Waters™ | TA Instruments

HIGH PRESSURE THERMOGRAVIMETRIC ANALYZERS

TGA Instruments with Magnetic Suspension Balance

High Pressure

High Temperature

Corrosion Resistant

HIGH PRESSURE THERMOGRAVIMETRY | INTRODUCTION

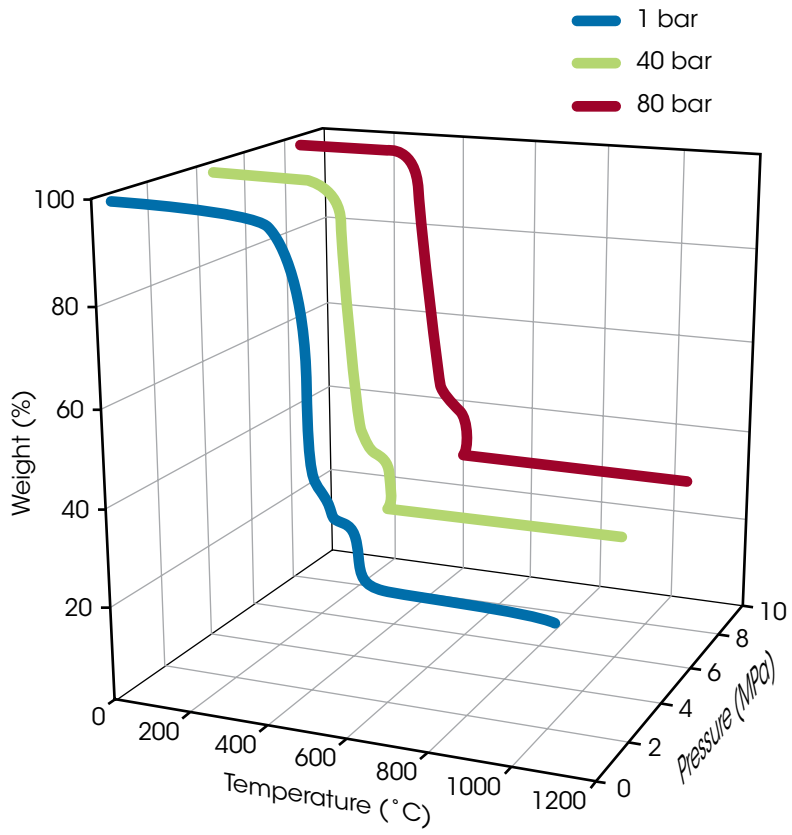
Thermogravimetric Analysis (TGA) is a well-established and frequently applied technique measuring the weight of a material as function of temperature. TGA measurements provide information about a material's stability and decomposition rates and help improve the lifetime and safety of many commercial products. However, many materials are exposed to extreme conditions, such as high pressure or the presence of reactive gas atmospheres or steam, in their normal use. In these cases, standard TGA data does not provide sufficient information and high pressure TGA is the better solution.

Adding the 3rd Dimension to Thermogravimetry

Standard TGA instruments measure thermal stability and decomposition kinetics of materials as weight change, mainly as a function of temperature. Heating rate and - in some cases-reaction atmosphere can be changed to provide insight about their influence on the mass change. High pressure TGA adds a third dimension to thermogravimetric analysis: in addition to temperature, heating rate, and atmosphere, the influence of pressure on the weight change of a material can be evaluated.

TA Instruments' suite of high pressure TGA analyzers allow you to assess the thermal stability of your material under application relevant conditions. Accurate weight measurements can be obtained under the following extreme conditions:

- In vacuum
- At pressures up to 80 bar
- At temperatures up to 1700 °C
- In reactive gas atmospheres
- In steam as reaction atmosphere

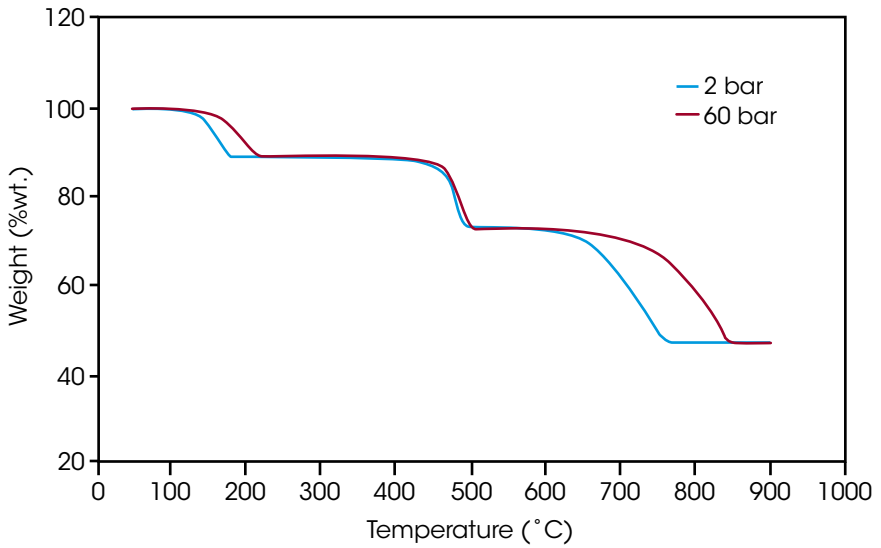


High Pressure Impacts the Results of TGA Measurements

Calcium Oxalate monohydrate $CaC_2O_4 \cdot (H_2O)$ is a widely characterized material with well-known and understood weight loss behavior. Upon heating it decomposes in three discrete step changes in weight. The steps are caused by the loss of H_20, CO and CO_2 resulting in Calcium Oxide CaO as residual product.

In the diagram on the right, two Calcium Oxalate decompositions measured at 2 and 60 bar are compared. The weight changes in each decomposition step are identical and match the expected stoichiometric theoretical change. However, the decomposition temperatures of the steps are shifted towards higher temperatures at higher pressures. Notably, the impact of pressure is different for each step. This is not surprising, since the steps represent different thermal reactions. But it is impossible to predict the influence of pressure on the decomposition temperature and/or kinetics if only low pressure TGA data are available.

The impact of elevated pressure on TGA data depends on the decomposition characteristics of the sample. TA Instruments High Pressure TGA systems can provide decomposition data under application-relevant conditions including not only pressure, but also humidity or reactive gas atmospheres.



Pressure changes the decomposition temperatures and kinetic behavior.
Steps in a TGA of Ca-Oxalate shift when 60 bar pressure is applied

The TA Instruments **HIGH PRESSURE TGA** are uniquely suited for challenging **THERMOGRAVIMETRIC APPLICATIONS**

HIGH PRESSURE THERMOGRAVIMETRY | APPLICATIONS

High pressure TGA instruments allow thermogravimetric experiments to be carried out under realistic application conditions. This data provides a better understanding of:

- thermal stability, decomposition and lifetime
- corrosion, oxidation and reduction
- catalyst activation and deactivation
- solubility and sorption processes of high-performance materials which are applied under high pressures
- pyrolysis and gasification

Thermal stability, decomposition and lifetime

High performance polymers are lightweight, durable and corrosion-resistant materials. Due to these properties, they are used in countless applications, e.g. in the chemical or oil & gas industry as contruction materials for containers, reactors and piping, or also as fittings, seals and sealant materials.

In these applications the polymeric materials are regularly exposed to elevated temperatures and high pressures as well as potentially reactive chemicals. The compatibility and stability of the materials cannot be evaluated based on ambient pressure testing. Compared to classical long-term autoclave pressure testing of the materials high pressure thermogravimetry is much more sensitive. In addition to determining the material compatibility, the influence of pressure or reactive atmospheres on the kinetics of decomposition is also assessable. TGA data can be measured under realistic application conditions in less time and provide more insight into a material's behavior. It is possible to understand and predict the lifetime of a material much more effectively than by performing long and cost intensive autoclave testing.

