High Pressure TGA
Technology and Application Examples

TA Instruments UK – 2018 Materials Characterisation Seminar
Weybridge

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Outline

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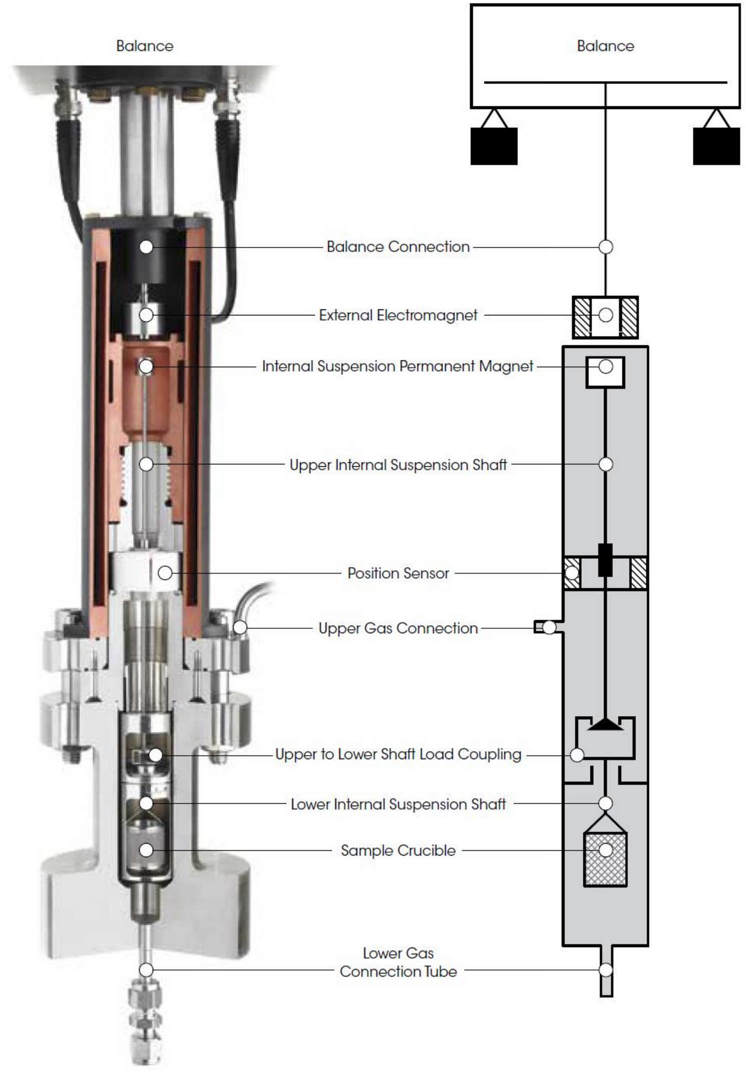
2	NEW MAGNETIC LEVITATION BALANCE	▪ Motivation for a new HP-TGA design ▪ Working principle, features
3	NEW DISCOVERY HP-TGA	▪ Setup and functional parts ▪ Specifications
4	APPLICATION EXAMPLES	▪ Influence of pressure on TGA ▪ Comparisons of TGA at ambient and elevated pressure
5	CONCLUSION	▪ Summary

TA

Principle of the Magnetic Suspension Balance

Weighing under extreme conditions



- Sample in reaction chamber connected to external balance by magnetic coupling
- Measuring sample weight in vacuum, at high pressures and temperatures, in corrosive atmospheres and vapors

- Based on research since the 1940s in the US and Germany
- Commercial instruments by Rubotherm since 1990

- Main application area: gravimetric sorption analysis – measuring gas sorption on porous particles for gas separation and storage (CO_2, H_2, CH_4).
- High pressure TGA

Company History

Rubotherm is part of TA Instruments

- Rubotherm was founded 1990 as spin-off of the Thermodynamics Department at Ruhr-University Bochum, Germany
- Key technology: Magnetic Suspension Balance instruments for thermogravimetric measurements under extreme conditions (high temperature, high pressure, vapor, corrosive atmospheres)
- Collaboration with universities and research organizations

- Main markets: Europe, Asia, North America
- Acquisition of Rubotherm by TA Instruments effective September 2016
- All operations in Germany: R&D, laboratory, and product management in Bochum, manufacturing facilities in Hüllhorst

Motivation for a new HP TGA design

Simplify operation of high pressure TGA

RUBOTHERM Series DynTHERM TGA

HP-TGA: 1100°C – 40 bar

Large custom made experimental installations

Unique specifications: high pressures, vapor, reaction gases

Drawbacks: size, price, sample handling, data analysis

Features for a new advanced instrument design

Benchtop HP-TGA

Compatible with high pressures, vapor, reaction gases

Small sample size

High balance resolution

Easy operation, Standard data analysis software

TGA 5500

High performance benchtop TGA

Autosampler

Easy operation

Sophisticated data analysis software

Magnetic Levitation Balance

Inventor of the Patented New Working Principle

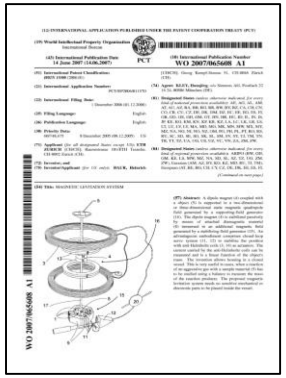
Patent for a new Magnetic Levitation Balance

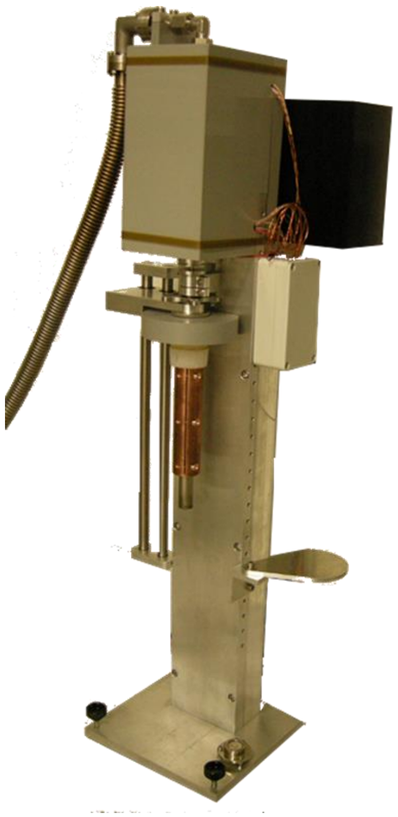
Dr. Heinrich Baur,

ETH Zürich, Institute of Geochemistry

High resolution balance for research on extraterrestial particles.

