Thermal abuse on 18650 Li-ion cell: time, temperature and correlated gases emission

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PhD students' seminar on fire safety science

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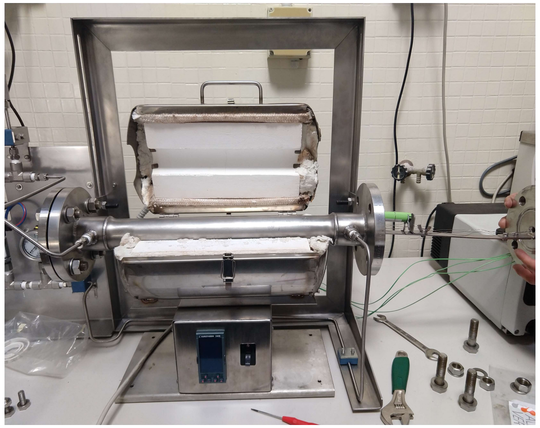
Summary

Lithium Ion Batteries (LIBs)

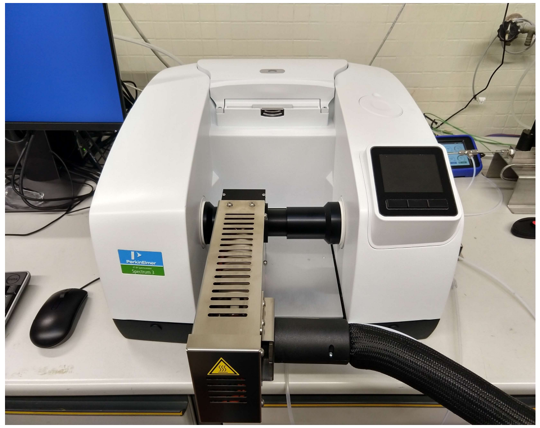
NCR 18650B Li-cell

Thermal abuse



Chamber in oven

Analysis



Cell gas for FT-IR analysis

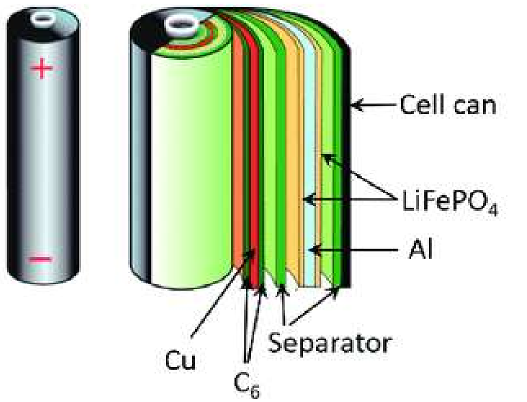
Scope: study of the time, temperature and correlated gases emission by a Li-ion cell subject to a thermal abuse in a controlled environmental under precise conditions.

Li-ion cells

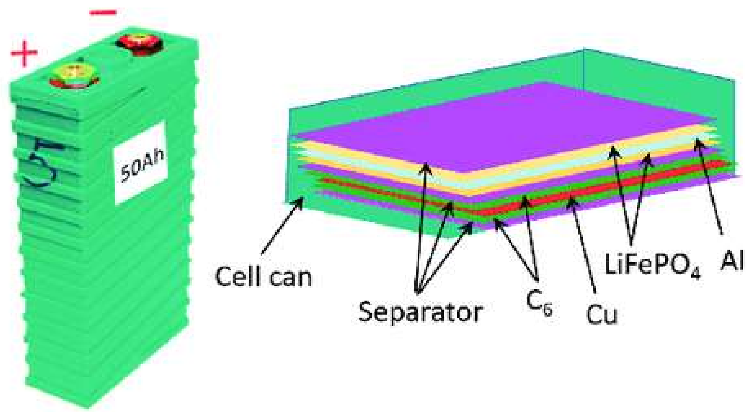
1. General aspect
2. NCR 18650: specification
3. NCR 18650: chemical composition analysis
    1. Anode material
    2. Cathode material
    3. Electrolytic solution

Li-ion cells: general aspect

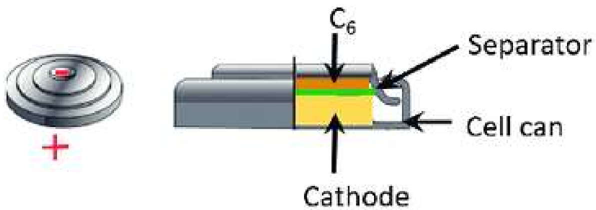
- Similar internal components
- Different shape
- Different chemical composition



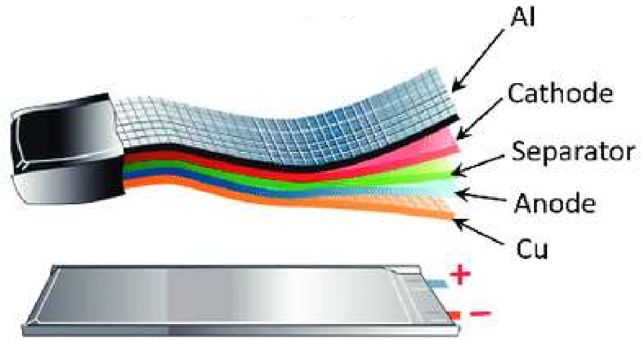
Cylindric



Prismatic



Bottom



Pouch

Li-ion cells: specification

Features & Benefits

- High energy density
- Long stable power and long run time
- Ideal for notebook PCs, boosters, portable devices, etc.

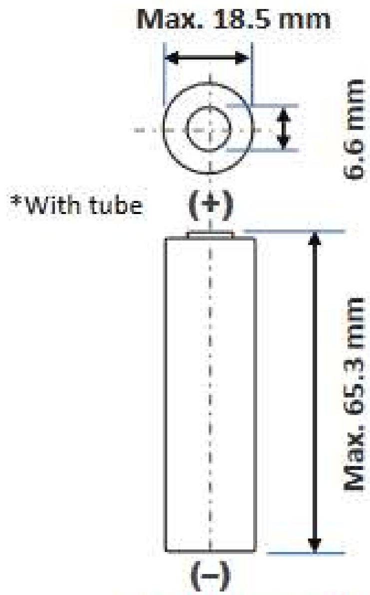
* At temperatures below 10°C, charge at a 0.25C rate.

Specifications

Rated capacity[1]	Min. 3200mAh
Capacity[2]	Min. 3250mAh Typ. 3350mAh
Nominal voltage	3.6V
Charging	CC-CV, Std. 1625mA, 4.20V, 4.0 hrs
Weight (max.)	48.5 g
Temperature	Charge*: 0 to +45°C Discharge: -20 to +60°C Storage: -20 to +50°C
Energy density[3]	Volumetric: 676 Wh/l Gravimetric: 243 Wh/kg

[1] At 20°C [2] At 25°C [3] Energy density based on bare cell dimensions

Dimensions



For Reference Only

The data sheet provides information on capacities, dimensions, and conditions of the safety window (temperature – voltage) but not on the internal chemical composition.

Li-ion cells: chemical composition

XRD method

Philips Analytical PW1830 X-ray diffractometer, equipped with Cu Kα (1.54056 Å) radiation

Range: 2θ range from 15 to 70 with a step size of 0.02° and a time for step of 3.5 s.

Voltage and current: 40 kV and 30 mA

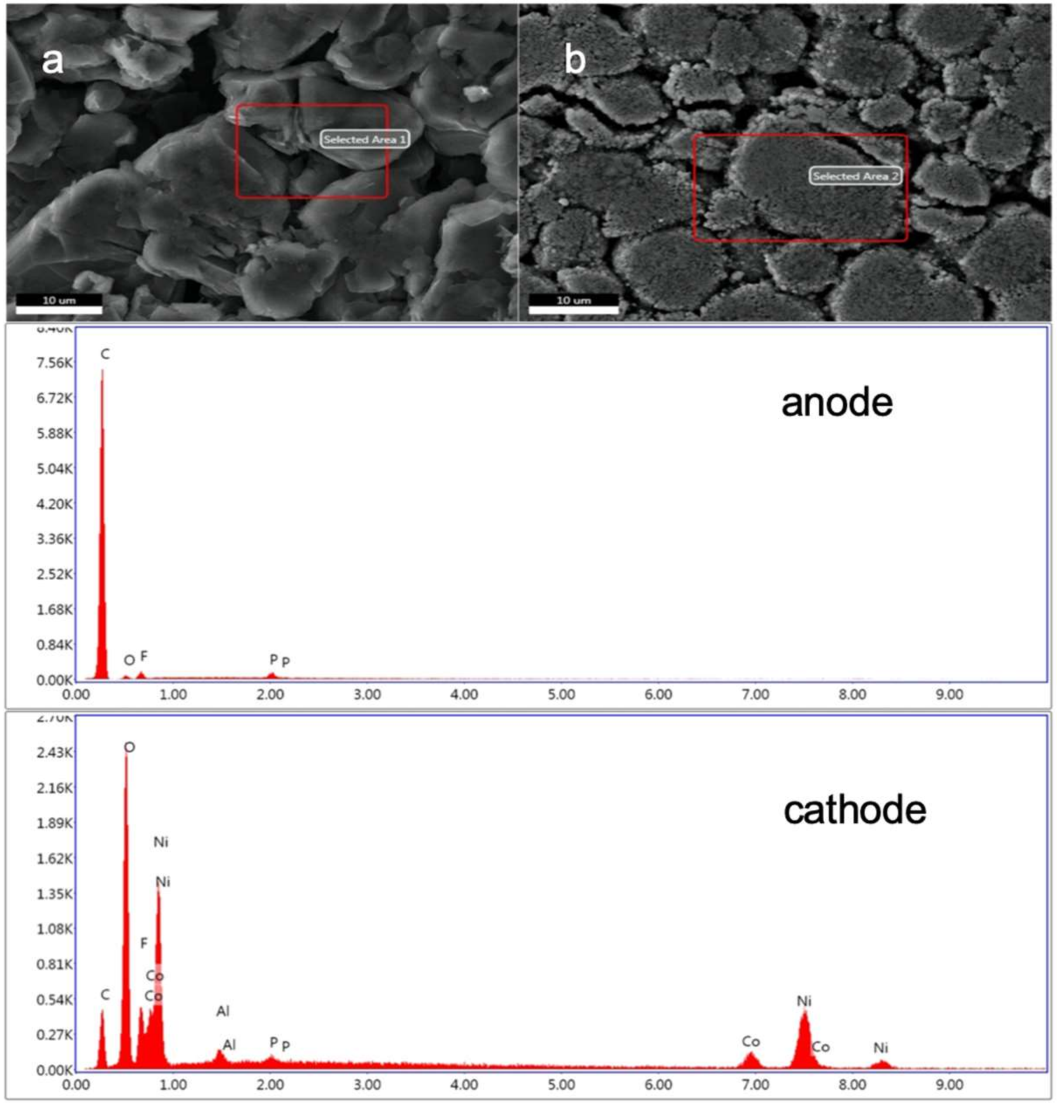
Library: COD (Crystallography Open).

