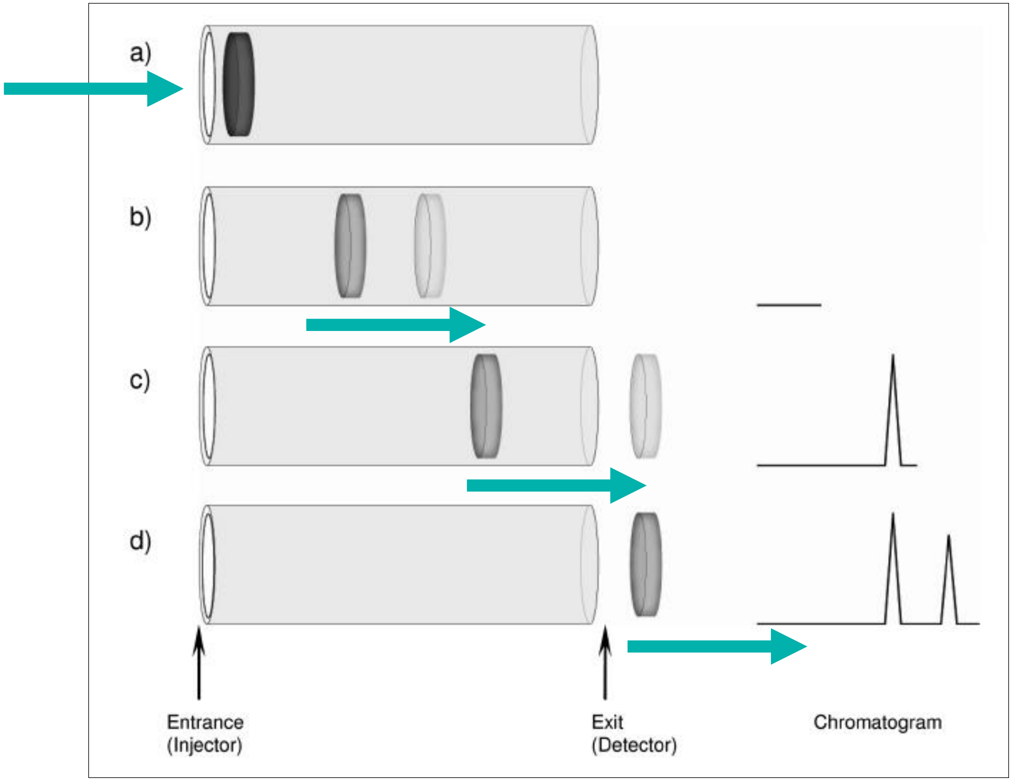
The TG-GC-MS Coupling Principle

- Mass spectra can be complicated. GC separation prior to identification in a mass spectrometer can make it easier for analysis but adds time to analysis