Similar lifetime and stability experiments can be applied for other materials as well; these can be metals, oils, lubricants or other materials that are used under challenging conditions.

Optimization of catalytic reactions

Catalytic reactions are of tremendous commercial importance. Over 90% of all chemicals worldwide are manufactured with the aid of solid catalysts. In a high pressure TGA instrument, it is possible to investigate reactions of solids with the gas phase under realistic working conditions. Activation (e.g. by reduction) and deactivation (by oxidation or coking) of a catalyst material is related to a weight change that can be measured in the HP-TGA. Simultanously, the yield and kinetics of the reaction can be monitored by evolved gas analysis with online MS, FTIR or other methods. Compared to standard fixed bed reactors the advantage of a high pressure TGA is the in-situ weighing of the catalyst material. This is extremely useful to optimize reaction conditions and develop improved catalyst materials.

Corrosion, oxidation and reduction studies

New metallic alloys are required for improving the performance of power plants or jet engines used in aircrafts. Thermodynamic efficiency of steam and gas turbines is directly related with their maximum operation temperature. The key for improvements are corrosion, oxidation and reduction resistant metal alloys which can be used as construction materials. High temperature corrosion studies to test and optimize novel metal alloys can be performed in HP TGA instruments. Oxidative or reductive corrosion is always associated with a weight change of the metal. In TA Instruments' high pressure TGA instruments this can be measured at high temperatures with the realistic atmosphere over long time intervals.

Pyrolysis and Gasification

Gasification is a technical process to generate syngas from solid carbonaceous fuels that is most energy efficient in a pressure range from 10 to 40 bar. High pressure TGA instruments are the best suited tool to study and optimize the gasification process and to test and compare different feedstock materials as solid fuel for gasification. The solid materials are pyrolyzed and react with a gasification agent that can be steam or carbon dioxide. Pyrolysis and gasification are additional examples of technical processes with reactive atmospheres under pressure that can only be optimized with the help of the HP-TGA systems by TA Instruments.

Unique Magnetic Suspension Balance Technology

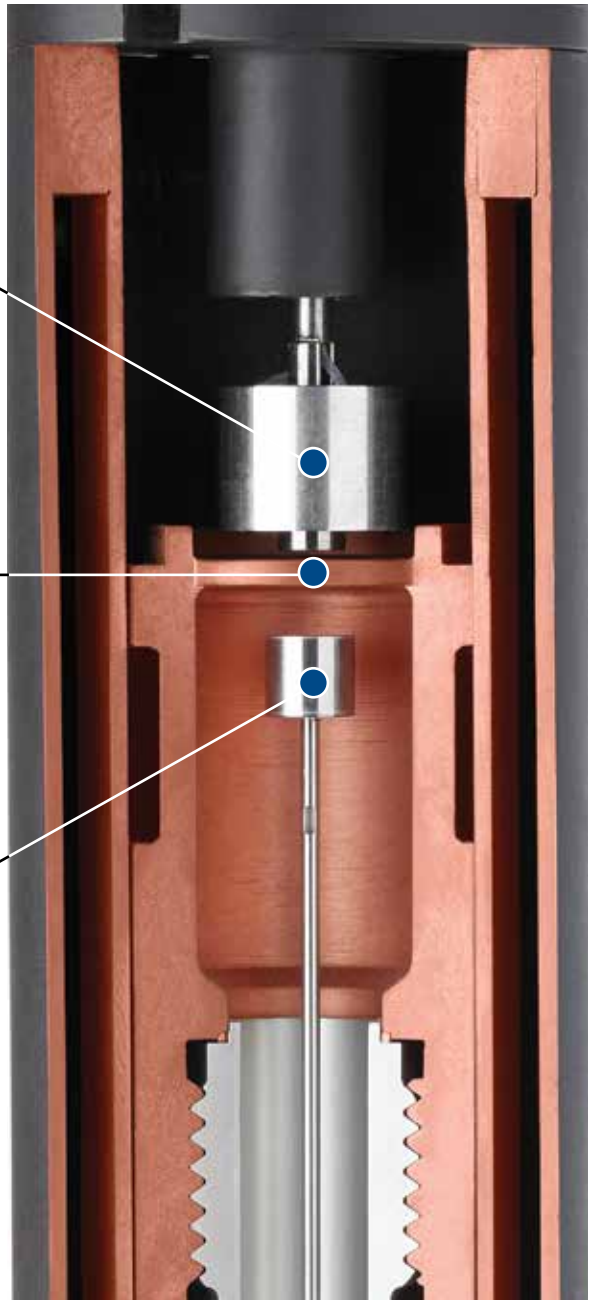
At the heart of every TA Instruments high pressure thermogravimetric analyzer is a patented* Magnetic Suspension Balance (MSB), which weighs a sample in a closed reactor cell with an externally located microbalance. This is realized by means of a magnetic suspension coupling that transmits the weight force through the wall of the sample cell. MSBs were originally developed and commercialized by Rubotherm, which is now a part of TA Instruments.

MSBs provide a complete separation of the external balance and the sample at high temperature and high pressure in the reaction atmosphere. The weight of the sample located in the pressure and temperature resistant reaction chamber is transferred without contact to the balance outside the reactor by a magnetic coupling.

With this technique, it is possible to apply extreme conditions such as reactive gas atmospheres, high pressures and temperatures to the sample in the reaction chamber without affecting the external balance. Since Magnetic Suspension Balances are commercially available, they have been used in a broad variety of special applications in many fields of research. MSB applications include gas sorption analysis on porous materials or gas solubility in polymers, and thermogravimetric measurements in vacuum or high pressures and with reactive atmospheres.

Therefore, MSBs are the best analytical technology to design specialized TGA instruments for analysis conditions that include high pressure, vacuum, reactive gas atmospheres or even steam. All TA Instruments high pressure TGA analyzers are equipped with Magnetic Suspension Balances.

Magnetic Suspension Balance - the best tool for weighing under extreme conditions



THERMOGRAVIMETRIC TESTING under REAL PROCESS CONDITIONS

*European Patent: 1958323, U.S. Patent: 2009/0, 160.279 A1, German Patent: DE 10 2009 009 204 B3

Discovery HP-TGA and Rubotherm Series DynTHERM TGA: The right high-pressure TGA for every application

Only TA Instruments is in the great position to offer two types of Magnetic Suspension Balances. The proprietary new magnetic levitation balance in the Discovery HP-TGA uniquely combines an exceptionally large specification range with the design and ease of use of a standard TGA. The classical Rubotherm Series MSB has been successful for more than 30 years in many research areas, especially in gravimetric sorption analysis and high pressure TGA. With its robust, field proven design, the large sample capacity and modular setup makes the DynTHERM TGA the first choice for applications requiring customized solutions.

Discovery HP-TGA 75 / 750 / 7500

HP-TGA made easy: the world's first benchtop High Pressure TGA

The Discovery HP-TGA series of instruments evolve the technique of high pressure TGA to a new level. The heart of the instrument is a completely new patented magnetic levitation balance that allows the miniaturization of the pressurized reactor volume in combination with a high balance resolution of better than 0.1 µg.

The Discovery HP-TGA are the only benchtop high pressure TGA instruments in the market. While offering extraordinary specifications of 1100 °C maximum temperature at pressures up to 80 bar they are as easy to operate as any TA Instruments Discovery TGA instrument controlled by TRIOS software and touchscreen display.

For the first time, sophisticated high pressure data is attainable for routine analysis with a benchtop TGA instrument.