Commercial instrument by Rubotherm – TA





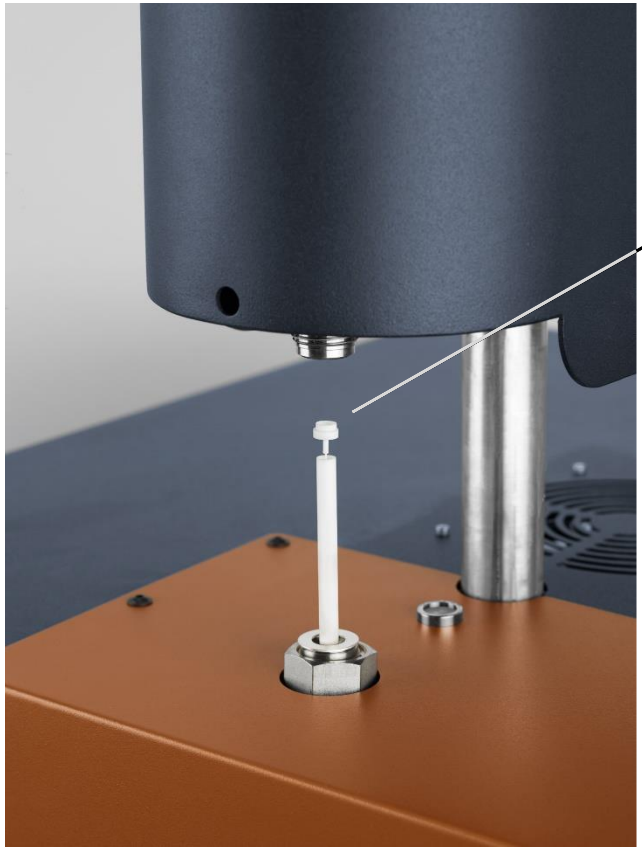
HP-TGA 750

Commercial instrument by Rubotherm – TA

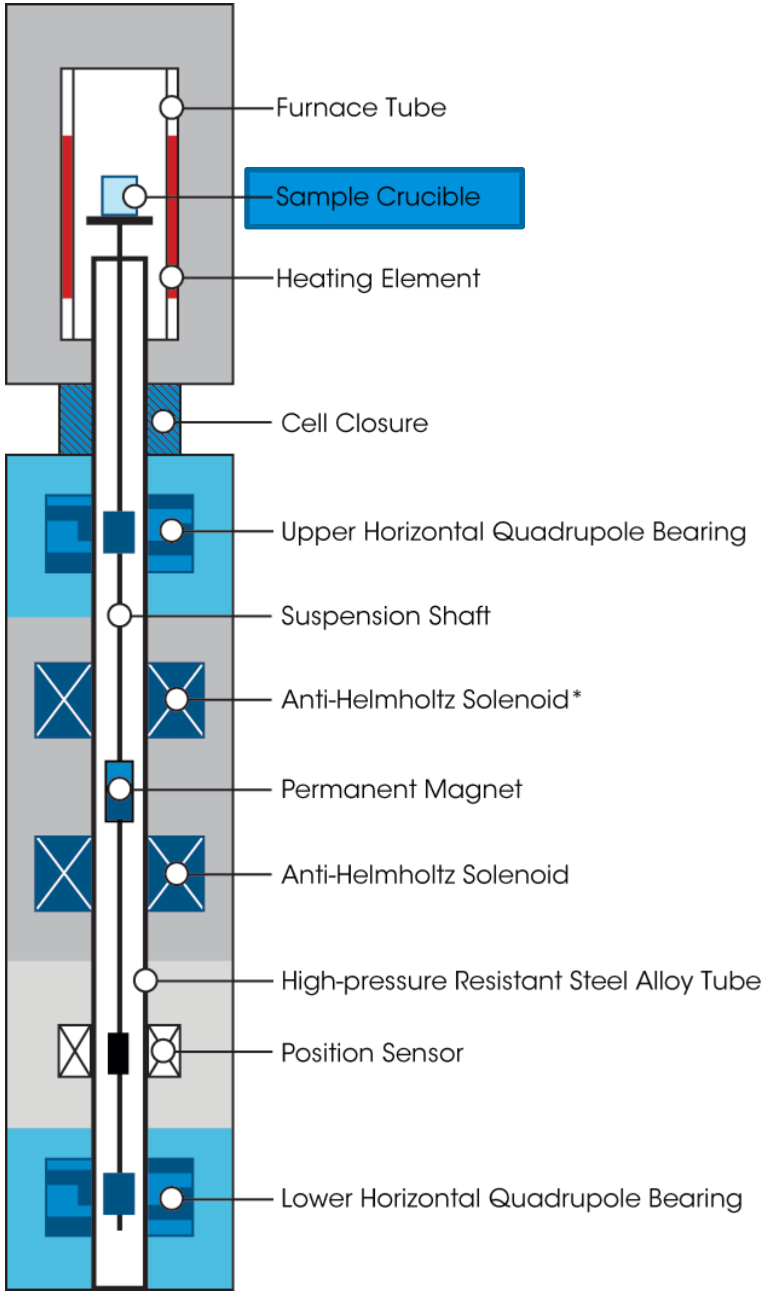
Top loading high pressure TGA based on a Magnetic Levitation Balance

New Magnetic Levitation Balance

Working Principle & Setup



Sample crucible
(top-loading)



New Magnetic Levitation Balance

Working Principle & Setup

Sample crucible located on suspension shaft with permanent magnet

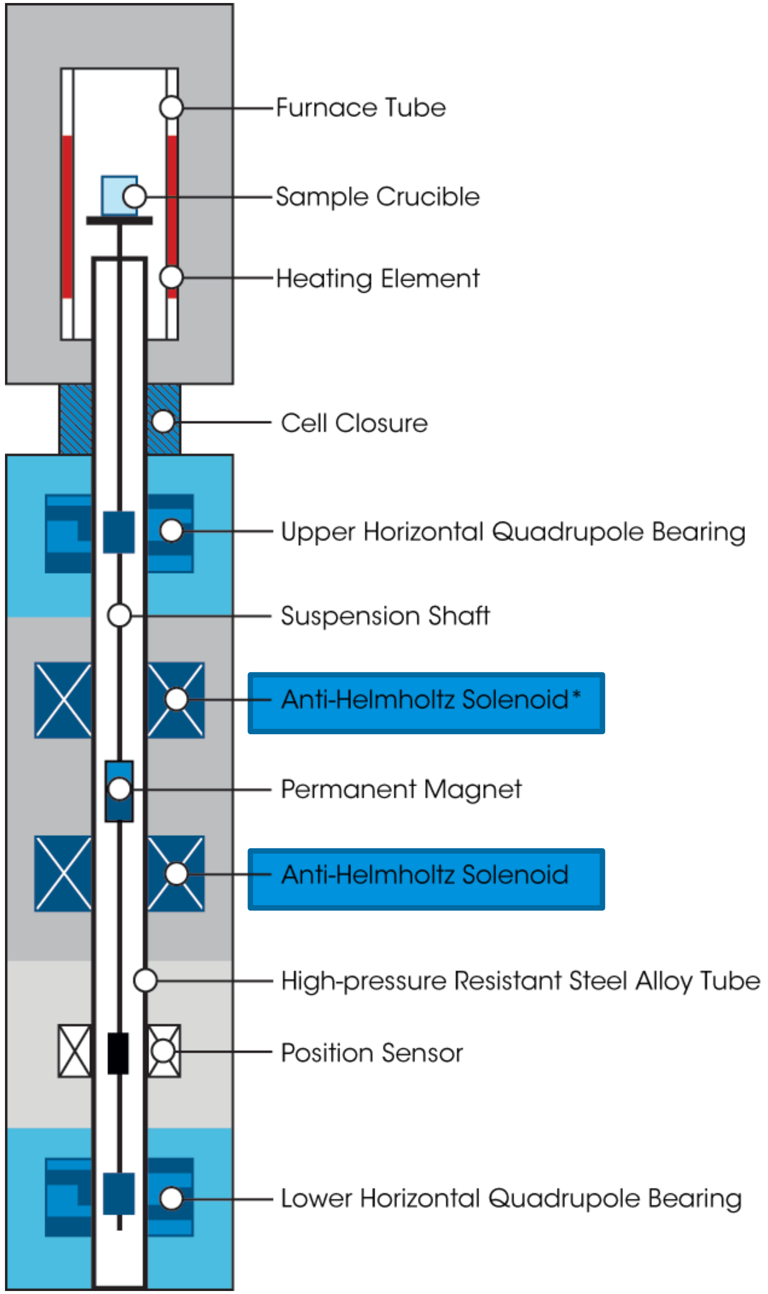
Suspension shaft positioned in small diameter steel tube

Electromagnetic field created by solenoids levitates permanent magnet, suspension shaft and sample crucible.