Li-ion cells: chemical composition

Anode: large amount of carbon, it can be said that the graphite particles are homogeneously distributed on the copper collector surface.

Cathode: presence of nickel, cobalt, aluminum and oxygen. The mixed lithium oxide particles are homogeneously distributed on the alumina collector surface.

In both cases traces of fluorine and phosphorus are visible, it can be attributable to the presence of traces of LiF6, the salt usually dissolved in the electrolyte solution.



Li-ion cells: chemical composition

GC-PID method

Perkin Elmer Gas Chromatography coupled with a Photo Ionization Detector (GC-PID).

Column: StabilWax-DA - Restek (30 m x 0.25 mm i.d. x 0.25 μm).

Gas carrier: 1 ml/min of He.

Tinjector: 200° C

Injection: 1,0μl of sample

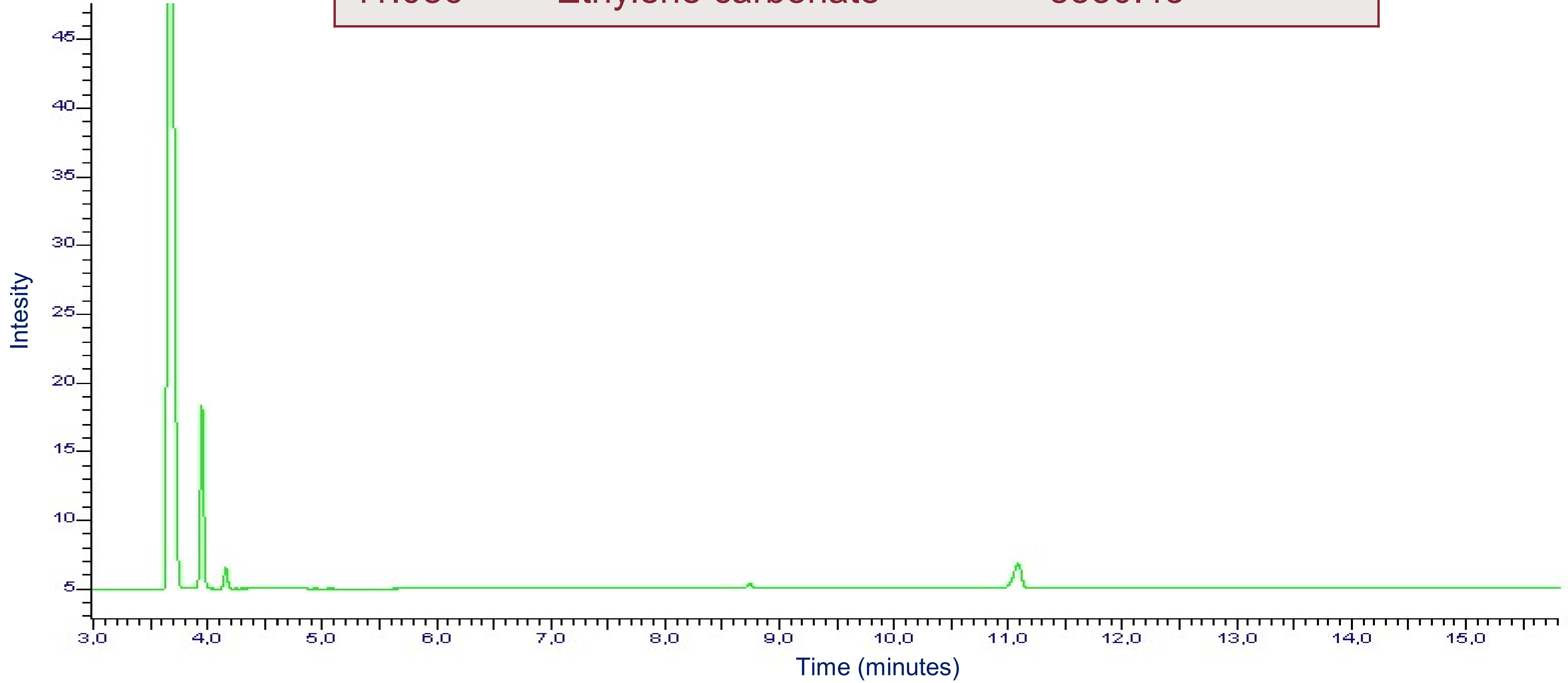
Split: 70:1.

Temperature program: 100° C (2,5 minutes) fino a 200° C (10 minutes) heat rate of 30° C/min.

Tdetector: 270° C.

Li-ion cells: chemical composition

t_R (min)	Compound	Area
3.948	Dimethylcarbonate	27676.93
4.157	Ethylmethyl carbonate	3237.08
11.086	Ethylene carbonate	8530.43



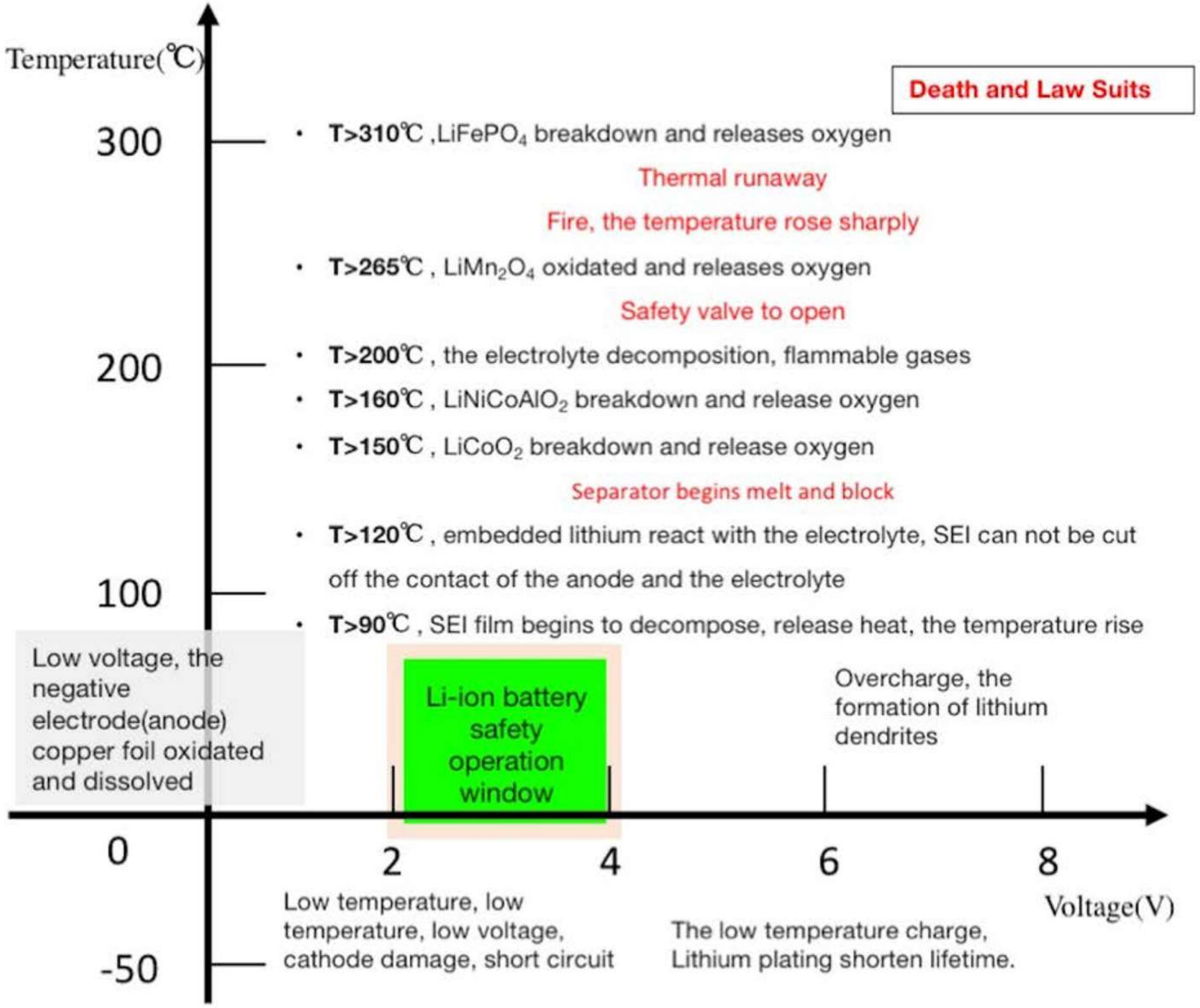
Thermal abuse

1. Abuses: thermal abuse

2. Test system and conditions
    1. Environmental conditions
    2. Maximum temperature
    3. Heat rate
    4. Transfer line
    5. FT-IR parameters