Rubotherm Series DynTHERM TGA

A modular research grade High Pressure TGA - with outstanding specifications for the most demanding applications

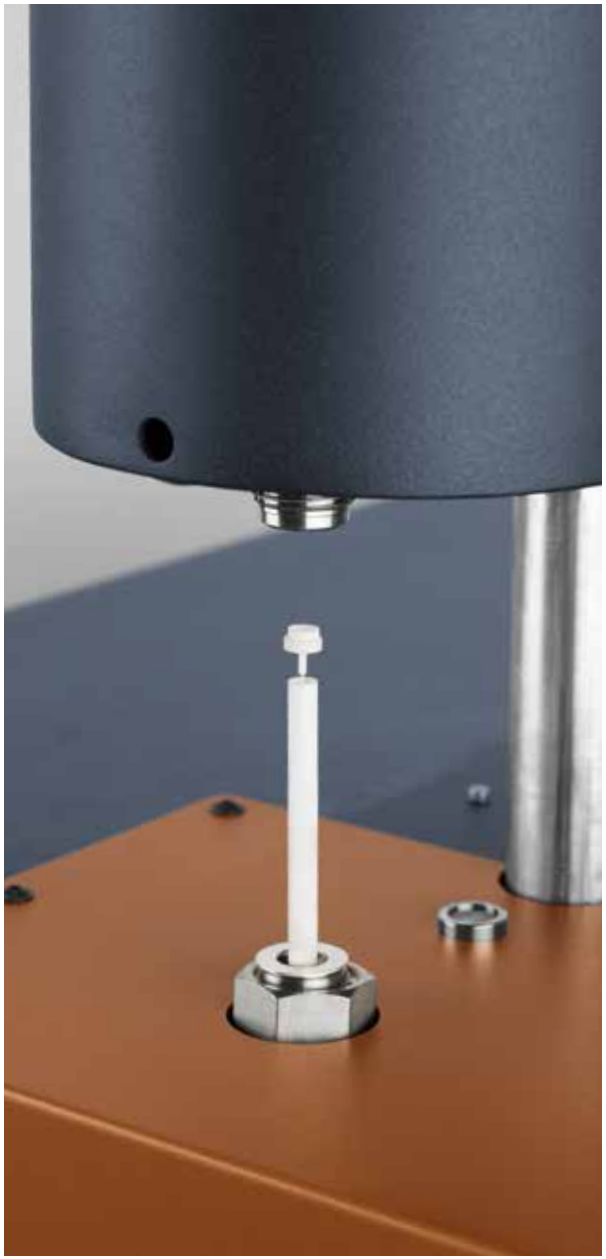
The DynTHERM TGAs are advanced gravimetric instruments featuring the classical Magnetic Suspension Balance. Weight changes of materials can be measured under high pressure, in the presence of a variety of gases, vapors, or steam, at temperatures up to 1700 °C and temperature-dependent maximum pressures up to 50 bar.

With the high weighing capacity and large sample volume the DynTHERM TGA are ideally suited for measurements with representative samples of inhomogeneous materials or complete assemblies.

DynTHERM TGAs are high-end research instruments for very challenging applications which require customized analyzers using the classic Rubotherm MSB technology.

KEY FEATURES | HP-TGA & DYNTHERM

	Discovery HP-TGA	DynTHERM TGA
Temperature Range	RT – 1100 °C	RT – 1700 °C
Pressure Range	Vacuum – 80 bar	Vacuum – 50 bar (T-dependent)
Max. Heating / Cooling rate	200 K/min	LP: 100 K/min HP: 20 K/min
Sample mass / Weighing range	500 mg / 500 mg	25 g / 20 g
Sample crucible volume	90 µl	635 µl
Max. sample dimensions (placed directly without crucible)	n/a	H = 25 mm W = 20 mm
Max. number of gases for blending	3	5
Steam generator and dosing	Yes	Yes



The Discovery HP-TGA features a new toploading MSB with standard ceramic crucibles (shown left), while the DynTHERM TGA to the right offers a larger volume crucible in a classic Rubotherm MSB.

HIGH PRESSURE THERMOGRAVIMETRY | DISCOVERY HP-TGA

Discovery HP-TGA 75 / 750 / 7500

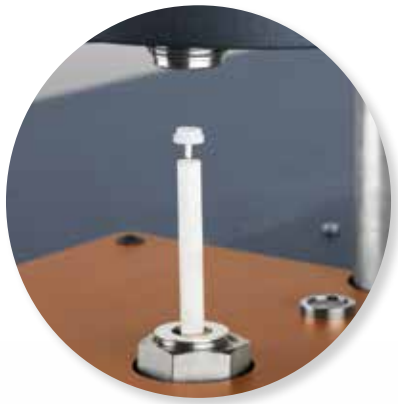
At the core of every Discovery HP-TGA is the new top-loading Magnetic Levitation Balance. Multiple patented technologies are combined to bring to life a highly sensitive and compact balance that can operate under high pressure.

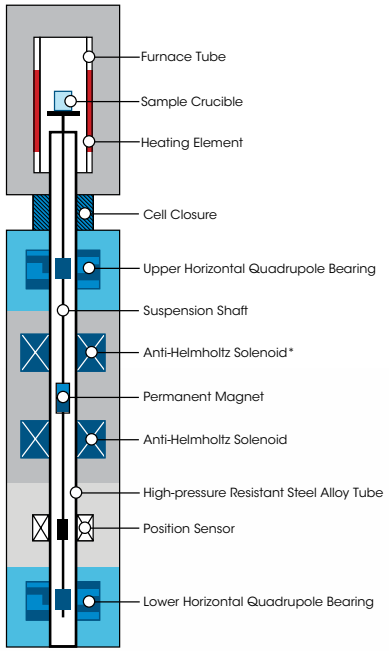
Magnetic Levitation Balance

In this unique top-loading Magnetic Levitation Balance, the sample crucible is located at the top of a ceramic suspension shaft. The suspension shaft is equipped with a permanent magnet and is positioned in a small diameter pressure-resistant steel tube. Levitation is achieved in an equilibrium between the total weight of sample, crucible and suspension shaft and the magnetic attraction of the permanent magnet and a magnetic field created by an array of Anti-Helmholtz coils located outside of the steel tube. In this sophisticated setup, the electric current applied to these coils is directly proportional to the weight of suspension shaft and sample and can be calibrated as weight signal.

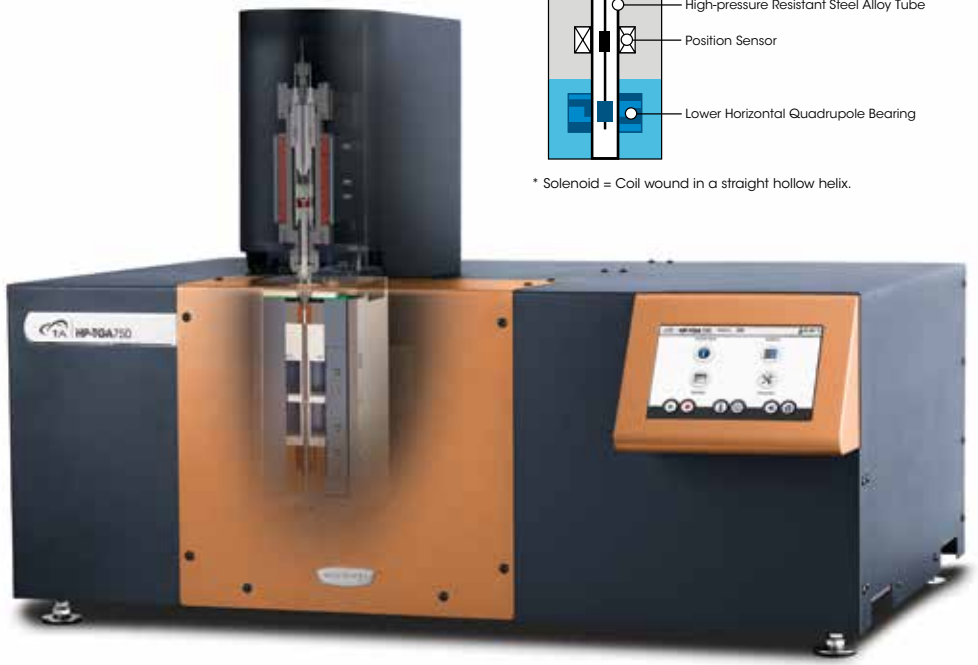
The vertical position of the suspension shaft is controlled by means of an LVDT position sensor: when the sample weight changes, the current on the electromagnetic coils is adjusted accordingly. Stabilization of the suspension shaft is achieved with two quadrupole bearings at the upper and lower end. All electronic parts, the coils, LVDT position sensor and quadrupole bearings are located outside the steel tube where they are separated from the pressurized reaction atmosphere and are kept at a constant temperature. This new Magnetic Levitation Balance is extremely precise and has an outstanding long-term weight stability.