Current applied to solenoids is proportional to levitated mass.

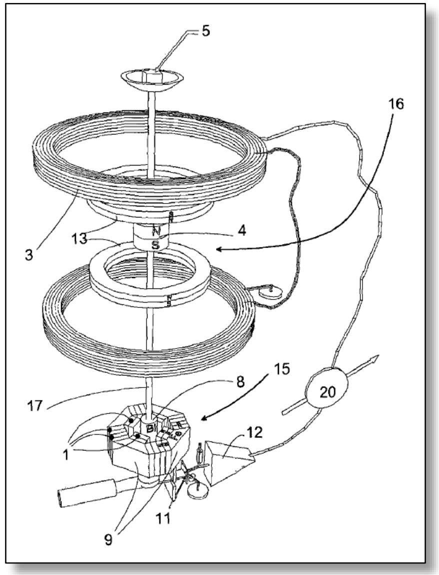
All electronic parts are located outside of the steel tube at ambient pressure and not in contact with the reaction atmosphere:
Separation of sample and balance electronics

Minimized internal volume: flexible and safe operation under pressure



New Magnetic Levitation Balance

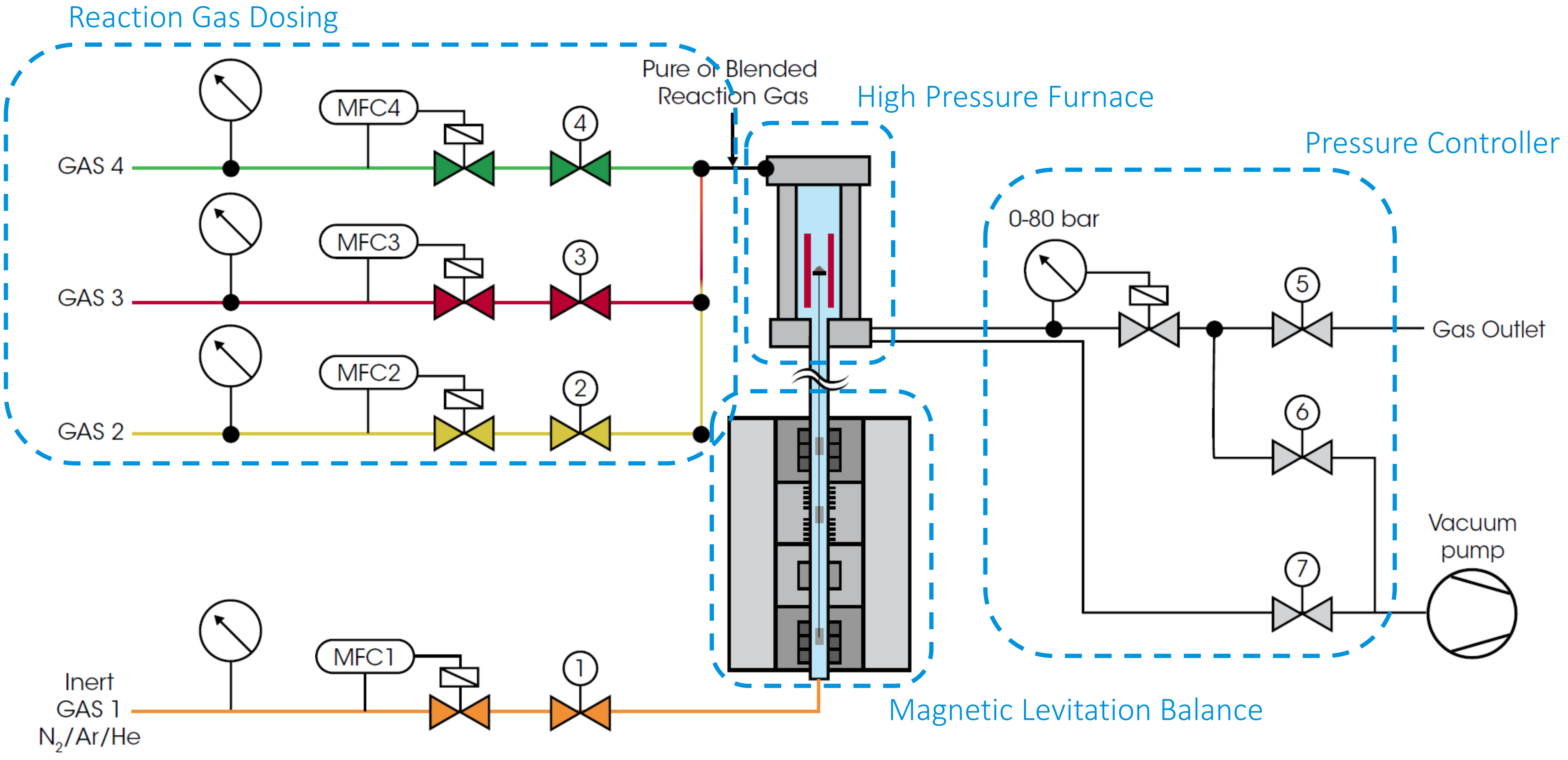
Unique Features



1	HIGHEST RESOLUTION	▪ Higher resolution than all other HP-TGA ▪ Perfect for low mass (change) samples & fast kinetics
2	ACCURATE BALANCE T-CONTROL	▪ Minimized drift – excellent base line stability ▪ Highest reproducibility
3	SMALL INTERNAL VOLUME	▪ High pressure and vacuum capable, safe ▪ Quick & clean gas changing, low gas consumption
4	CORROSION RESISTANT	▪ Can perform TGA with application relevant gases ▪ Extensive list of gases to select from in the software