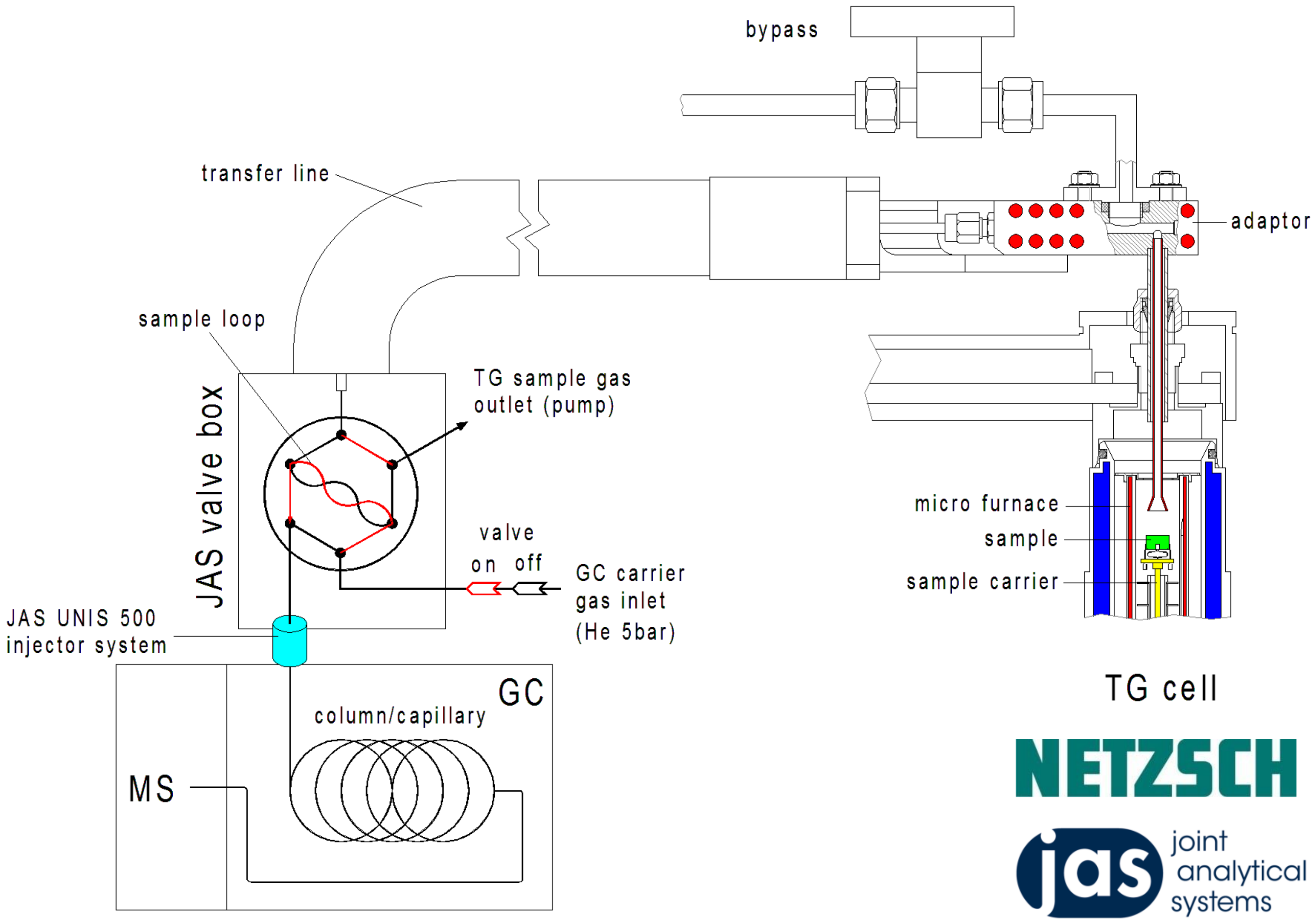


GC Principle

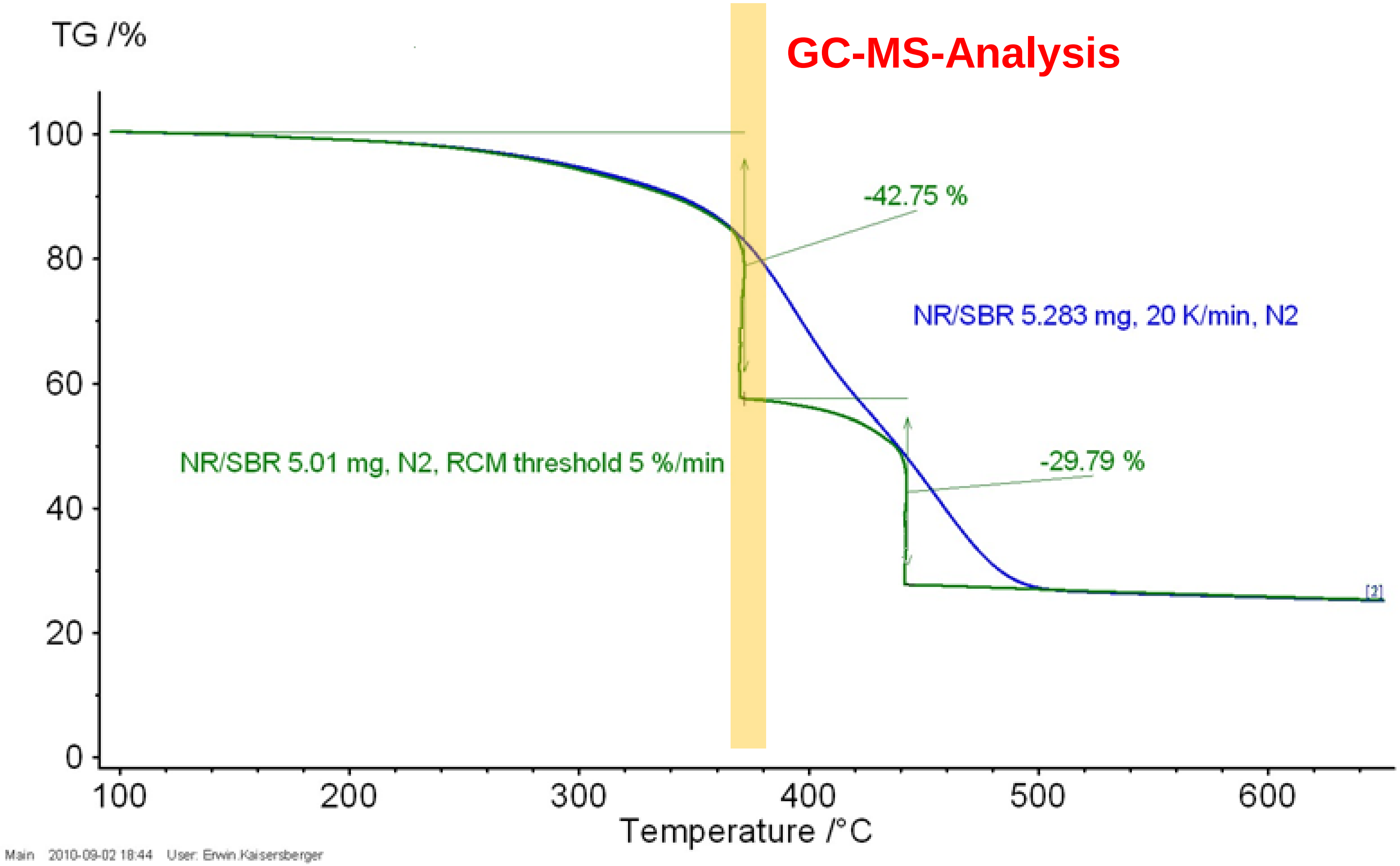
Gas mixture