1. Analysis
    1. Temperatures
    2. Gases analysis
    3. Solid analysis

Use and abuse



Lithium Ion Cell Operating Window

Abuse – outside Safety Window

Mechanical

Thermical

Electrical

Use – in Safety Window

Physico-chemical modification

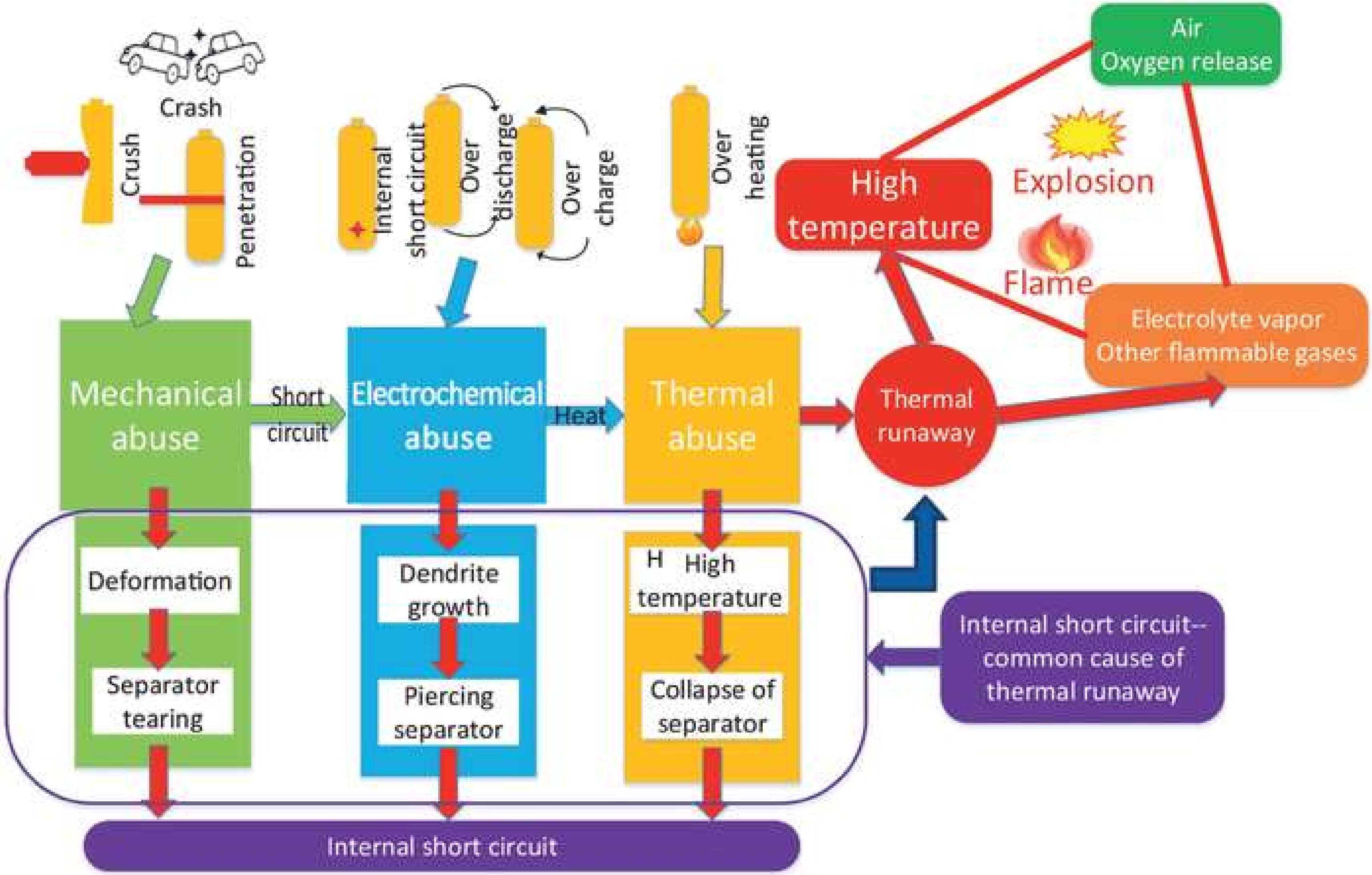
Mechanical:

1.Stress

2. Aging-relevant environmental

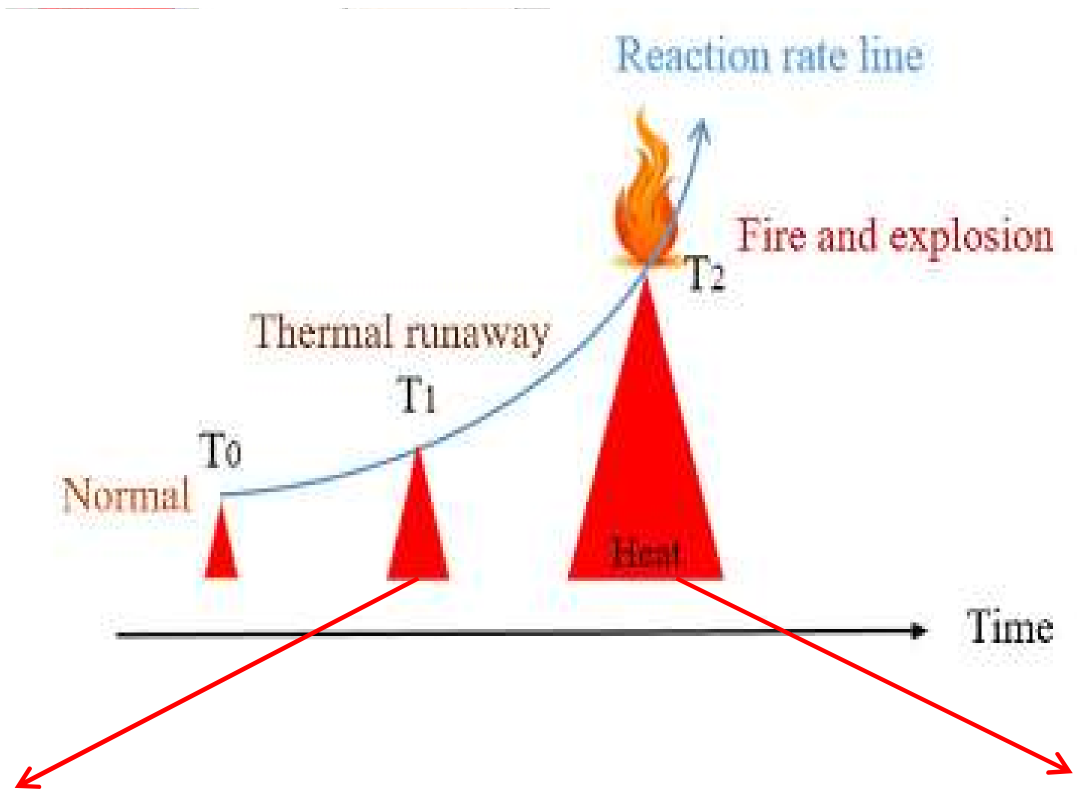
3. Operational condition

Abuses: mechanical, electrical and thermal



Thermal runaway

Once the thermal instability of the lithium-ion battery begins, an **unstoppable chain of exothermic reaction begins**.



The risk of thermal runaway begins at a T of 60° C and becomes extremely critical at 95-100° C.

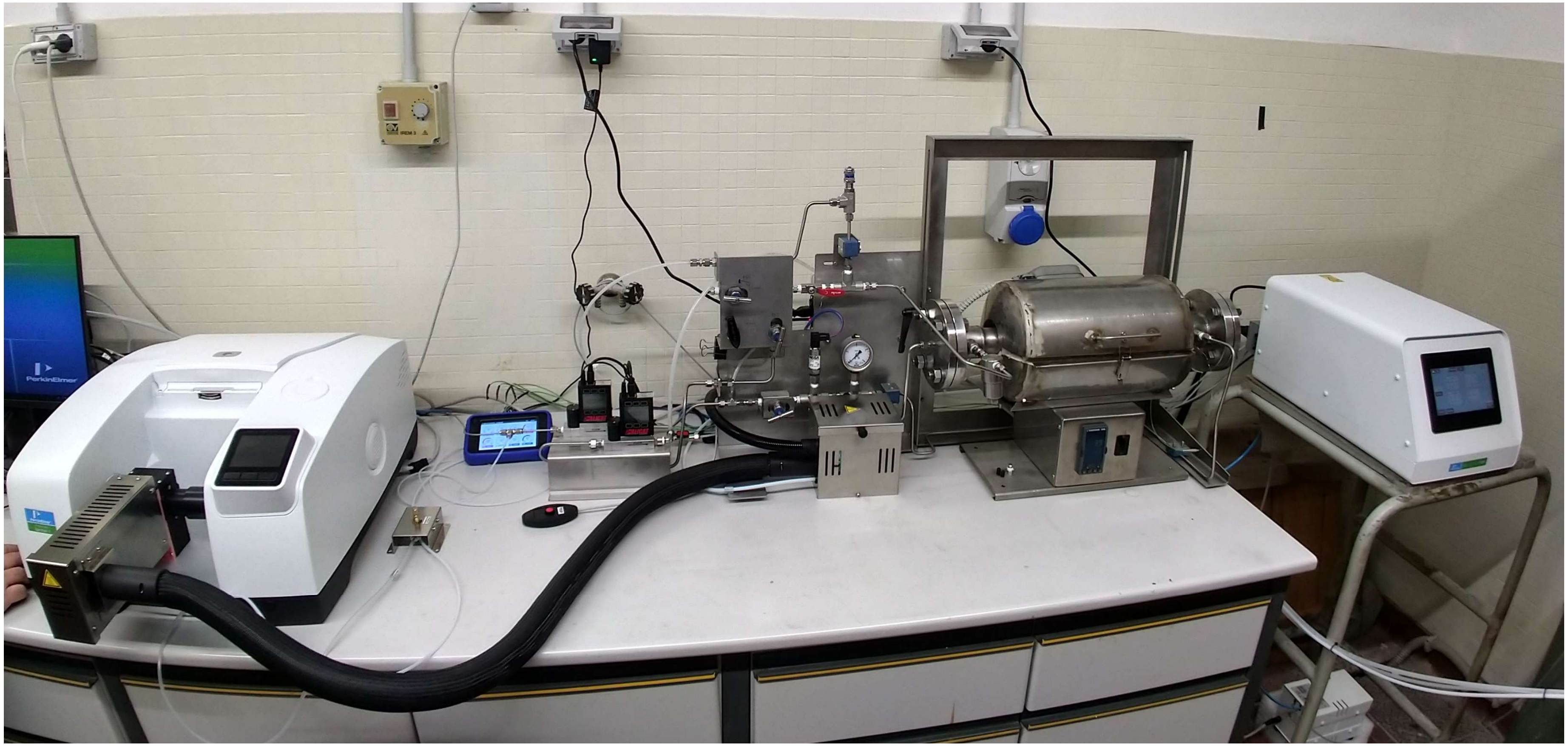
The T rises rapidly in a few seconds and the energy stored in the battery is suddenly released. In this way, T up to 400° C are generated and a fire breaks out which is difficult to extinguish with conventional agents.