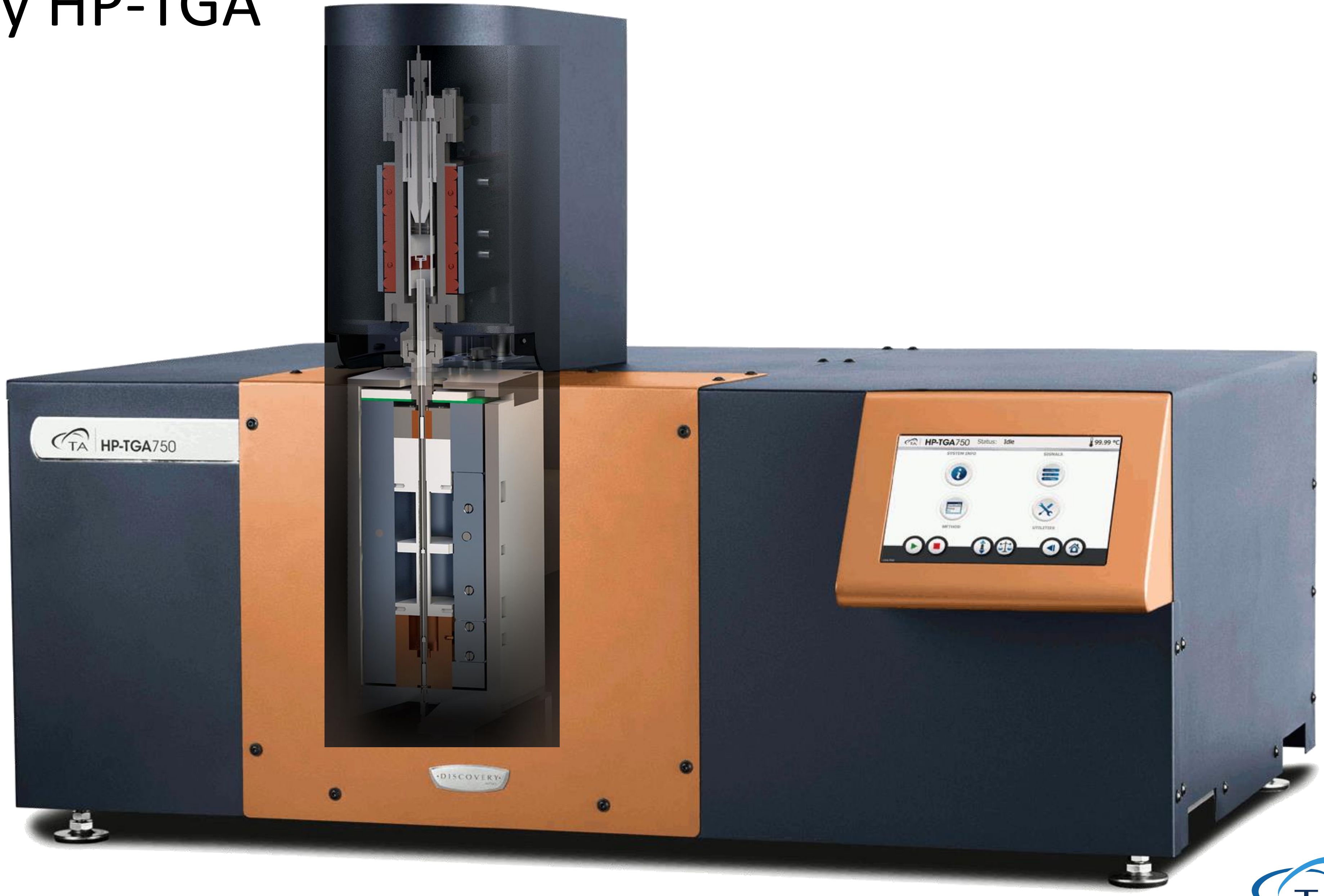
New Discovery HP-TGA

Functional Parts



New Discovery HP-TGA

Setup



New Discovery HP-TGA

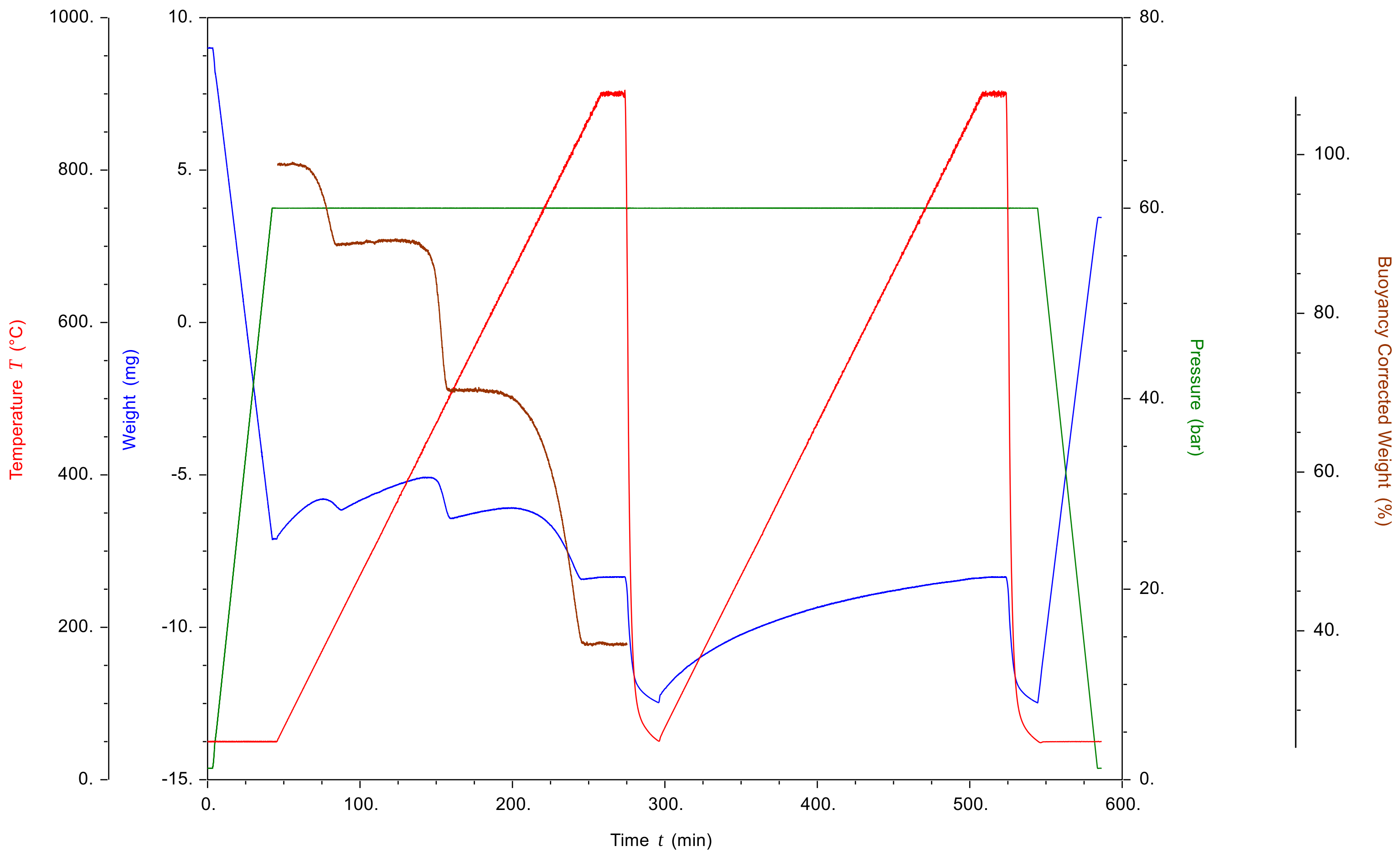
Specifications

Magnetic Levitation Balance	1	0.1 µg weighing resolution 500 mg weighing range / sample mass
High Pressure Furnace	2	Up to 1100°C, 250 °C/min heating and cooling rate Integrated Curie-Point T-calibration
Gas Dosing & Pressure Controller	3	3 reaction gas MFC for gas switching and blending Vacuum…80 bar, EGA sampling for QMS