(mobile phase)



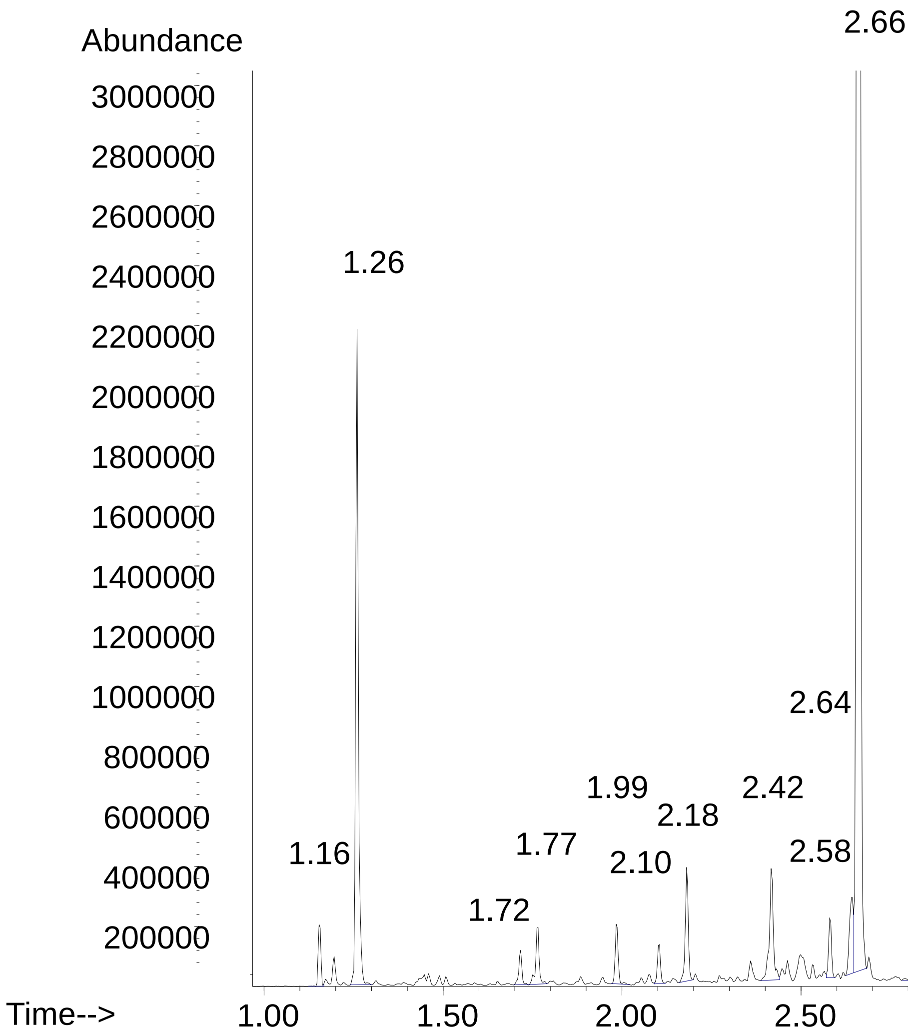
Coupling with Chromatographic Pre-Separation