The main advantage of the new design is the possibility to miniaturize the MSB technology: for the first time, a benchtop high pressure TGA is available with the complete gas and vapor dosing and pressure control included. This way, HP-TGA is finally available for routine sample testing, taking advantage of the sophisticated features of TRIOS software.





* Solenoid = Coil wound in a straight hollow helix.



TOP LOADING MAGNETIC LEVITATION BALANCE for highest weighing **RESOLUTION, PRECISION** and **STABILITY** in high pressure TGA

Dynamic High Pressure Reaction Furnace

An innovative high-pressure reaction furnace for accurate and responsive temperature control under all pressure and gas flow conditions.

The Discovery HP-TGA furnace features a robust corrosion-resistant ceramic tube with an embedded heating element capable of sample temperature control to 1100 °C. Due to the compact low mass design, this furnace can provide heating/cooling rates of up to 200 K/min. The sample temperature is measured with a thermocouple directly adjacent to the sample. A key feature is the Curie-point temperature calibration that can be performed at all pressures and temperatures with any reaction gas and thus can provide the most accurate temperature control available for a high pressure TGA instrument.

The low volume of the pressure-resistant balance tube and furnace is extremely important for precise control and fast exchange of reaction gas atmospheres and provides systematic advantages for safe operation at high pressures.

Corrosion Resistant
Heating Element

ADVANCED FURNACE DESIGN
for optimal **TEMPERATURE**
and **PRESSURE** control

Integrated Gas and Steam Dosing and Blending Systems with Pressure Control

In high pressure TGA, the reliability and accuracy of gas flow and pressure control is of utmost importance for the data quality. All Discovery HP-TGA models feature integrated gas dosing and blending systems with pressure control to provide the flexibility to address the widest range of applications. Pressure can be controlled in the range from 200 mbar to 80 bar and complete evacuation to ultimate vacuum is possible as well. All Discovery HP-TGA instruments include a mass flow controller connected to an inert gas for the balance purge.

The **Discovery HP-TGA 75** is equipped with a single reaction gas mass flow controller and three gas connections. One reaction gas can be selected from the three connected. During a measurement, the reaction gas can be switched through software controls.

The **Discovery HP-TGA 750** is equipped with three reaction gas connections and three independent reaction gas mass flow controllers, which enables the reaction gas to be a pure gas or a blend of up to three gases.

The **Discovery HP-TGA 7500** is additionally equipped with a high-pressure steam generator. An accurate HPLC pump controls a flow of liquid water into an evaporator where the steam is generated. The steam is mixed with the reaction gas or gas mixture coming from the reaction gas mass flow controllers. Anti-condensation heating enables measurement with high steam concentrations at high pressures without unwanted condensation.

TGA analysis under **CONTROLLED PROCESS ATMOSPHERES**
with integrated **GAS AND STEAM DOSING SYSTEMS**
and **PRESSURE CONTROLLER**

HIGH PRESSURE THERMOGRAVIMETRY
"APP" STYLE TOUCHSCREEN

Powerful HP-TGA performance at your fingertips

The Discovery HP-TGA instruments boast a brand-new One-Touch-Away™ app-style touch screen that greatly enhances usability by placing key instrument features at your fingertips.

Touch Screen Features and Benefits:

- Ergonomic design for easy viewing and operation
- Packed with functionality to simplify operation and enhance user experience.

The app-style touch screen includes:

- Start/stop runs
- Real-time signals
- Active method viewing
- Curie point temperature calibration
- System information
- Test and instrument status
- Real-time plot
- Advance method segments
- Loading/unloading samples

IT'S NEVER BEEN EASIER TO GET GREAT HIGH PRESSURE DATA!

TECHNOLOGY | TRIOS SOFTWARE

Discover powerful TRIOS software that delivers exceptional user experience in a combined package for instrument control, data analysis and reporting for thermal analysis and rheology. New features such as multiple calibration sets, real-time test method editing, and inter-laboratory data and test method sharing provide unmatched flexibility, while one-click analysis and custom reporting raise productivity to new levels.

TRIOS Features:

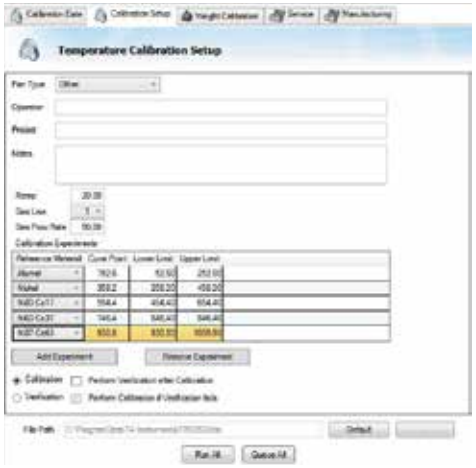
- Control multiple instruments with a single PC and software package
- Overlay and compare results across techniques including DSC, TGA, DMA, SDT and rheometry
- One-click repeated analysis for increased productivity
- Automated custom report generation including: experimental details, data plots and tables, and analysis results
- Convenient data export to plain-text, CSV, XML, Excel®, Word®, PowerPoint®, and image formats
- Optional TRIOS Guardian with electronic signatures for audit trail and data integrity

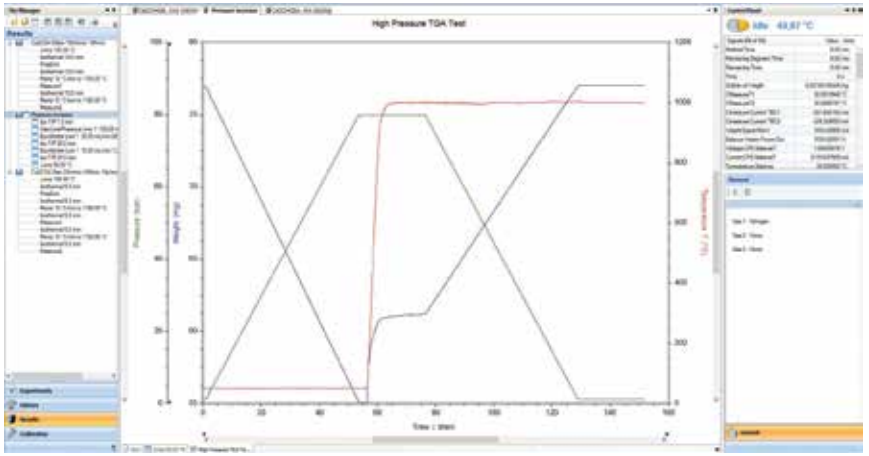
Ease of Use

TRIOS software makes calibration and operation of the entire line of Thermogravimetric Analyzers simple. Users can easily generate Curie-point temperature calibration data sets under varying experimental conditions (e.g. different pressures or gas selections) which are automatically applied to match the experimental conditions used for sample testing. Real-time signals and the progress of running experiments is readily available with the added capability of modifying a running method on the fly. TRIOS software offers a level of flexibility that is unmatched in the industry.

Complete Data Record

The advanced data collection system automatically saves all relevant signals, active calibrations, and system settings. This comprehensive set of information is invaluable for method development, procedure deployment, and data validation.