TGA at elevated pressures: Buoyancy

Increasing pressure: density of reaction atmosphere is affecting weight signal

Calciumoxalate, 4 K/min, Argon, 60 bar



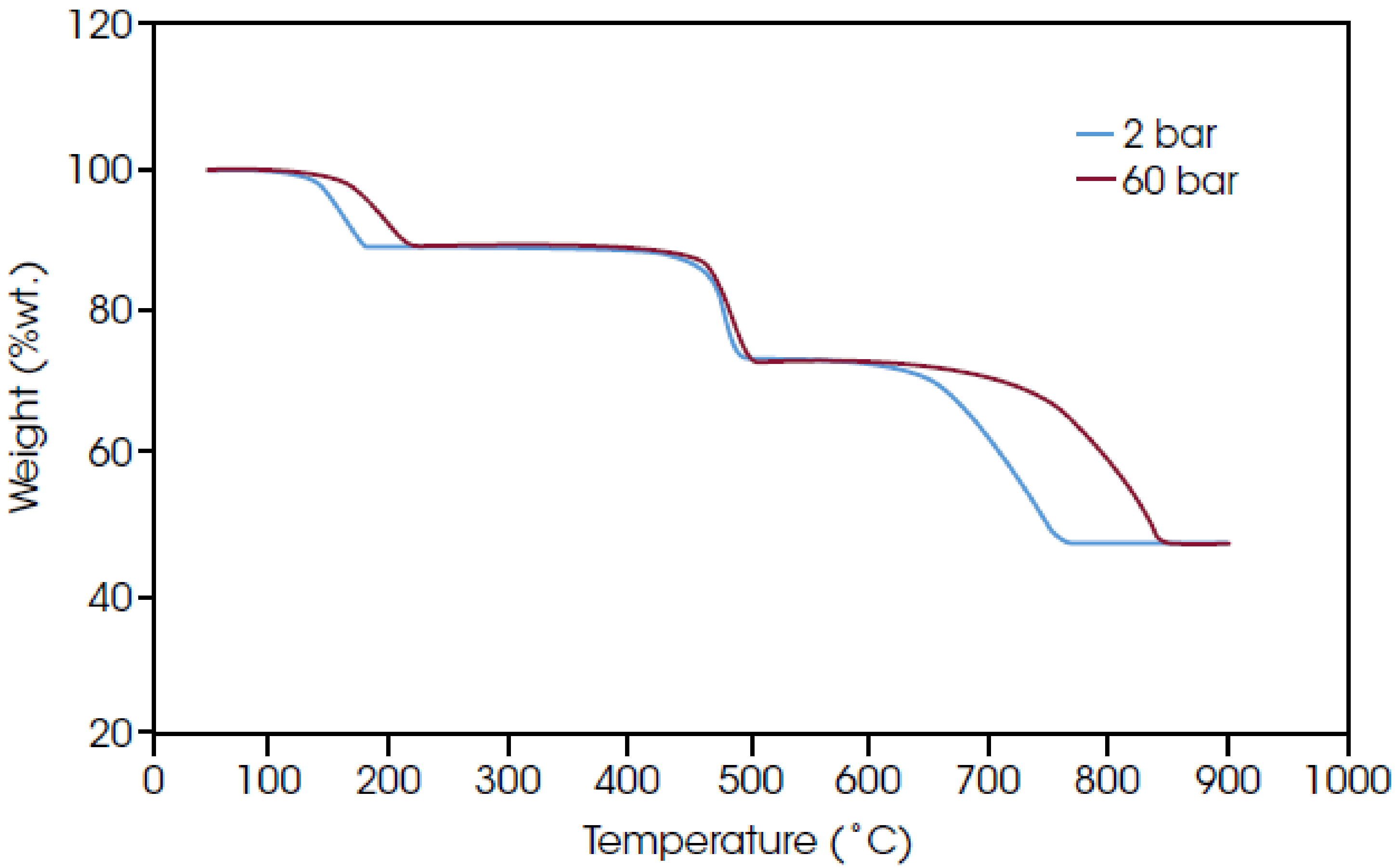
Buoyancy Mode:
Temperature ramp is repeated for automated data correction

Buoyancy corrected weight:
Weight change of sample under pressure

Calcium Oxalate

Influence of Pressure on Decomposition

Atmosphere: Ar, Heating Rate: 4°C/min, Maximum Temperature: 900°C



Mass change steps are independent of pressure and can be measured accurately.

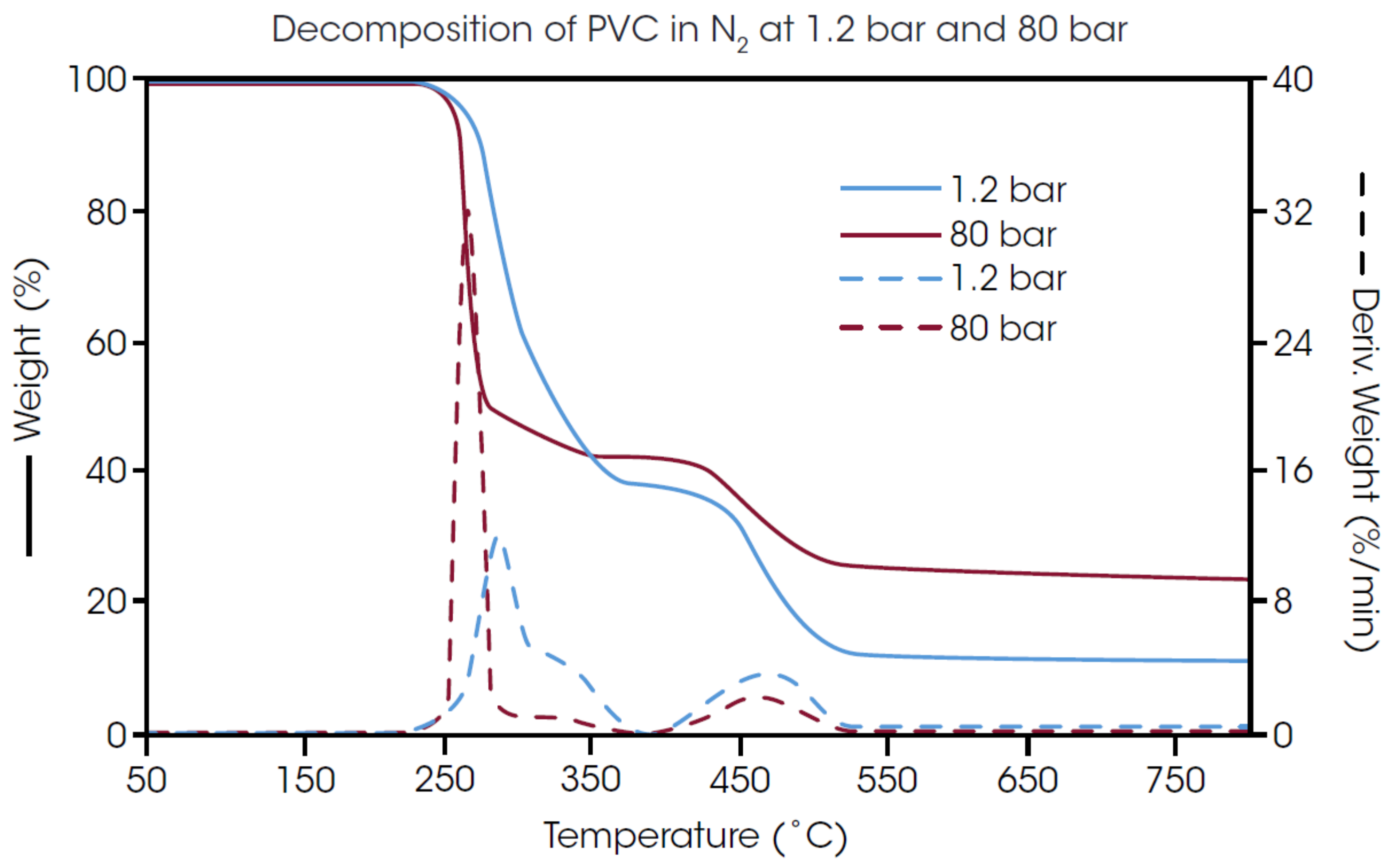
Decomposition temperatures can change with pressure.