Event-Controlled TG-GC-MS Separates NR and SBR Decomposition Steps



Help with Identification: Library Search Report @ designated temperatures



Search Libraries: C:\Database\NIST05.L Minimum Quality: 50
C:\Database\Wiley7N.L Minimum Quality: 0

Unknown Spectrum: Apex
Integration Events: Chemstation Integrator - events.e

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			2H-1,4-Benzodiazepin-2-one, 7-b...	186113	1000142-56-8	56
			Olean-9(11)-en-12-one, 3.beta.,...	186608	004409-10-3	10
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			1,3-Butadiene, 2-methyl-	446	000078-79-5	90
			Cyclobutane, methylene-	443	001120-56-5	83
			Cyclopropane, ethylidene-	453	018631-83-9	83
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			Cyclopentene, 1,5-dimethyl-	2847	016491-15-9	90
			Cyclobutane, (1-methylethylidene)-	2865	001528-22-9	87
			Cyclopropane, trimethylmethylene-	2864	034462-28-7	86
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			Toluene	2395	000108-88-3	86
			1,3,5-Cycloheptatriene	2413	000544-25-2	50
			Cyclobutene, 2-propenylidene-	2420	052097-85-5	38
5	1.99	1.26	C:\Database\NIST05.L			
			Cyclohexene, 4-ethenyl-	5296	000100-40-3	96
			Spiro[2.9]dodeca-4,8-diene	30817	062108-42-3	53
			1,5-Cyclooctadiene, (Z,Z)-	5309	001552-12-1	43
6	2.10	0.84	C:\Database\NIST05.L			
			p-Xylene	4944	000106-42-3	95
			o-Xylene	4945	000095-47-6	95
			Benzene, 1,3-dimethyl-	4970	000108-38-3	94
7	2.18	2.31	C:\Database\NIST05.L			
			Styrene	4749	000100-42-5	97
			1,3,5,7-Cyclooctatetraene	4757	000629-20-9	96
			Bicyclo[4.2.0]octa-1,3,5-triene	4759	000694-87-1	95
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			Cyclohexene, 1-methyl-4-(1-meth...	15365	005989-54-8	94
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			Cyclohexene, 1-methyl-4-(1-meth...	15372	007705-14-8	70
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			Spiro[2.4]heptane, 1,5-dimethyl...	15330	062238-24-8	76
			1-Decen-3-yne	15173	033622-26-3	72
			7-Propylidene-bicyclo[4.1.0]hep...	15272	082253-09-6	58
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			D-Limonene	15162	005989-27-5	94
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			Bicyclo[4.1.0]hept-2-ene, 3,7,7...	15317	000554-61-0	70