Test system: reactor ⟶ transfer line ⟶ FT-IR

Reactor: pressure and temperature tight analysis chamber. From 1 to 3 18650 cells.

Transfer line: connection line between the reactor and the FT-IR analysis gas cell.

FT-IR: analytical technique of interaction between an IR electromagnetic radiation and matter.



Test system and conditions

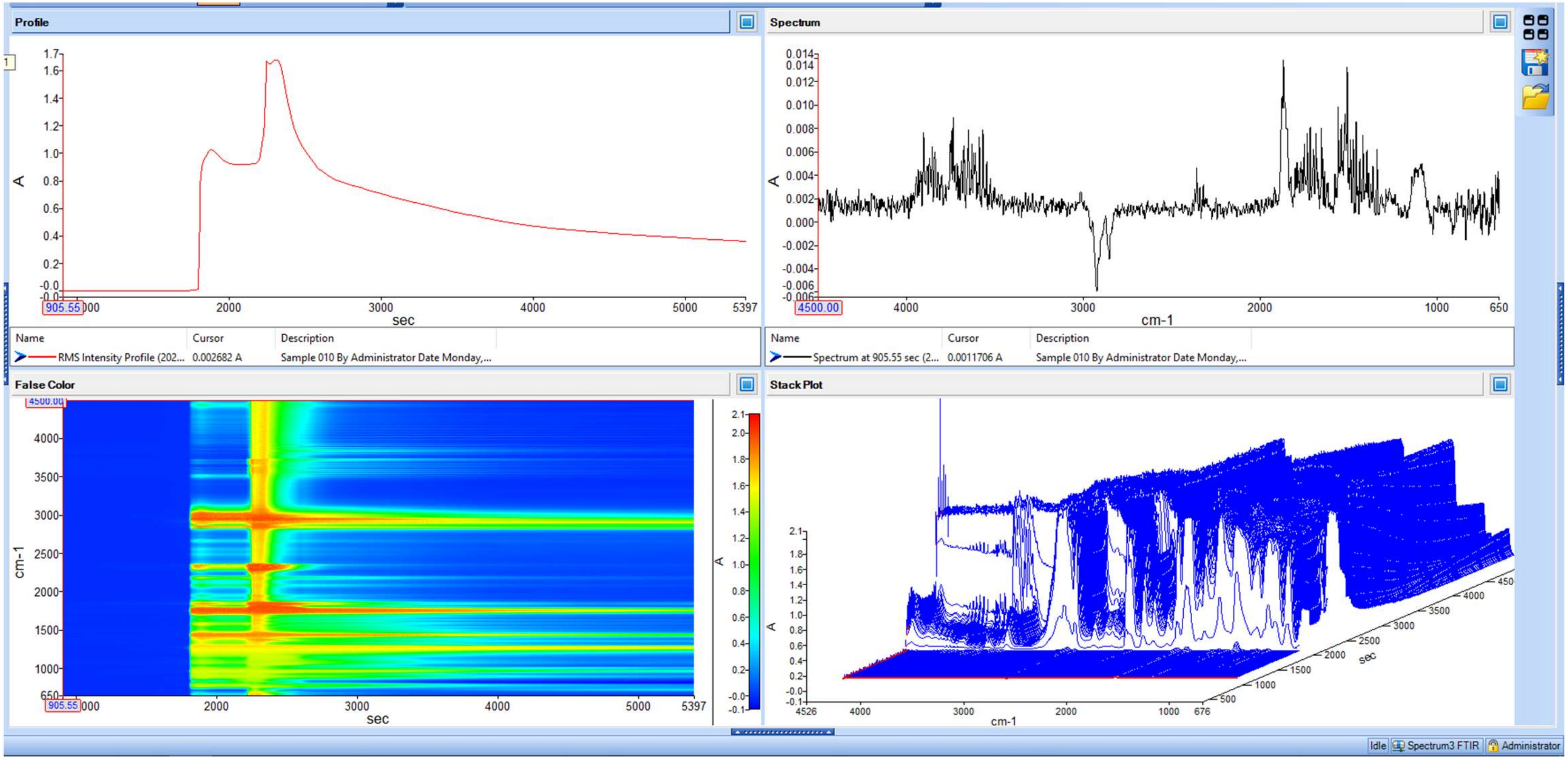
1. Temperature
   1. Thermocouples in reactor: placed both on the cell surface and in the reaction chamber to monitor temperatures.

2. Flow
   1. IN mass flow controller: flow rate of the inlet to the chamber.
   2. OUT mass flow controller: flow rate out of the chamber.
   3. Pump linked to transferline: flow rate to the gas cell.

3. Transferline
   1. Temperature filter units: 180° C
   2. Temperature transfer line: 180° C

4. FT-IR
   1. Number of scans: 8
   2. Resolution: 4cm-1
   3. Detector: MCT
   4. Time of acquisition: in continuous (Time Base)

Time Base: spectra in real time

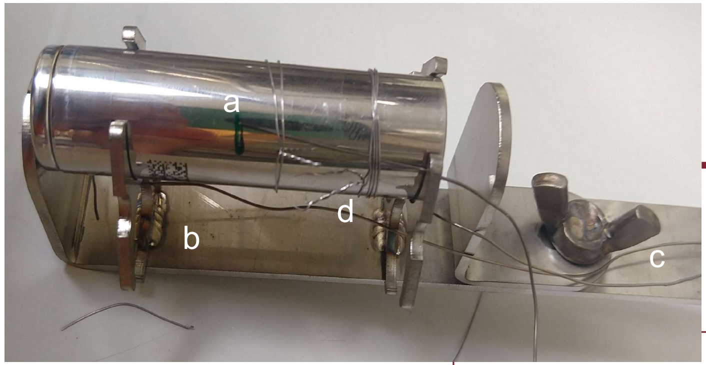


Analysis

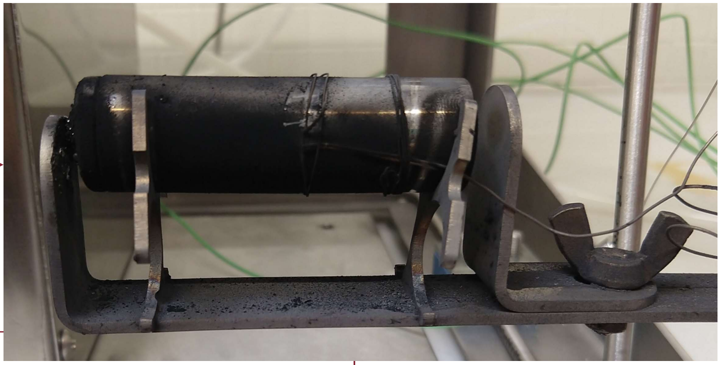
1. Thermal runaway temperature
    1. Oven controller
    2. Thermocouples on cell surface