	2 bar	60 bar
Step 1	172°C	191°C
Step 2	480°C	481°C
Step 3	739°C	798°C

Polymer Decomposition: PVC

Influence of Pressure on Decomposition

Atmosphere: Nitrogen, Heating Rate: 10 K/min



PVC decomposition is a multistage process with HCL and various hydrocarbons as reaction products.

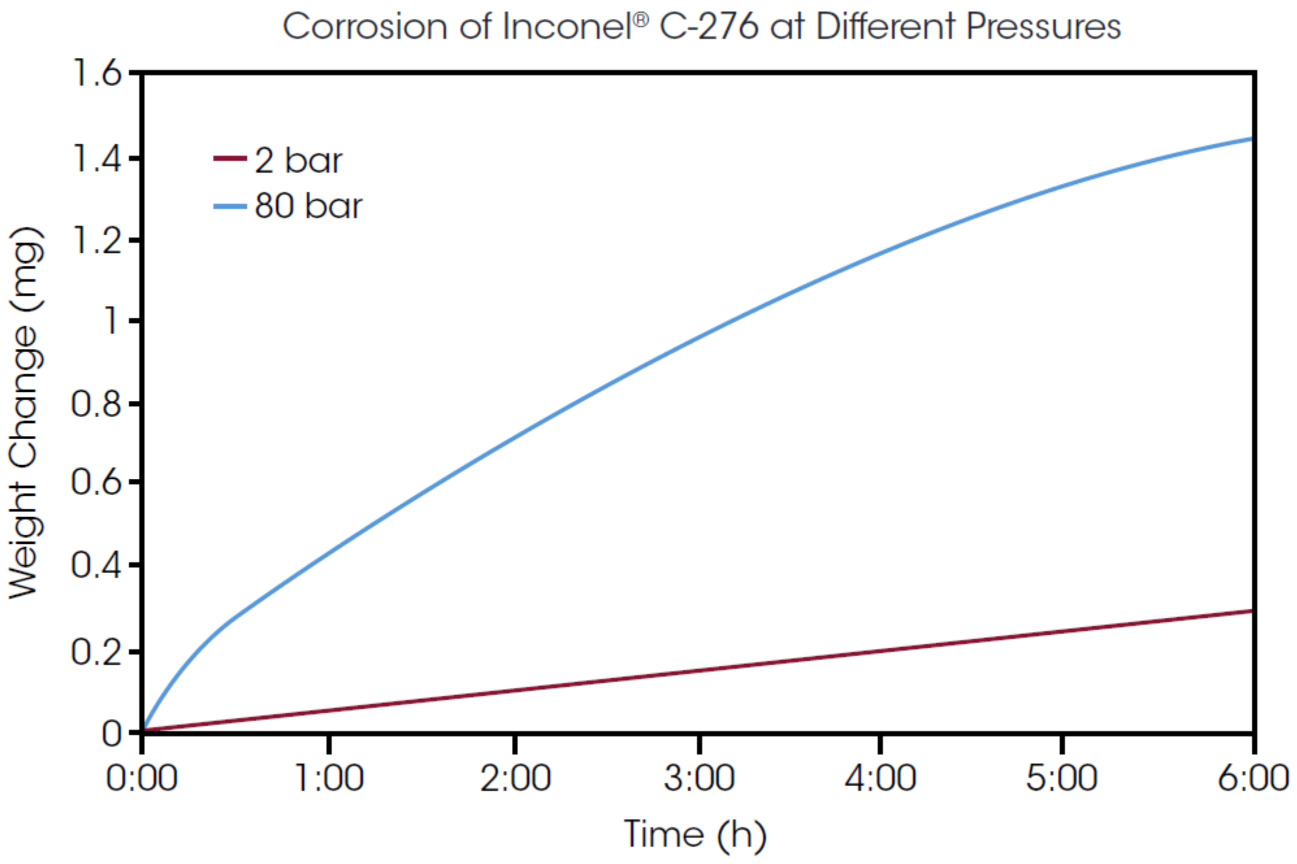
Changing pressure from ambient to 80 bar leads to:

- No significant change in decomposition temperatures
- Faster reaction rate in step 1
- Clear separation of step 1 and step 2
- 23 %wt residue (only 10 %wt at normal p)

Corrosion: Oxidation of High Performance Metal Alloy

Influence of Pressure on Oxidation

Atmosphere: Air



Temperature: 1000°C
Pressure: 2 bar and 80 bar
Sample surface 0.47 cm2

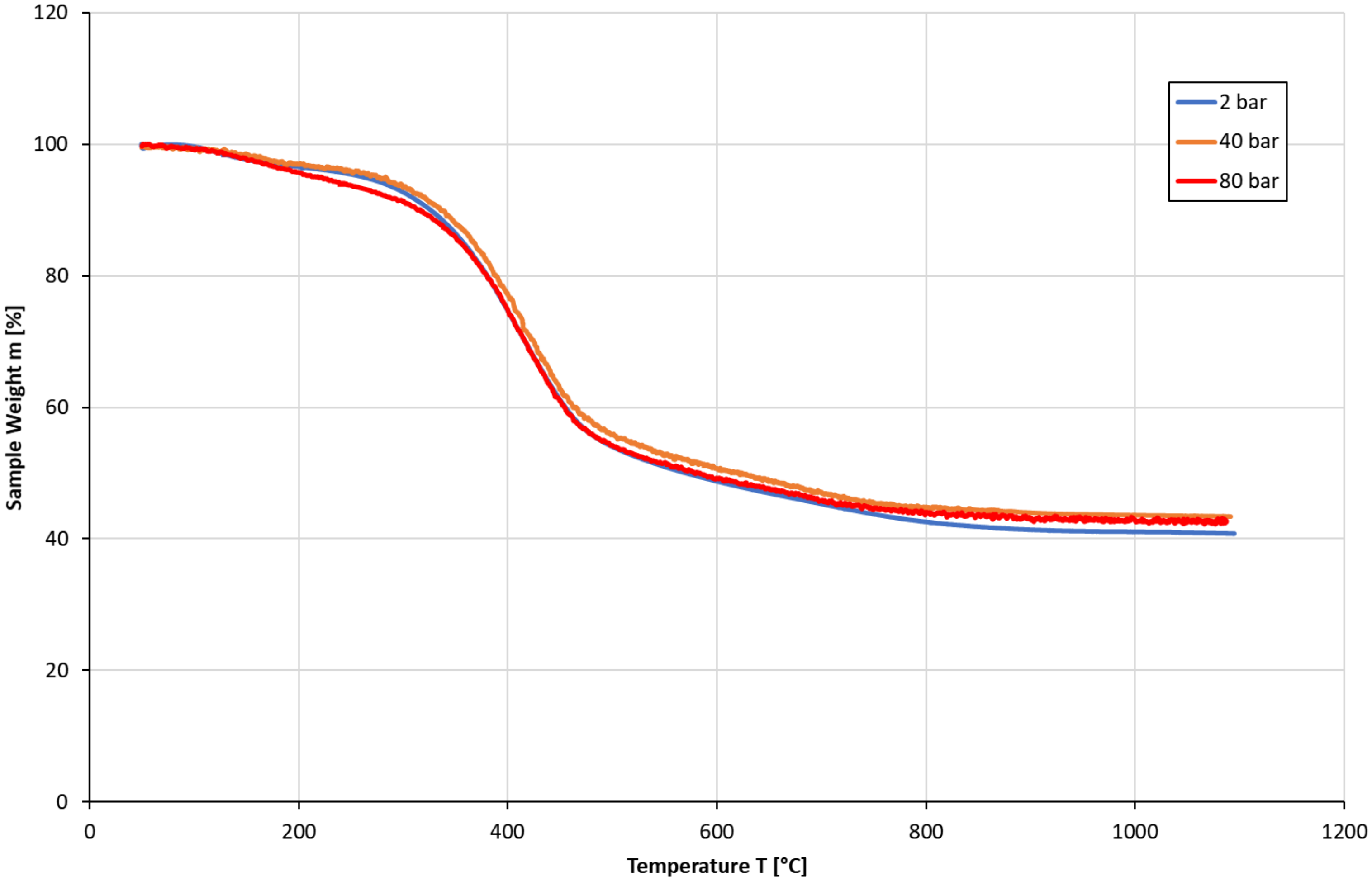
Corrosion rate is 5 times higher at high pressure
Oxidative weight gain after 6 hours:
- 610 mg/cm^2 at 2 bar
- 3078 mg/cm^2 at 80 bar