The Most **VERSATILE CONTROL** and **ANALYSIS SOFTWARE!**

Complete Data Analysis Capabilities

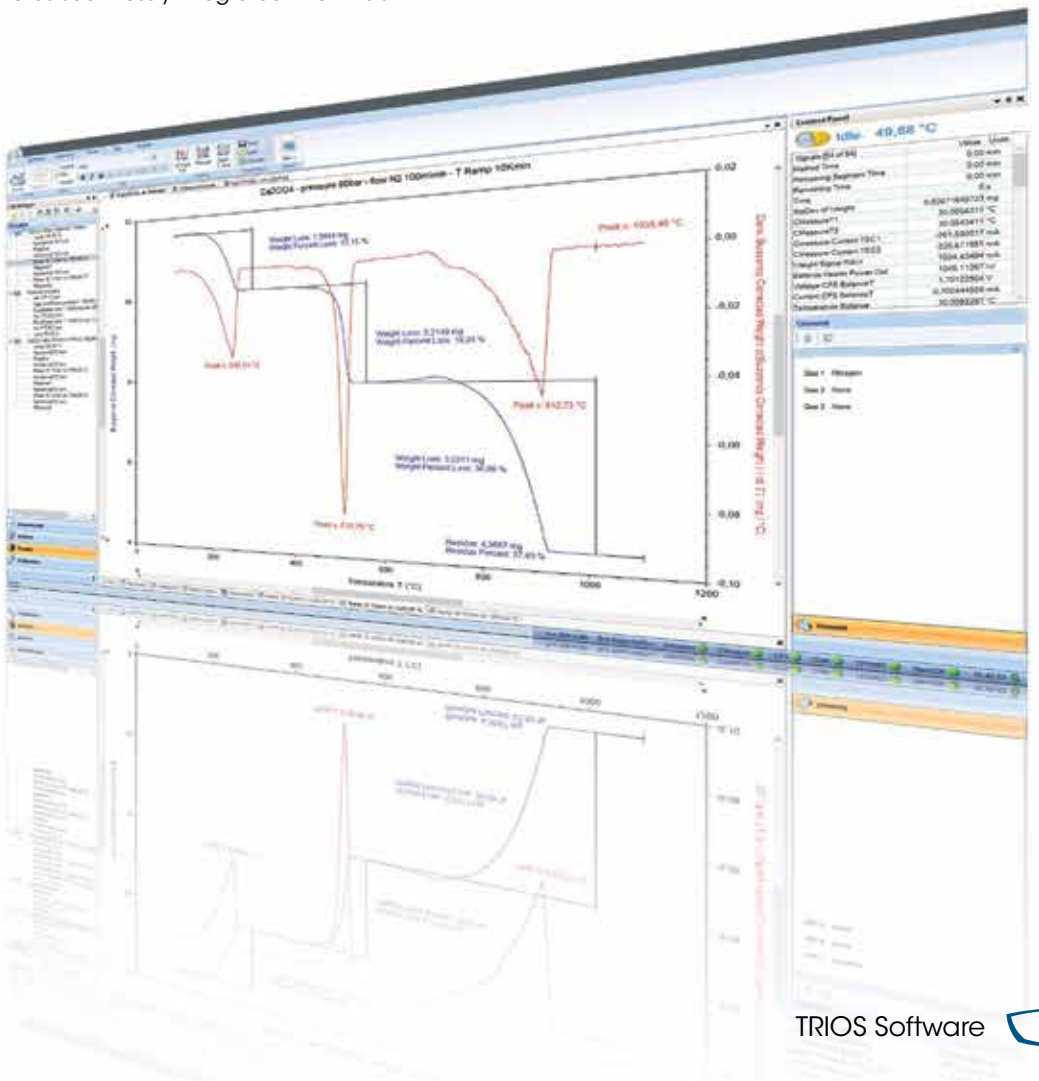
A comprehensive set of relevant tools are available for real-time data analysis, even during experiments. Gain actionable insights into material behavior through a powerful and versatile set of features seamlessly integrated into TRIOS.

All Standard TGA Analyses:

- Weight change (absolute and as a percentage)
- Residue content
- 1st and 2nd derivatives
- Weight at a specified time or temperature
- Weight loss at a specified time or temperature
- Peak height and area
- Temperature at peak maximum
- Onset and endset analyses
- Step transition analysis
- Easily import and export TGA data with TRIOS

Advanced Analysis Capabilities:

- Decomposition kinetics
- Advanced custom analysis with user-defined variables and models



HIGH PRESSURE THERMOGRAVIMETRY | DYNTHERM TGA

Rubotherm Series DynTHERM TGA

At the heart of every Rubotherm Series instrument is the patented Magnetic Suspension Balance (MSB), which weighs a sample in a closed reactor cell with an external microbalance.This is realized by means of a magnetic suspension coupling that transmits the weight force through the wall of the sample cell.

In this design, a permanent suspension magnet is attached at the top of an upper internal suspension shaft. A lower internal suspension shaft is connected to a crucible holding a sample material. Between the upper and lower suspension shafts is a load coupling mechanism. The upper and lower shafts and the sample crucible are enclosed within the sample cell.

An external electromagnet is controlled to attract the internal permanent magnet. This raises the internal suspension magnet and engages the load coupling and, as a result, raises the sample crucible. The electromagnet control continues to apply attractive force until the system reaches a constant measuring point height.

The weight of the sample in the cell is determined by the external microbalance, to which the electromagnet is connected, with high resolution and accuracy.

FIELD PROVEN MAGNETIC SUSPENSION BALANCE provides **LARGE SAMPLE** weighing for high pressure TGA **IN CHALLENGING ATMOSPHERES**

UNRIVALED LONG-TERM MEASUREMENT ACCURACY

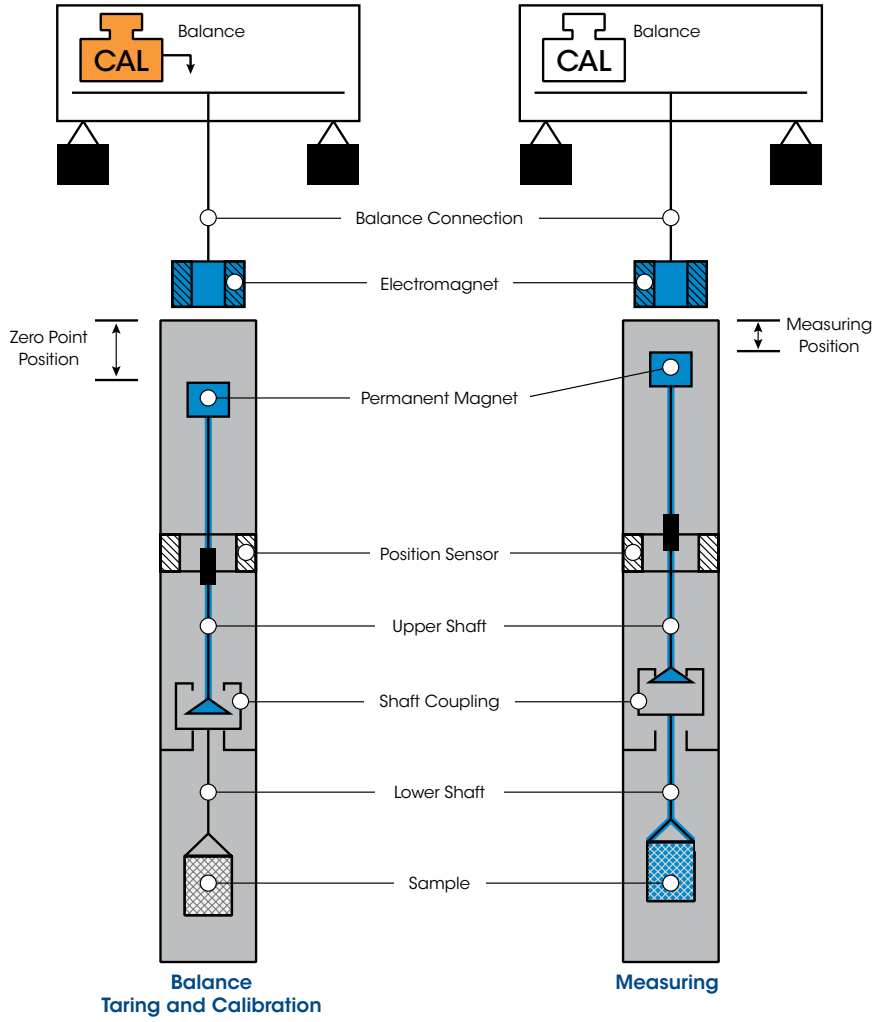
Automatic Sample Decoupling Feature (ASD)