2. Gas analysis
    1. Gas cell for FT-IR analysis

Overview of the results

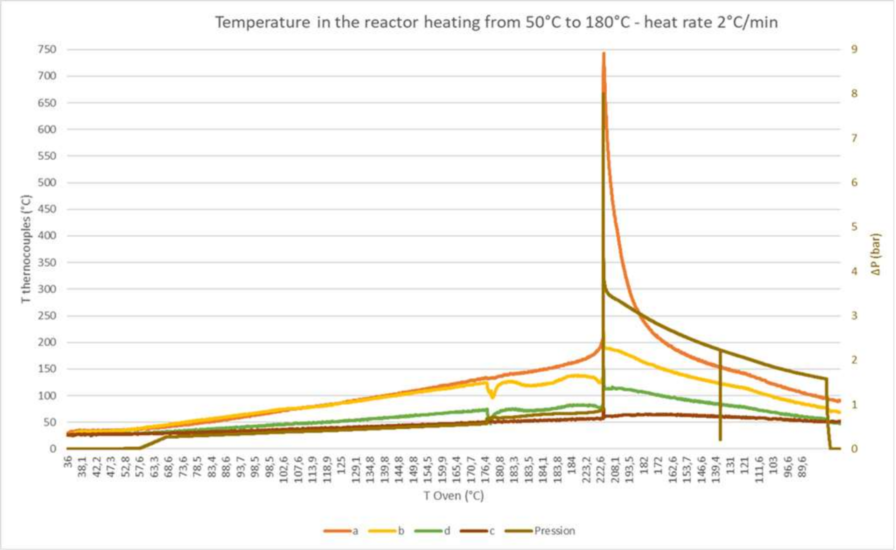


Heating

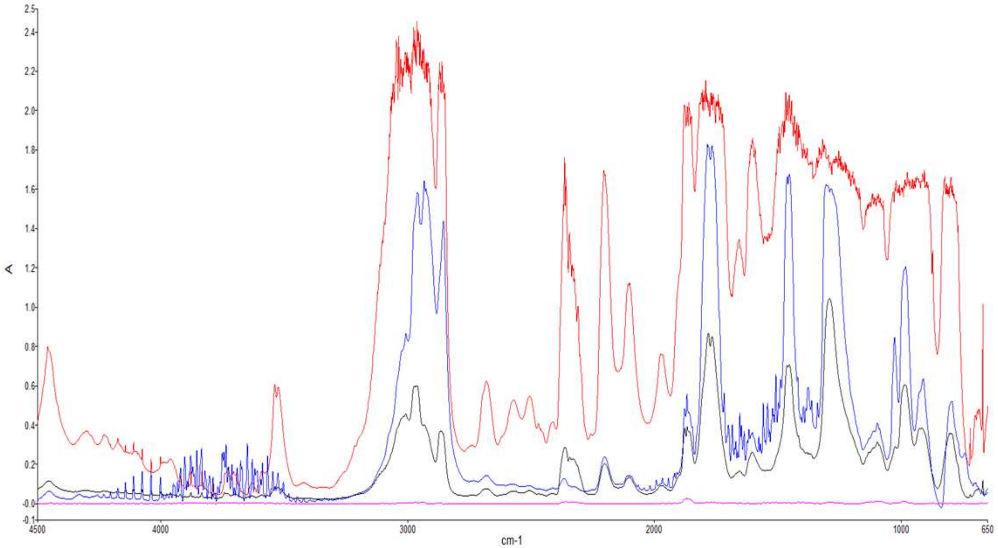


Thermal runaway process

Gas analysis

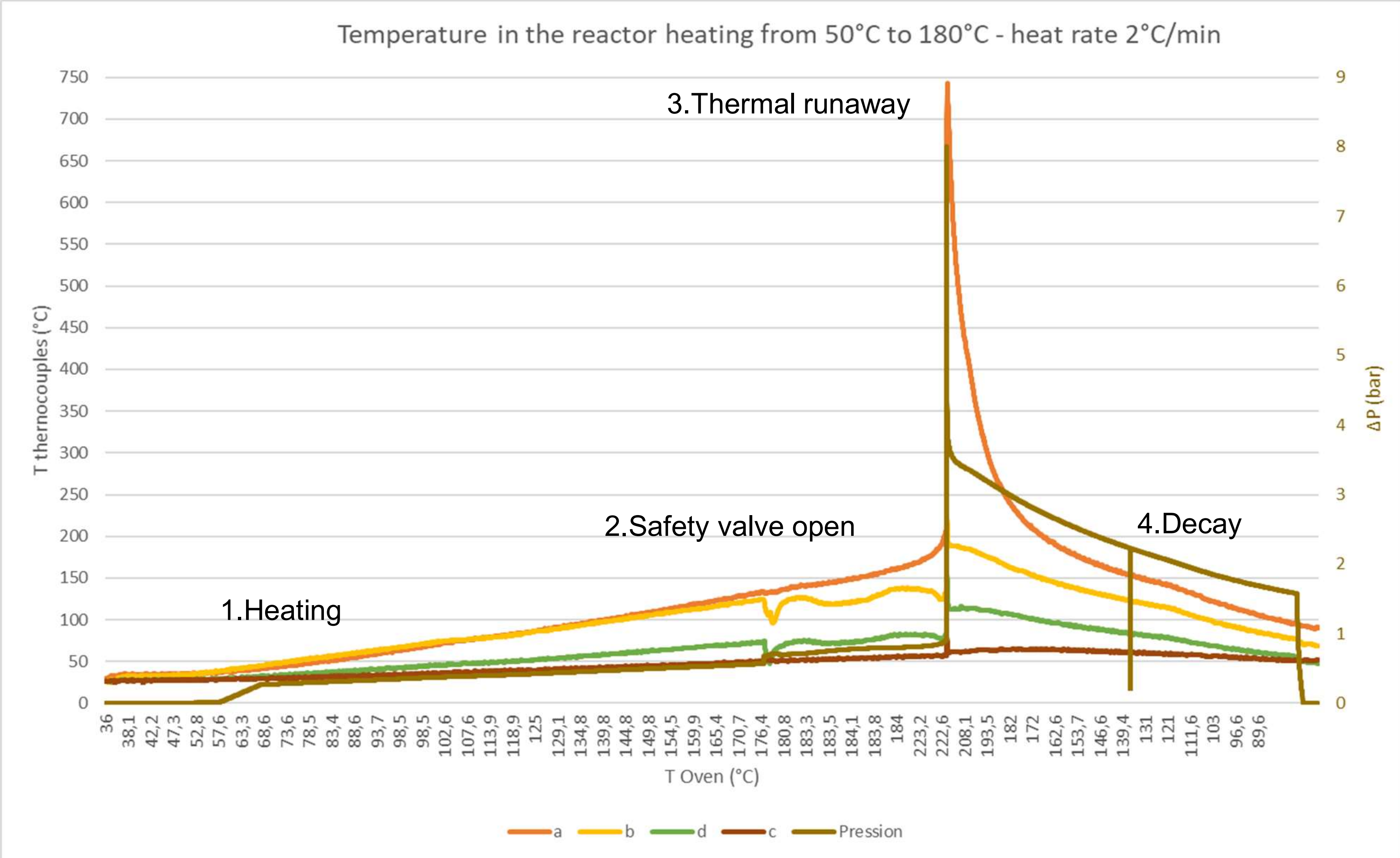


1.Heating 2.Safety valve open 3.Thermal runaway 4.Decay

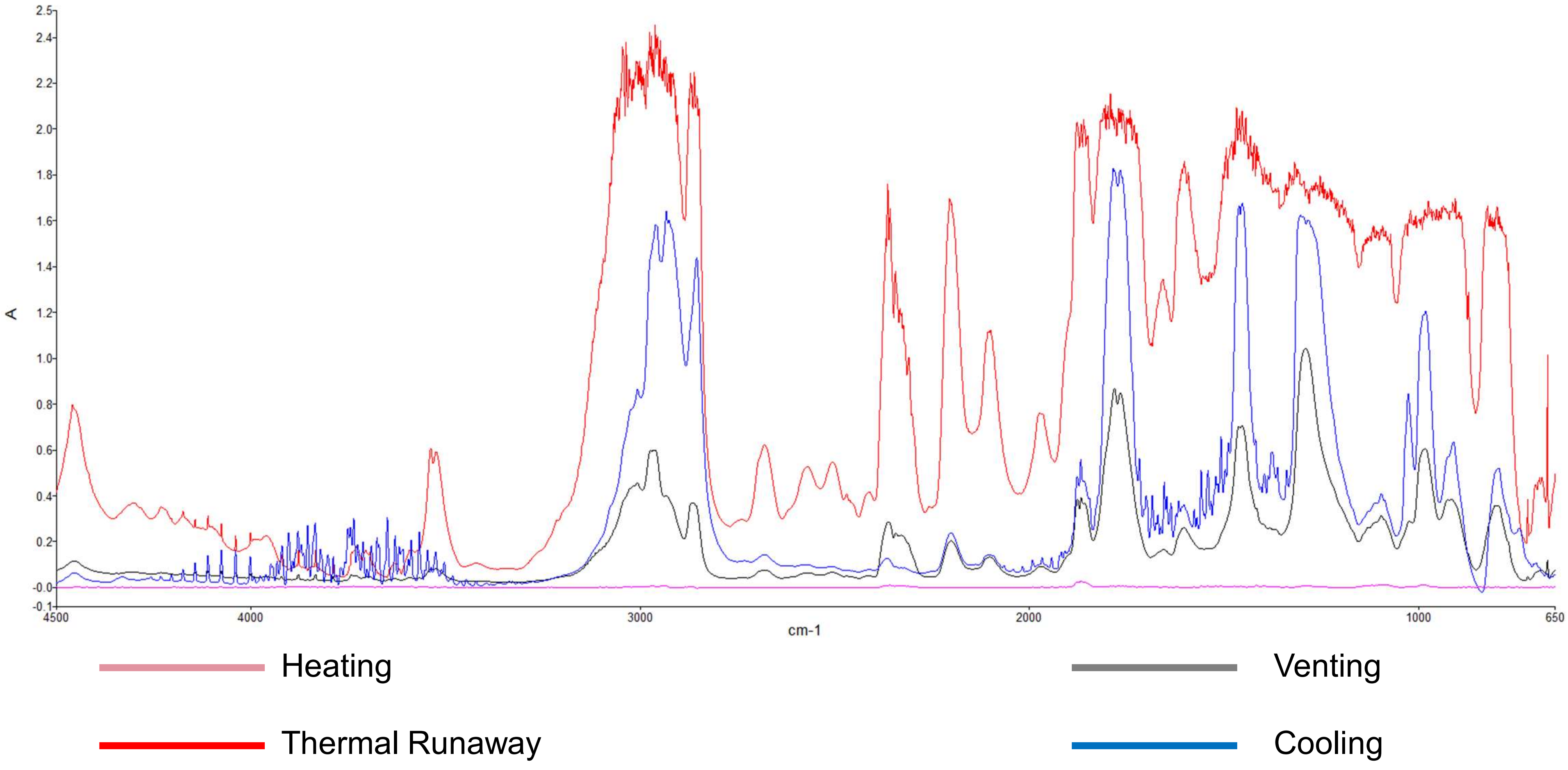


CO CO_2 HCl HPO_3 HF C_2H_4 CH_4