Thermogravimetric Analysis of Cathode

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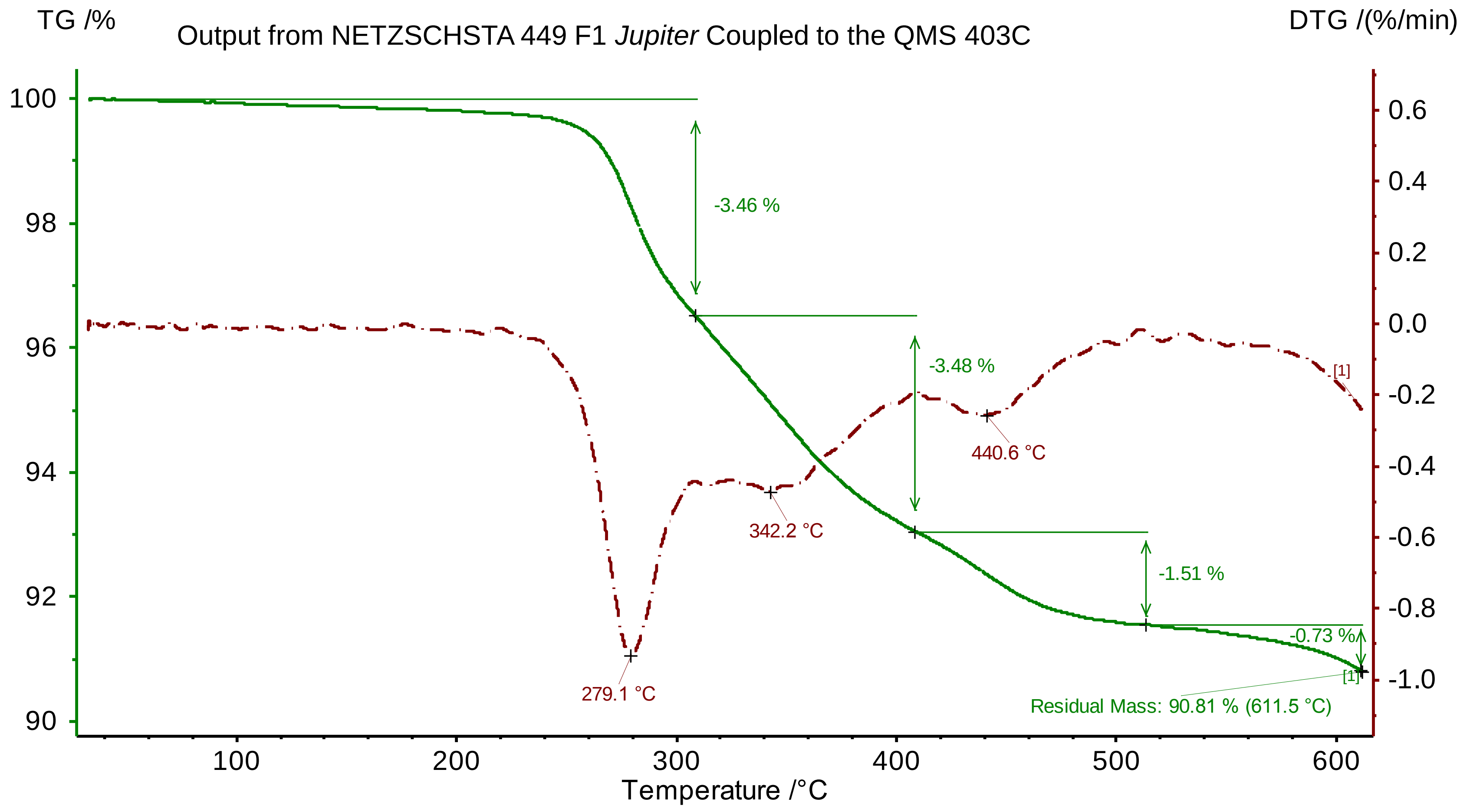
Understanding thermal stability of battery components