At the start of any gravimetric experiment, the balance is automatically tared and calibrated to establish a "zero-point" for the weight measurement. This zero-point is the value used for all subsequent measurements. However, as experiment time frames can vary from hours to weeks, the ability to accurately measure small weight changes over extended times can be diminished by drift in the zero-point. Drift is typically due to external factors such as fluctuations in laboratory temperature and air pressure or humidity.

Attempts to improve signal accuracy have traditionally been to conduct empty crucible baseline runs and subtracting them from the sample run. This method is not ideal as it doubles experiment times, and is inherently flawed as no two experiments are ever exactly the same. TA's DynTHERM TGA, with patented MSB technology, provides the unique Automatic Sample Decoupling (ASD) feature for real-time drift corrections, increasing weight accuracy to previously unattainable levels, especially for long-term measurements.

How ASD Works:

As shown in the figure to the right, the MSB design includes a shaft load coupling. When the electromagnet is energized, it attracts the permanent magnet that is connected to the upper shaft. The upper shaft lifts upward, engages the coupling, and raises the crucible to the measuring point to make the weight measurement. At any time during the experiment, the permanent suspension magnet can be moved downward to decouple from the sample crucible. During this downward movement, the shaft load coupling is placed at rest on a support. The suspension magnet remains in a free-floating state, transferring only its weight to the balance. By moving to this new zero-point position corresponding to an unloaded balance, taring and calibrating are possible during measurements, even under process conditions (pressure, temperature) in the sample cell. This unique automatic software-controlled calibration of the balance during measurements is an exclusive feature of TA Instruments' DynTHERM TGA analyzers.



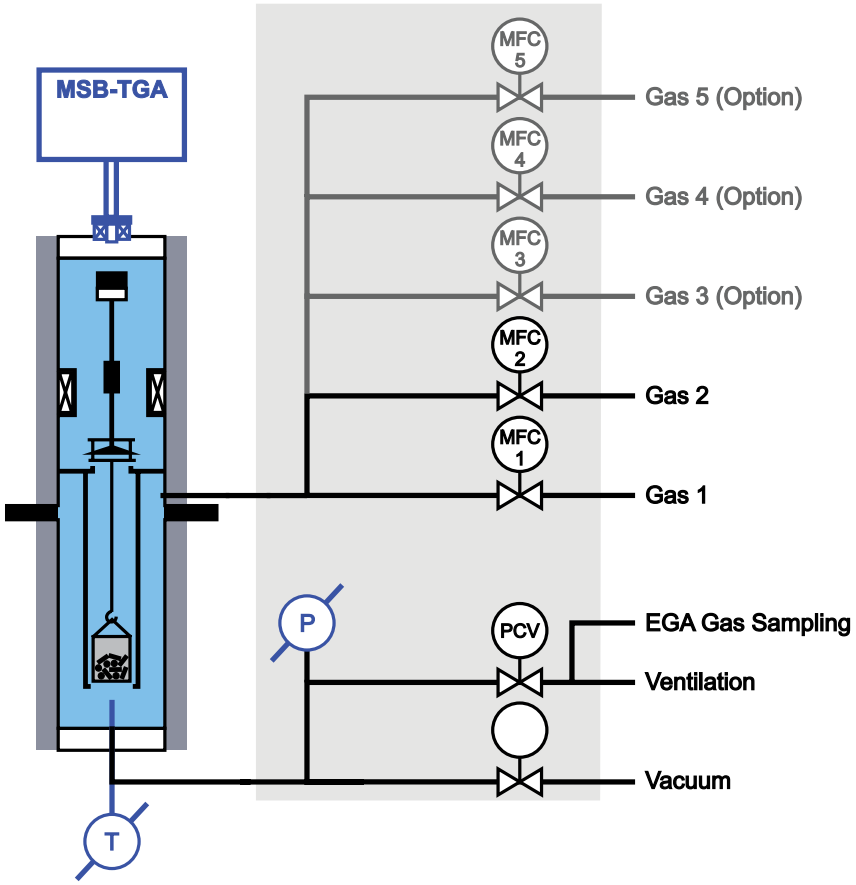
Gas & Vapor Dosing, Blending and Pressure Control Systems

The accuracy of TGA measurements rely on accurate control of the pressure and the composition of the reaction atmosphere. The DynTHERM TGA features sophisticated gas & vapor dosing and blending systems with pressure controllers which ensure the highest data quality while providing flexibility to address the widest range of applications. These systems provide a continuous flow of pure reaction gas, a gas mixture, or gas and vapor mixture with controlled composition to the sample reactor cell of the TGA. A dynamic backpressure controller in the outlet flow maintains pressure with the highest stability and precision.

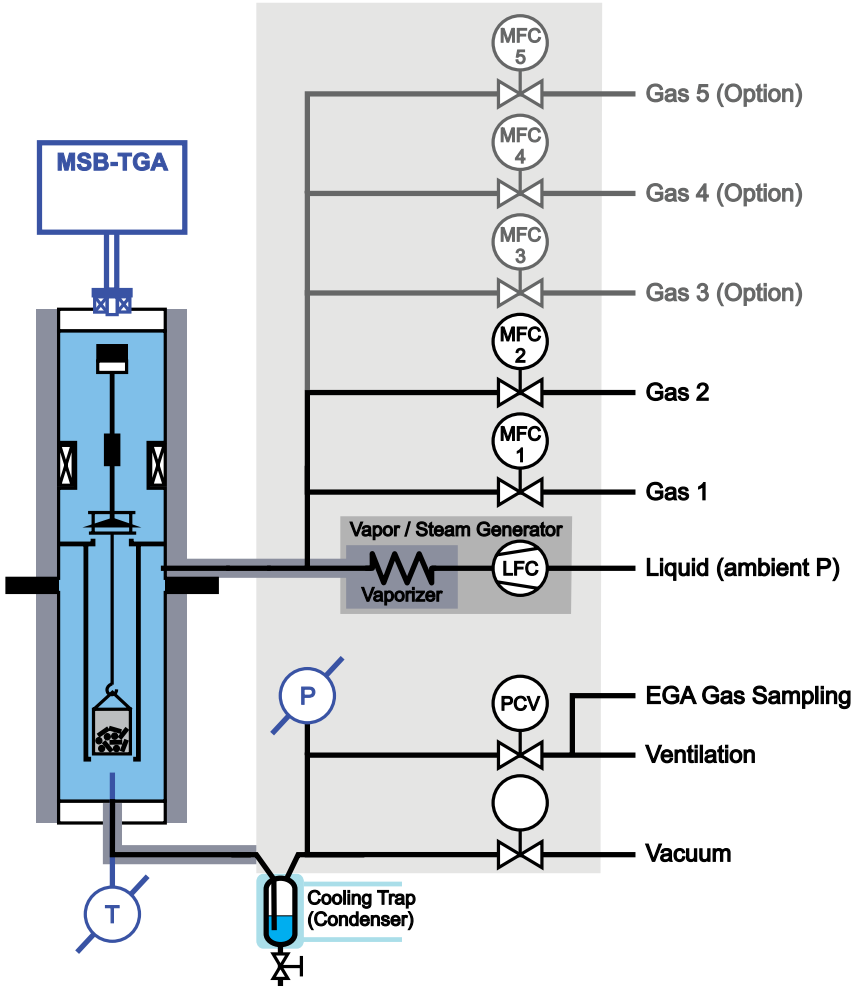
Each dosing system includes two mass flow controllers (MFC 1, MFC 2) for dosing pure gas or blending gas mixtures and dosing into the TGA reactor, an accurate pressure sensor (P), a PID controller, a pressure controlling valve (PCV) in the gas flow at the reactor exit, and a gas sampling connection for evolved gas analysis (EGA). Additional gas lines with mass flow controllers are optional.