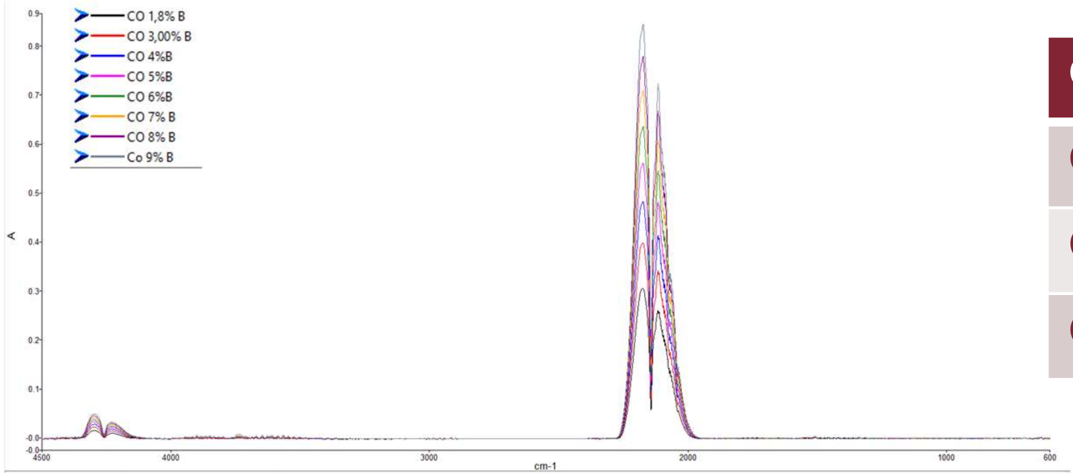
Thermal runaway: temperature



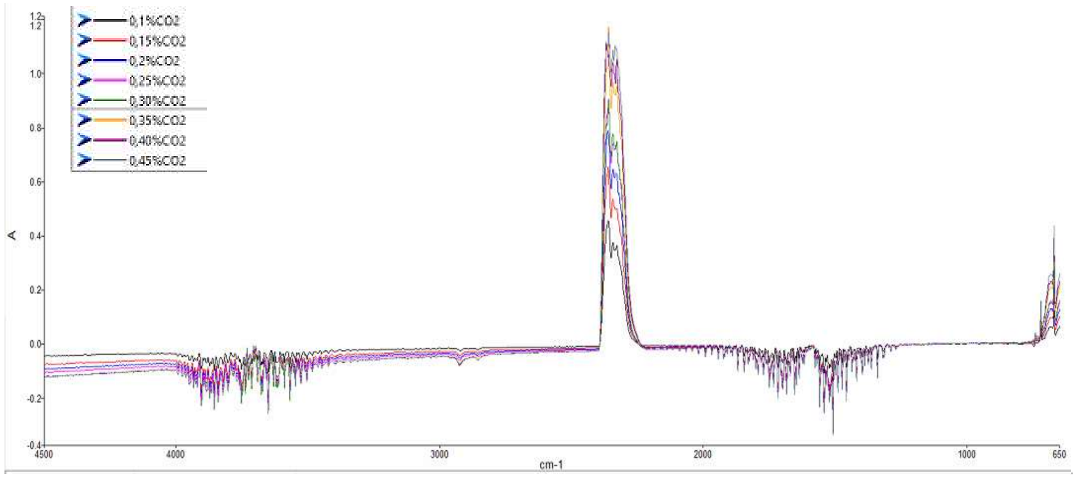
Evolution of gases in relation to temperature

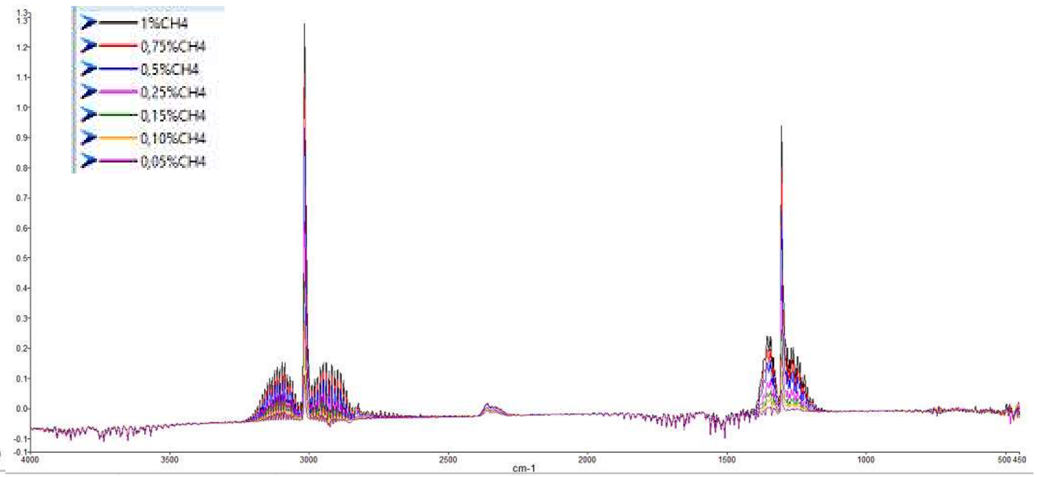


Gases calibration: CO, CO_2, and CH_4



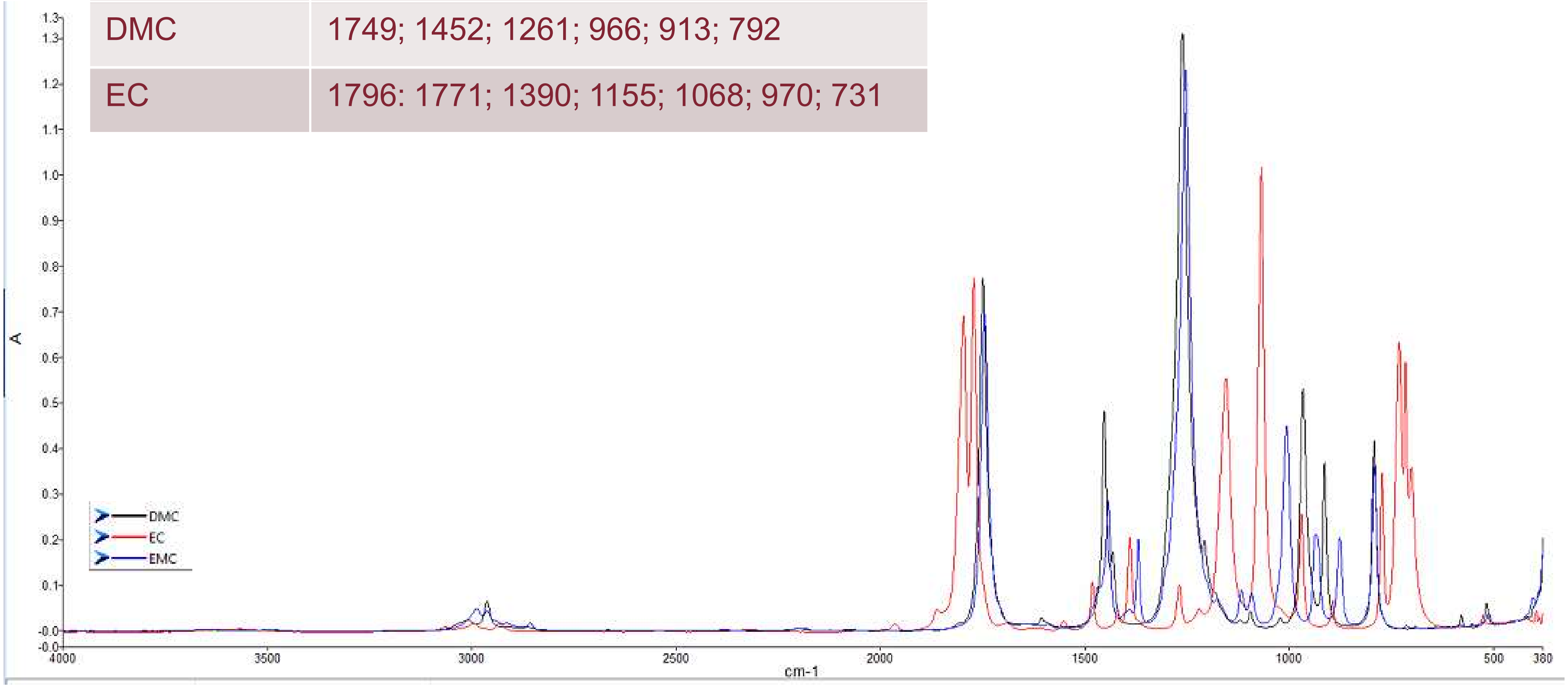
Gases	Wave number (cm-1)	Calibration range
CO	2176; 2114	1,8% - 9%
CO_2	2363; 2344	0,1% – 0,25%
CH_4	3016	0,05% - 0,25%