Cathode Material Example Using Evolved Gas Analysis

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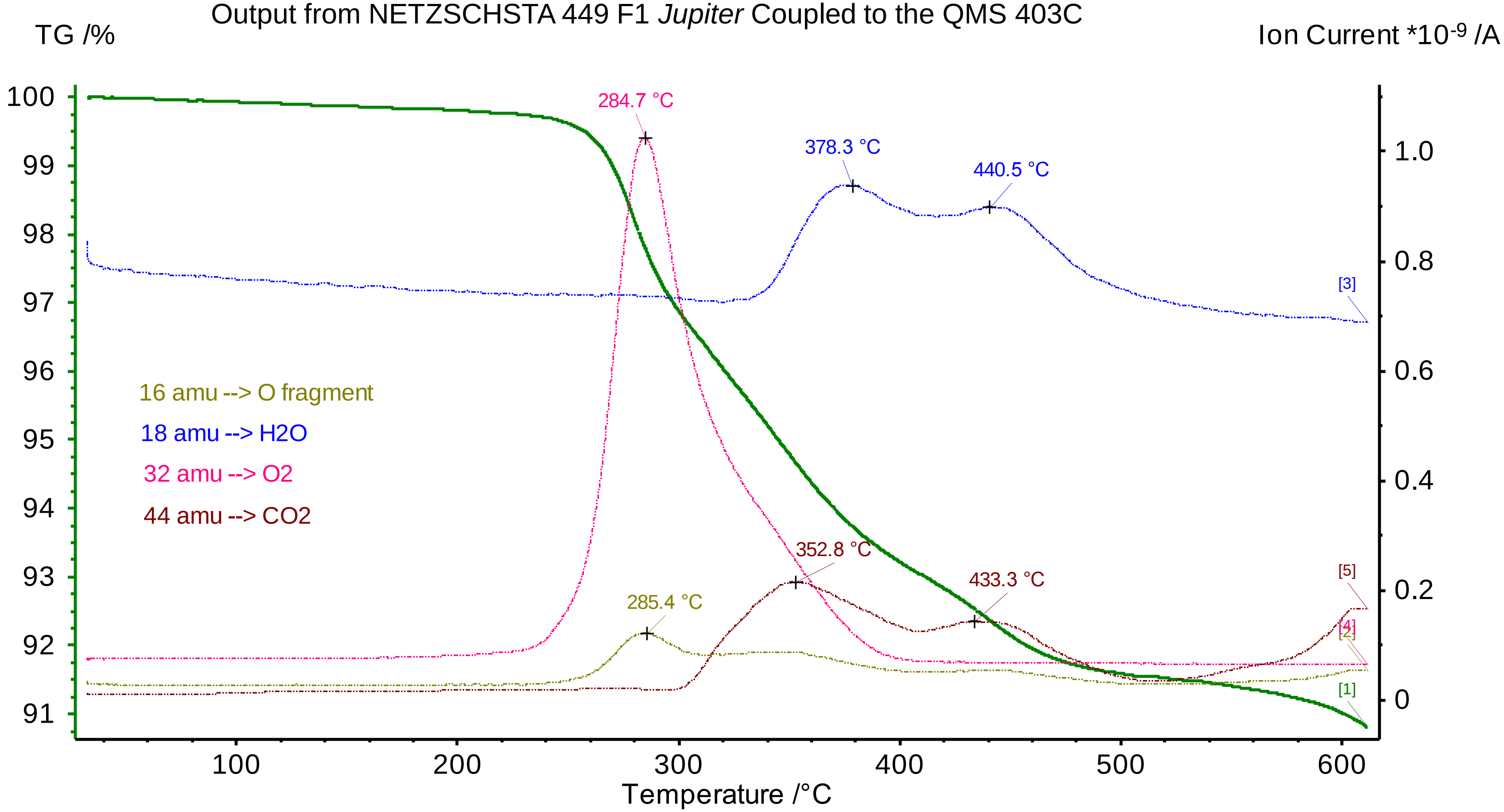
MS ion-current for the 16; 18; 32 and 44 amu mass numbers and TG for the delithiated LiCoO2 cathode material with 10 K/min heating rate

Output from NETZSCHSTA 449 F1 *Jupiter* Coupled to the QMS 403C



Conclusion

- TGAs are standard in Research and Development as well as Quality Assurance of Automotive Parts

- Simultaneous TG-DSC instruments (STA) are standard in research and development, for example, in the organic or inorganic chemistry.

- Coupling to MS or FT-IR yields additional information on the material's behavior at high temperatures and the nature of the evolved gases.

Thank you for your attention!

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Questions?

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