Gas and Vapor (steam) Dosing Systems are additionally equipped with a vapor/steam generator consisting of a liquid compressing and flow control pump (LFC) for dosing a controlled flow of liquid into a vaporizer in which the steam is generated. The steam is then mixed with the gas flow(s) coming from the MFC's and flowing into the TGA reactor through heated transfer lines.

Gas Dosing System with Pressure Controller



Gas & Vapor Dosing System with Pressure Controller



High Pressure Furnace Reactor

The DynTHERM TGA instruments are equipped with low or high pressure sample cells with electrical heaters for accurate temperature control under all pressure and gas flow conditions.

Cold wall reactor design

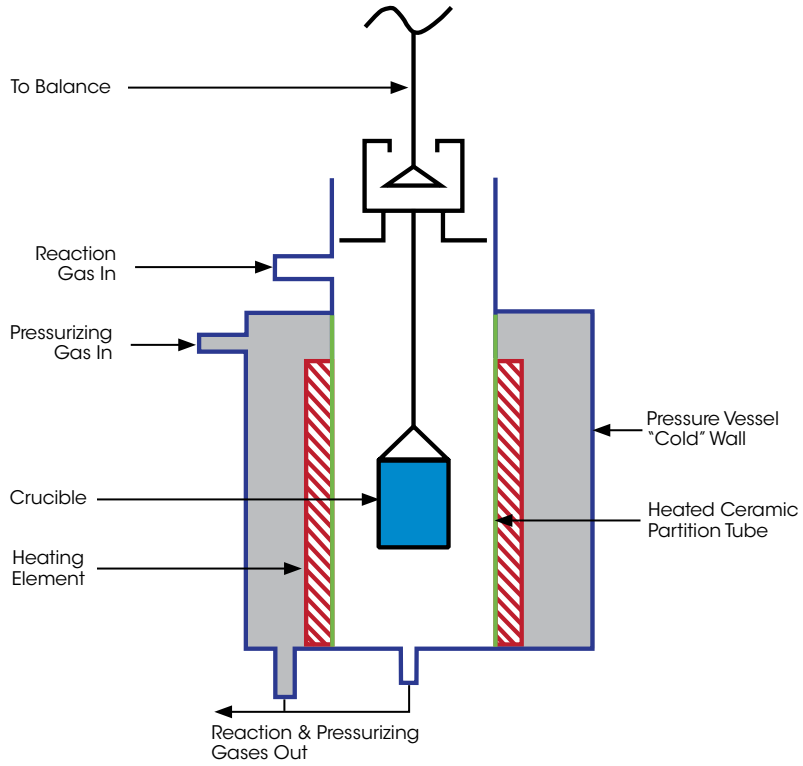
Installation of the electrical heater into a pressure vessel – the cold wall reactor setup – allows the use of only corrosion-resistant ceramic materials in the high temperature zone. The cold wall heaters can be applied using very corrosive reaction atmospheres in a temperature range up to 1700 °C* and at pressures up to 50 bar*.

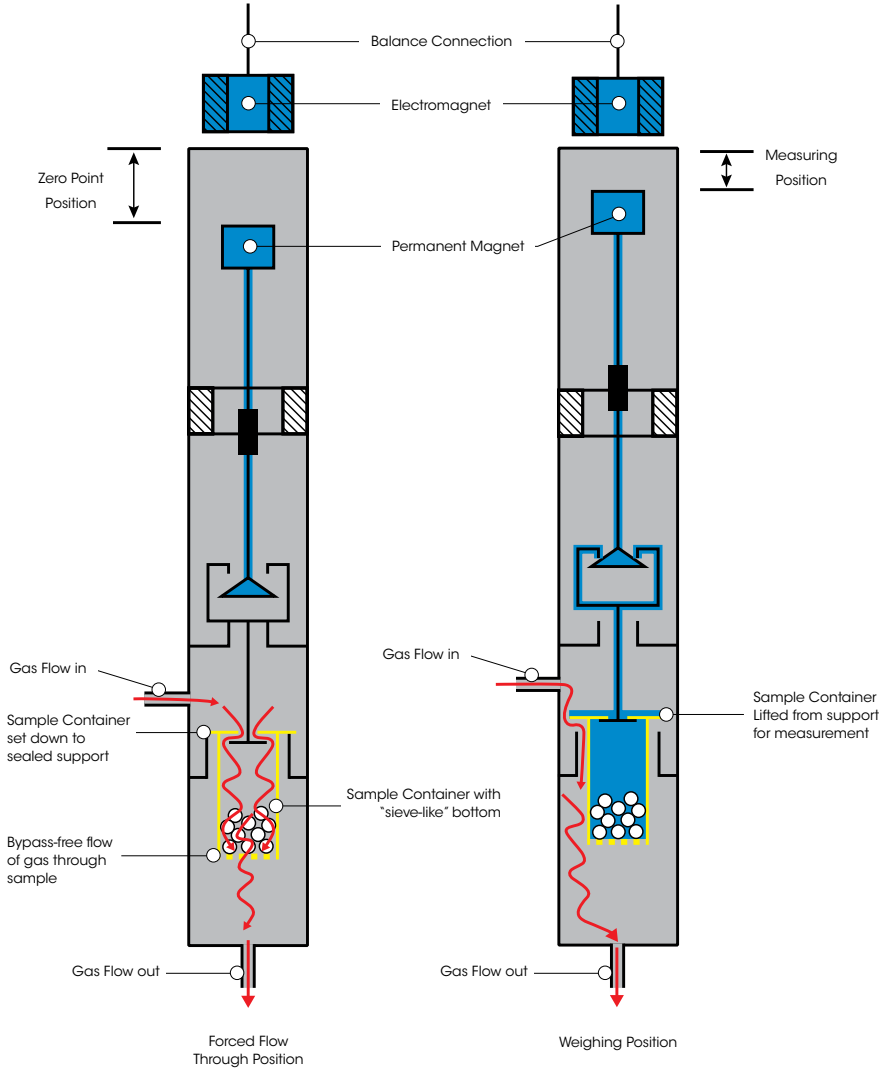
Temperature control

Sample temperature is measured by a thermocouple directly adjacent to the sample inside the reaction gas. Furnace temperature and temperatures in other parts of the reactor are measured with additional thermocouples. A fast PID temperature controller realizes precise temperature control of the sample under all operating conditions.

* Specifications are model-dependent

Cold-Wall Reactor Design





Forced Gas Flow Through Bulk Material Bed

The DynTHERM TGA features a unique forced gas flow through option for applications that require a forced flow of reaction gas through the sample material bed. This capability, which enables mimicking real process conditions of a material in a bulk reactor, is demonstrated in the schematic to the left.

For forced gas flow measurements, the sample is placed in a container with a "sieve-like" bottom and a flanged lid with an opening in the center. When the balance is in the zero point position, the flange of the sample container sits in a rest position on top of a bypass-free support. The sample container is disconnected from the balance and reaction gas is forced to flow into the container from the opening at its top and passes through the sample to finally exit through the "sieve-like" bottom.