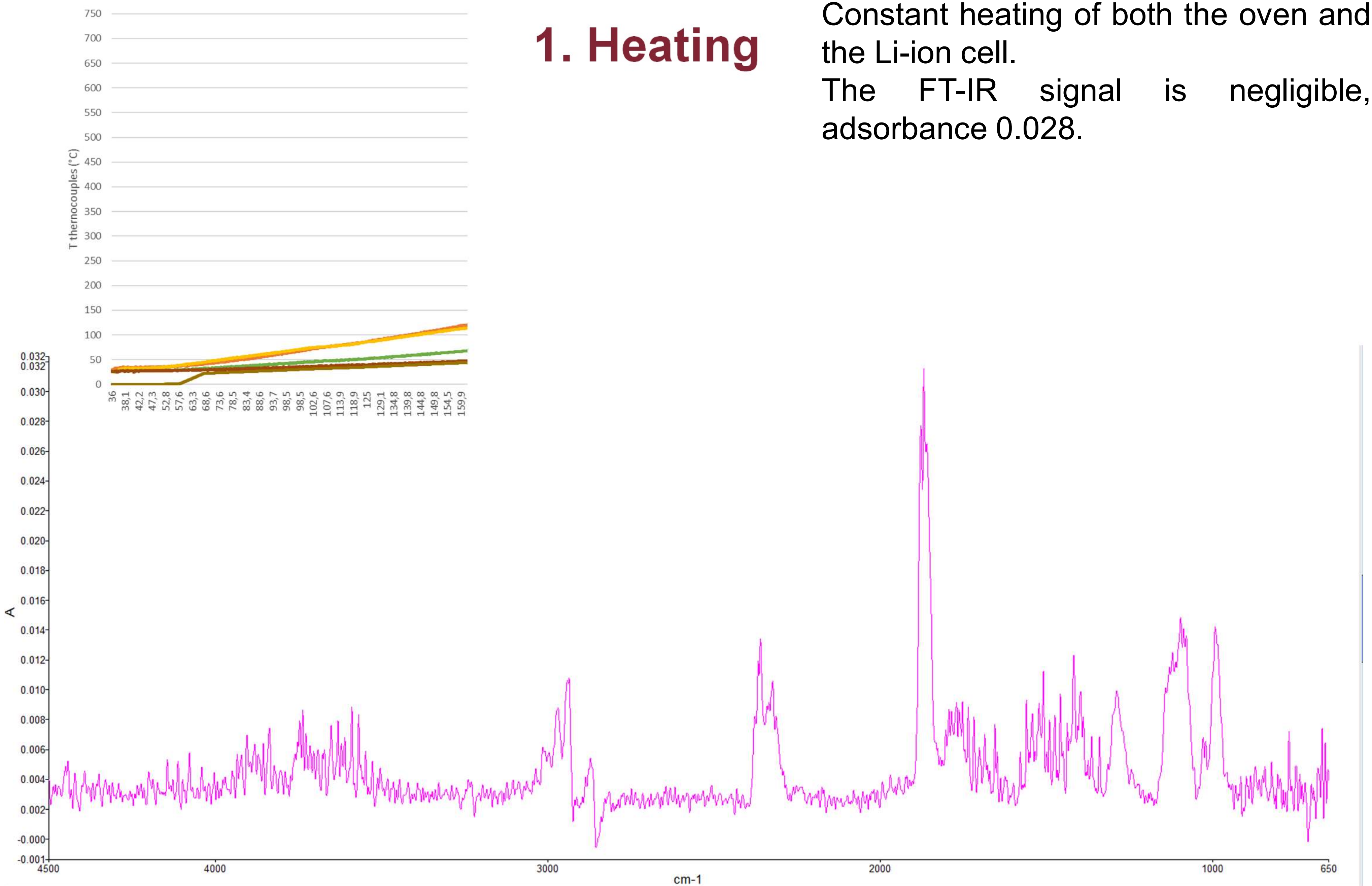
Other gases: electrolytic solution

Gases	Wave number (cm-1)
EMC	1745; 1442; 1253; 1006; 791
DMC	1749; 1452; 1261; 966; 913; 792
EC	1796: 1771; 1390; 1155; 1068; 970; 731



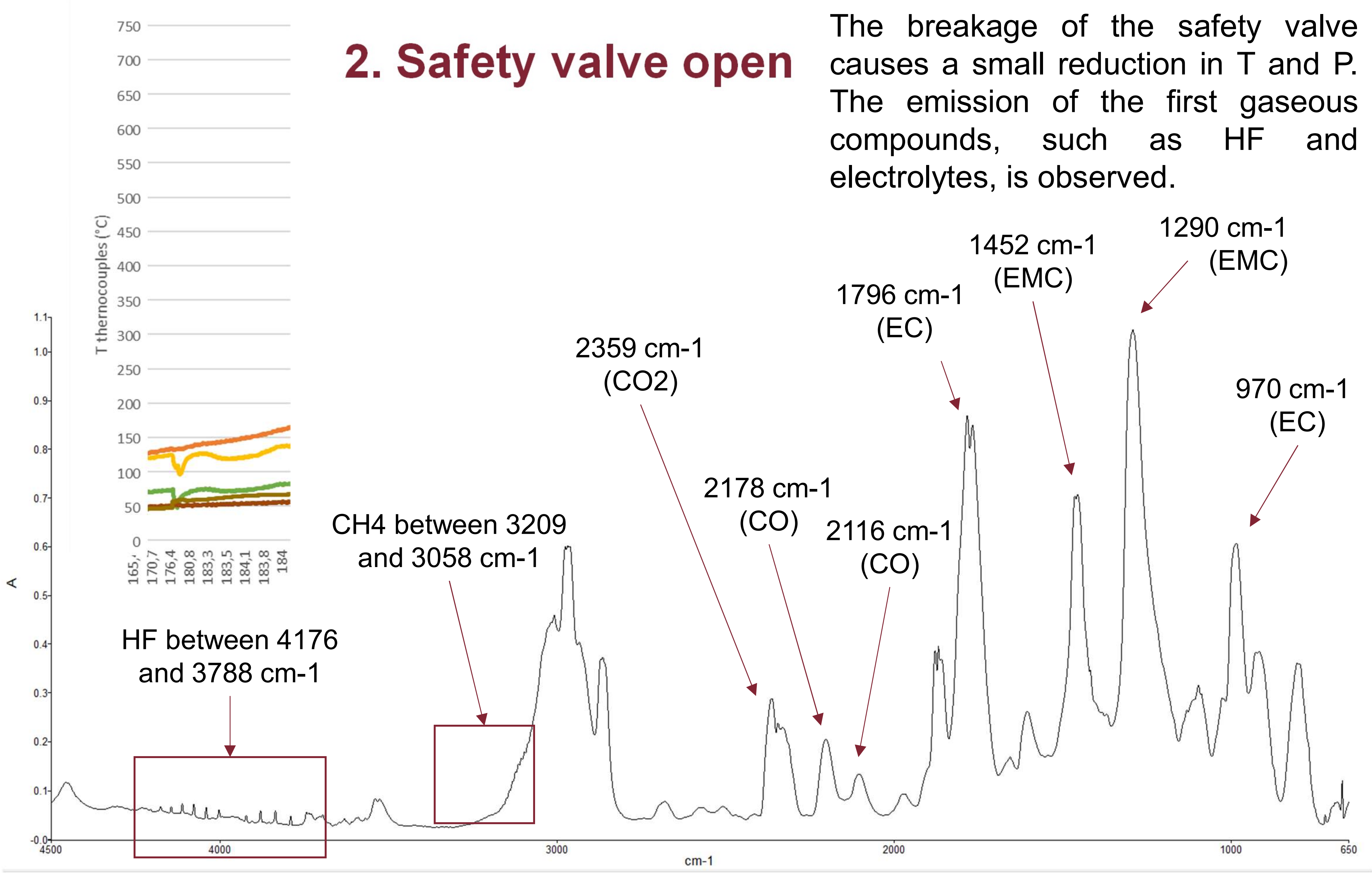
1. Heating

Constant heating of both the oven and the Li-ion cell.
The FT-IR signal is negligible, adsorbance 0.028.