High pressure corrosion seems to approach saturation – oxidic layer

Coal Gasification: Lignite Pyrolysis in N_2

Influence of Pressure on Reaction Kinetics

Atmosphere: N_2, Heating Rate: 10°C/min, Maximum Temperature: 1100°C



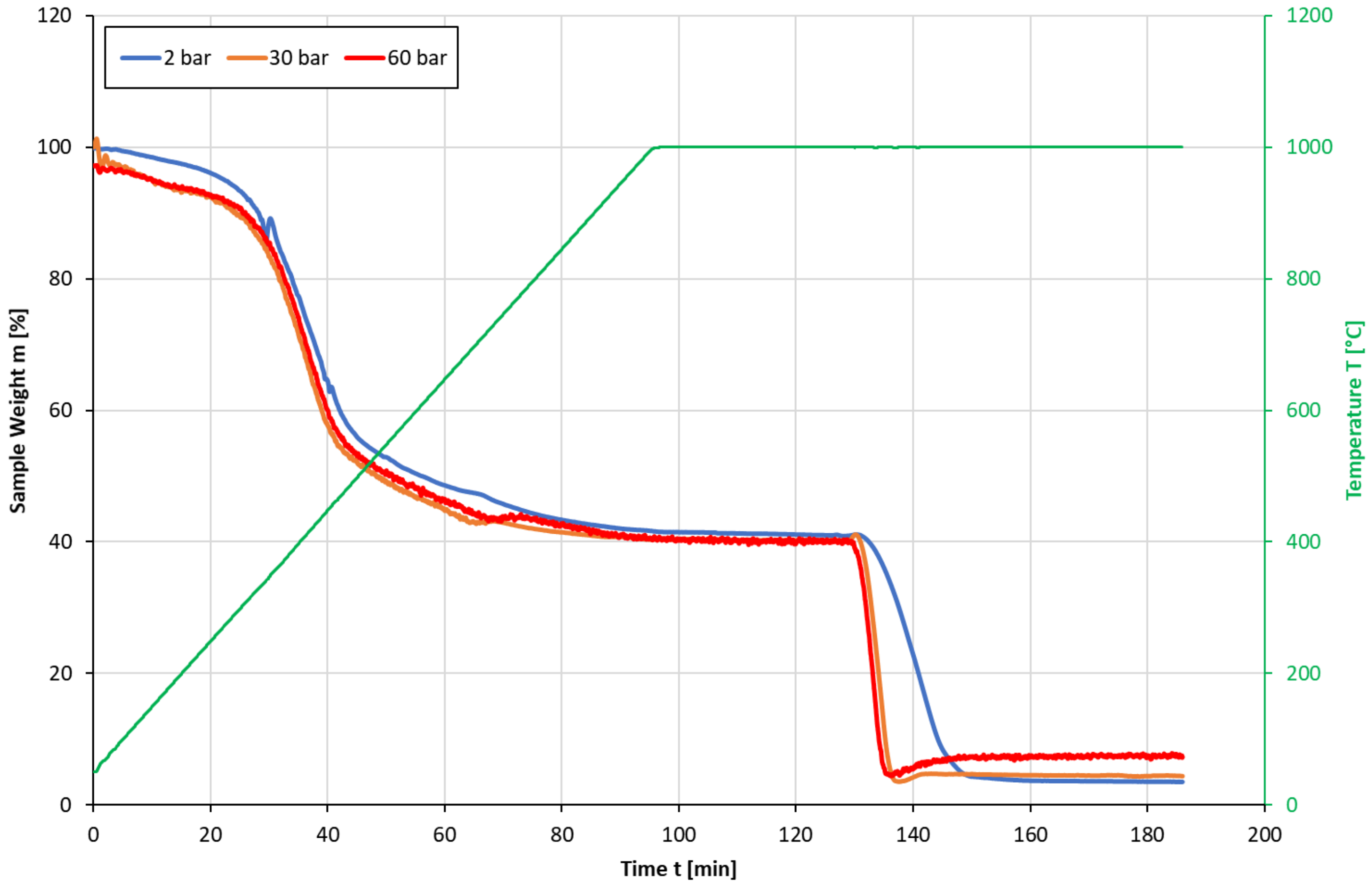
No significant influence of pressure

Coal Gasification: Lignite reacts with CO_2

Influence of Pressure on Reaction Kinetics

Heating Rate: 10°C/min, Maximum Temperature: 1000°C

Atmosphere: Ar during Temperature Ramp, then switch to 30% CO_2 in Ar



$$\frac{dm}{dt} \leq 3.0\ \%/min$$

$$\frac{dm}{dt} \leq 5.9\ \%/min$$

$$\frac{dm}{dt} \leq 5.8\ \%/min$$

$m_\infty = 3.5\%$

$m_\infty = 4.4\%$

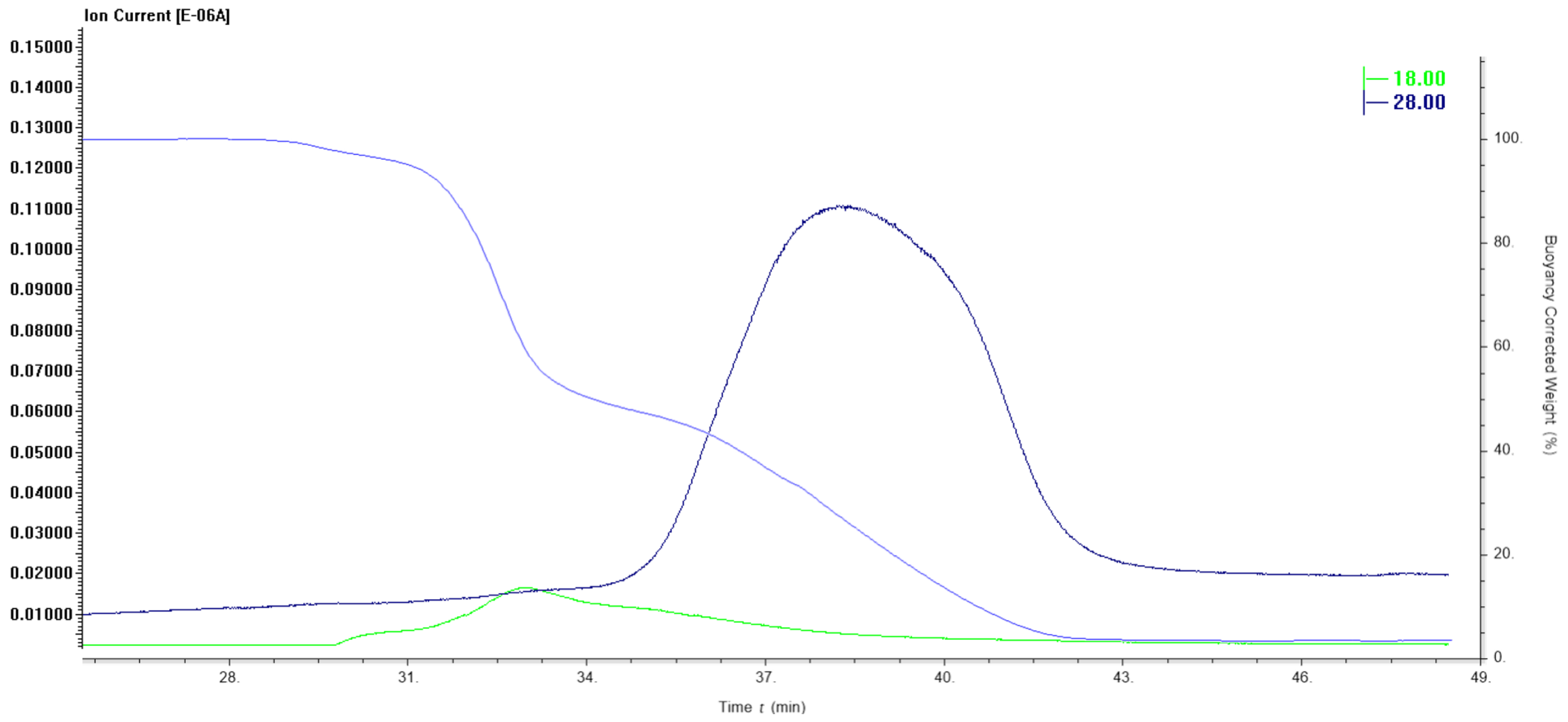
$m_\infty = 7.3\%$

EGA of Lignite Gasification

QMS coupled to TGA

Atmosphere: 30% CO_2 in Ar, Pressure: 2 bar,

Temperature: 100K/min to 1000°C,



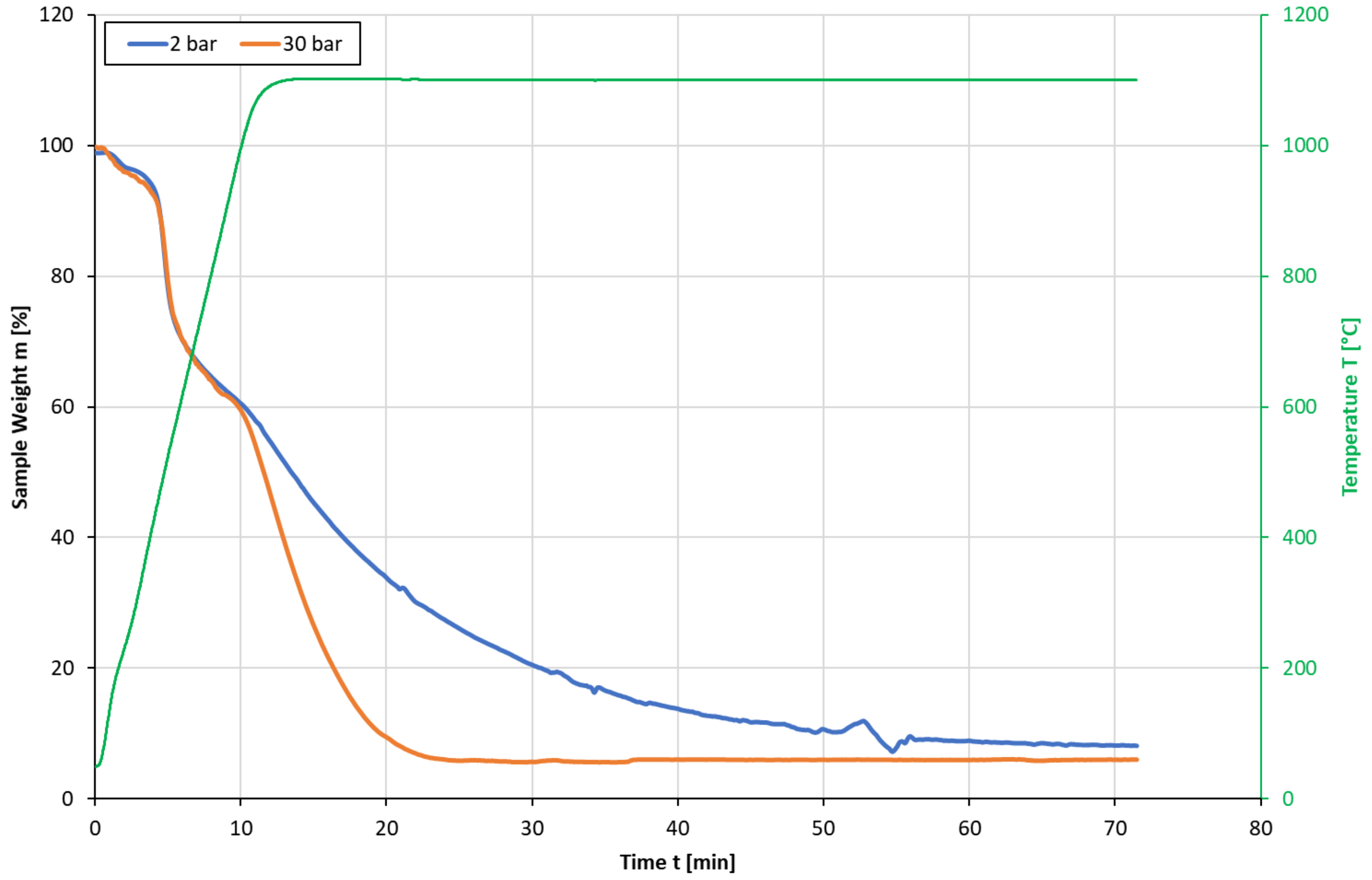
m/z 18: H_2O, mass loss due to drying of lignite

m/z 28: CO generated as product of gasification reaction

Anthracite Gasification

Influence of Pressure on Reaction Kinetics

Atmosphere: 30% CO_2 in Ar, Heating Rate: 100°C/min, Maximum Temperature: 1100°C



$\frac{dm}{dt} \leq 3.1\ \%/min$

$\frac{dm}{dt} \leq 6.6\ \%/min$

$m_\infty = 8.1\ \%$

$m_\infty = 6.0\ \%$

Summary

- Magnetic Suspension Balance: weight measurements at extreme conditions by separation of sample and balance
- New Magnetic Levitation Balance integrated in Discovery HP-TGA
- Top loading balance with high resolution allows measurements with small samples
- High heating and cooling rate, Integration with TA's TRIOS software
- Applications show influence of pressure on TGA experiments:
    - Ca-Oxalate: steps 1 and 3 shifted towards higher decomposition temperatures
    - PVC polymer: similar decomposition temperatures but different kinetics
    - Inconel alloy oxidation in air: 5 times faster at 80 bar
    - Gasification of lignite and anthracite coal: no influence on pyrolysis but faster reaction with CO_2 reactand gas
- Evolved gas analysis with QMS shown with gasification of lignite example

Thank You

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