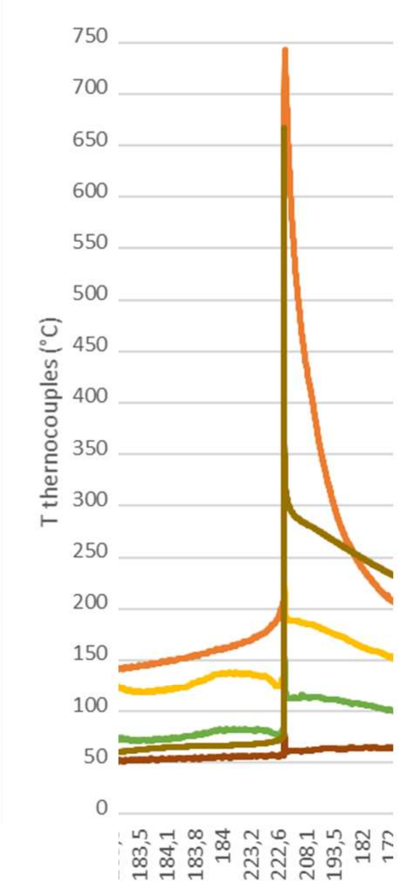
2. Safety valve open

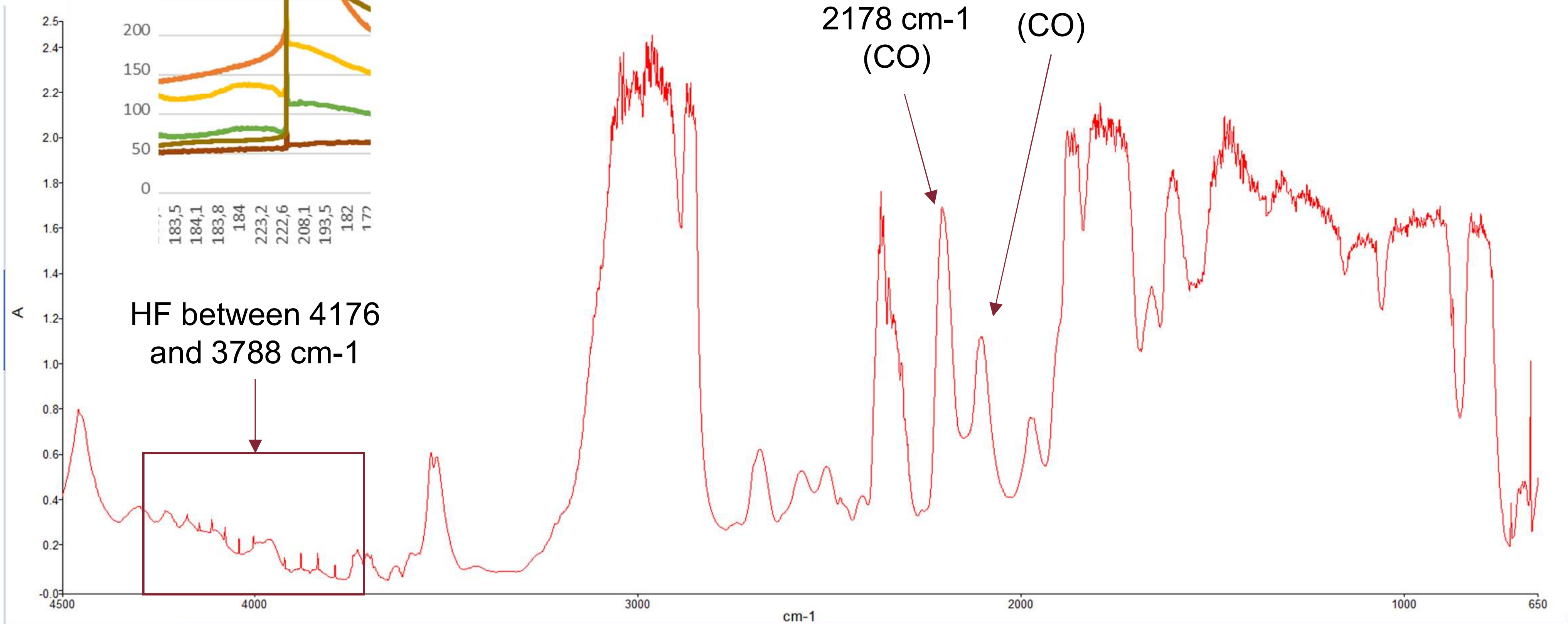
The breakage of the safety valve causes a small reduction in T and P. The emission of the first gaseous compounds, such as HF and electrolytes, is observed.



3. Thermal runaway

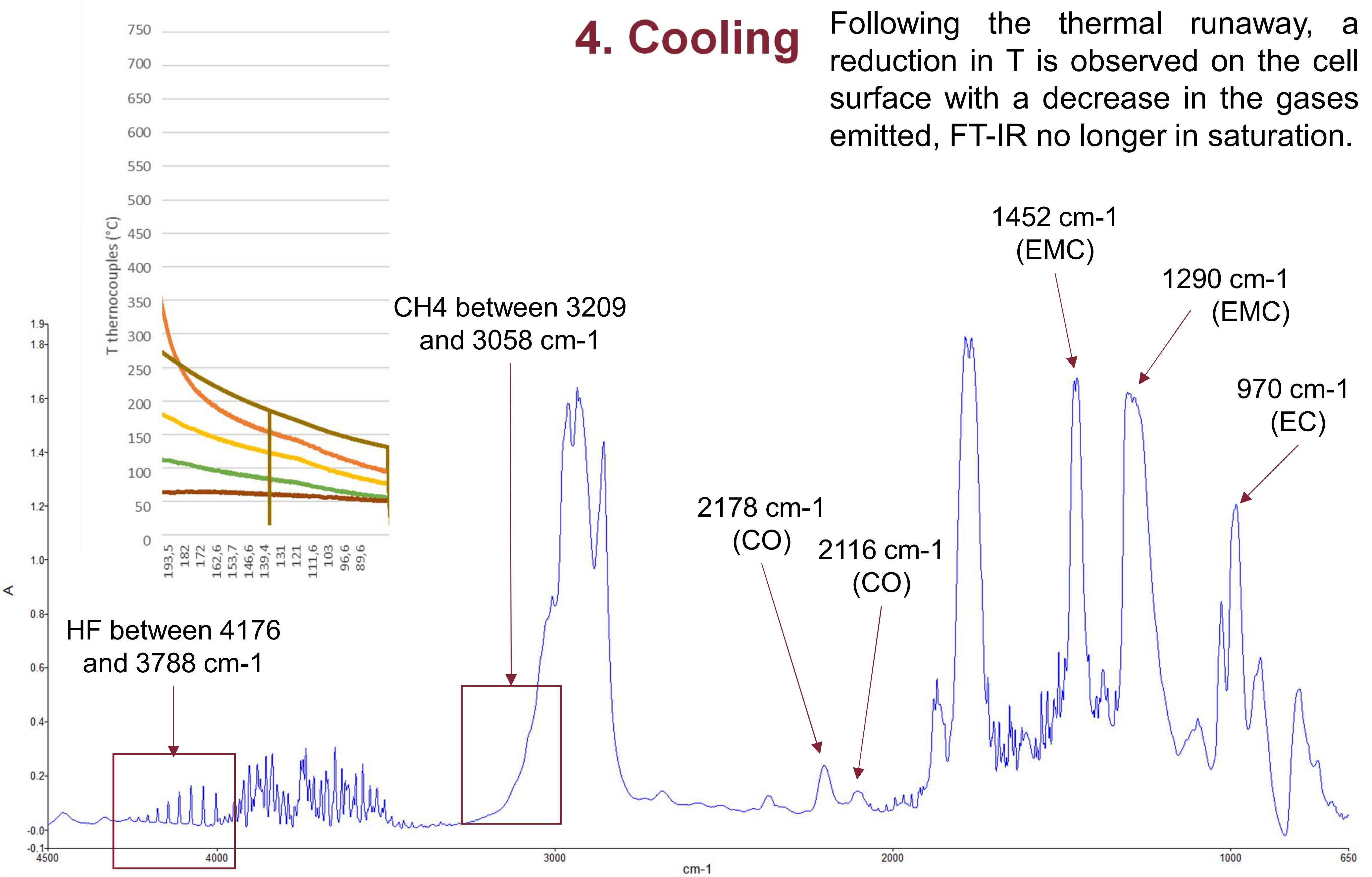
The continuous heating leads to the thermal runaway, with a max T on the cell surface of 750° C. Due to the high quantity of gases emitted, the FT-IR spectrum results in saturation for many cm-1, A>1.5, However, it is possible to identify some compounds.



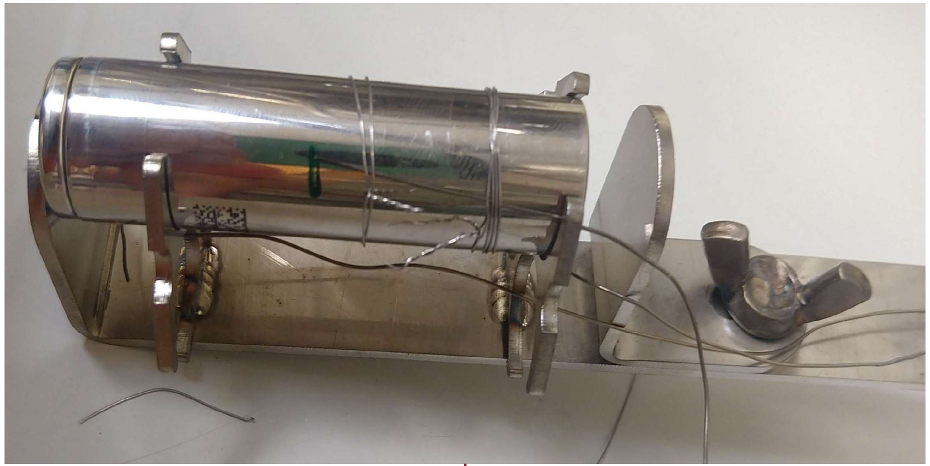


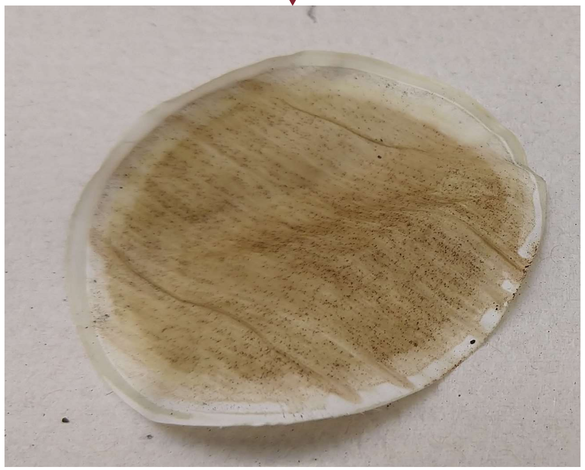
4. Cooling

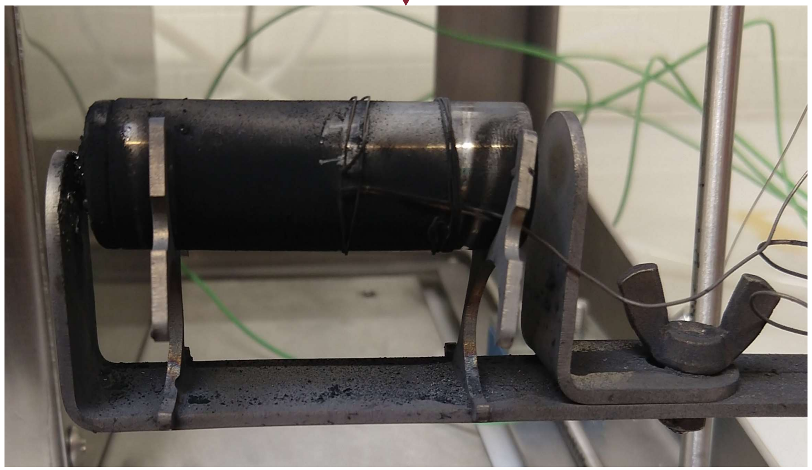
Following the thermal runaway, a reduction in T is observed on the cell surface with a decrease in the gases emitted, FT-IR no longer in saturation.



Future analysis: solid residue







Thank you for your attention