The sample is weighed over specified intervals of time by raising the MSB into measuring position, which lifts the sample container from the supports. Once the weight measurement is completed, the sample container is returned to the rest position to start the process again.

HIGH PRESSURE THERMOGRAVIMETRY | SPECIFICATIONS

Product Line	Model	Max. Sample Temperature	Maximum Pressure	Weighing Resolution	Weighing Range / Sample Mass	Reaction Atmosphere
Discovery HP-TGA	75	1100 °C	80 bar	0.1 µg	500 mg / 500 mg	Pure Gas (select and switch between 1 of 3)
	750	1100 °C	80 bar	0.1 µg	500 mg / 500 mg	Pure Gas & Gas Blends (of 3 gases)
	7500	1100 °C	80 bar	0.1 µg	500 mg / 500 mg	Pure Gas & Gas Blends & Gas and Steam Blends (of 3 gases and 1 steam)
DynTHERM TGA	1100-1, LP-G 1100-1, LP-G+V	1100 °C	1 bar	10 µg	20 g / 25 g	Pure Gas & Gas Blends (of up to 5 gases) Pure Gas & Gas Blends & Gas and Steam Blends (of up to 5 gases and 1 steam)
	1700-1, LP-G 1700-1, LP-G+V	1700 °C	1 bar	10 µg	20 g / 25 g	Pure Gas & Gas Blends (of up to 5 gases) Pure Gas & Gas Blends & Gas and Steam Blends (of up to 5 gases and 1 steam)
	1100-50, HP-G 1100-50, HP-G+V	1100 °C	50 bar*	10 µg	20 g / 25 g	Pure Gas & Gas Blends (of up to 5 gases) Pure Gas & Gas Blends & Gas and Steam Blends (of up to 5 gases and 1 steam)
	1500-50, HP-G 1500-50, HP-G+V	1500 °C	50 bar*	10 µg	20 g / 25 g	Pure Gas & Gas Blends (of up to 5 gases) Pure Gas & Gas Blends & Gas and Steam Blends (of up to 5 gases and 1 steam)

*Maximum pressure is temperature dependent

Broadest range of **HP-TGA MODELS** with the **RIGHT SPECIFICATIONS** for **EACH APPLICATION**

DISCOVERY SERIES II QUADRUPOLE MASS SPECTROMETER

The Discovery Series II Quadrupole Mass Spectrometer is a benchtop, quadrupole mass spectrometer designed for chemical analysis of all gases evolved during thermogravimetric analysis experiments. The mass spectrometer is designed by MKS Instruments to specifically interface with TA Instruments thermogravimetric analyzers for seamless integration of hardware and software.

The spectrometer includes a heated stainless steel capillary for efficient transfer of gas products from the TGA furnace/reactor to the MS. Parts per billion (ppb) sensitivity over the mass range 1-300 amu (gas dependent) is achieved with a state-of-the-art quadrupole detection system, including a closed ion source, a triple mass filter and a dual (Faraday and Secondary Electron Multiplier) detector system. This analyzer configuration is selected to optimize sensitivity and long term stability performance.

Control of the experimental parameters and analysis of the mass spectral data is achieved through a user-friendly, recipe-driven Windows® software interface. Data collection can be triggered directly from the TGA software, and the resulting MS data (trend scans) can be combined directly for overlaying with the corresponding TGA results.

Parameter	Performance
Mass range	1-300 amu
Mass Resolution	>0.5 amu
Sensitivity	< 100 ppb (gas-dependent)
Ionization Source	Electron Ionization
Detector System	Dual (Faraday and Second Electron Multiplier)
Sample Pressure	1 atm (nominal)
Data Collection Modes	Bar graph and Peak Jump
Transfer Line	2 meters, flexible
Filaments	Dual, customer changeable
Capillary	Stainless Steel, changeable
Capillary size	I.D. = 0.22 mm
Inputs	Data collection controlled by TGA Trigger

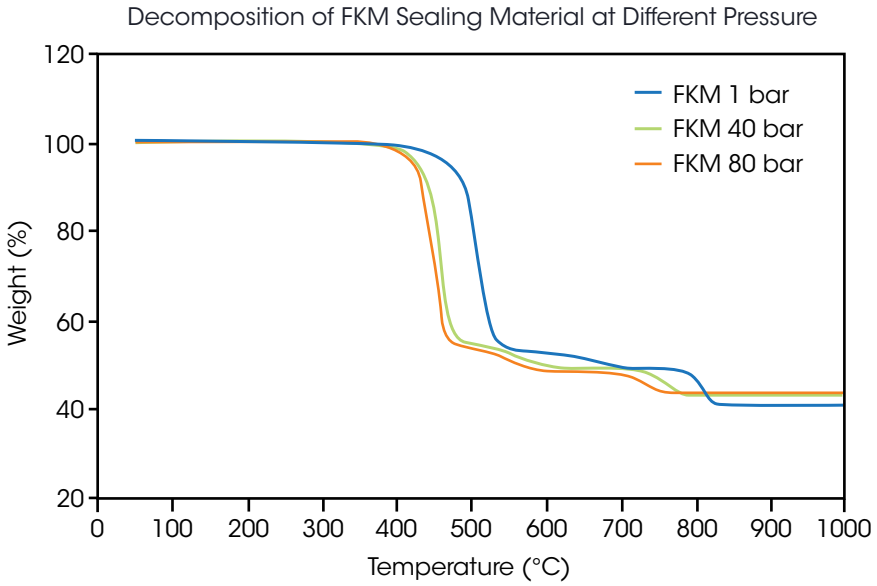
Polymers

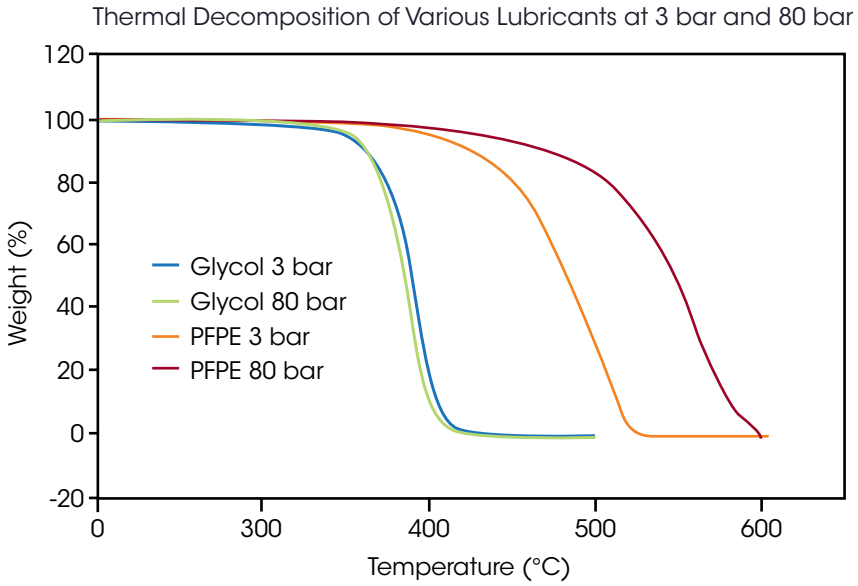
Polymer products are exposed to high temperatures and pressures already in many manufacturing processes like injection molding or 3D printing. Additionally, they are exposed to elevated pressure, aggressive media or steam in countless application areas. The stability and decomposition of polymeric materials under application relevant conditions can be studied by high pressure TGA.

Polymer Sealing Materials

A very sensitive application area is the use of polymer materials for sealing purposes, e.g. as sealant or O-ring type seals in autoclaves or tubing. Many processes in industries like electronics, automotive, chemical or oil & gas require the handling of gases or liquids under pressure. Whenever pressure is involved, a leak due to a failed seal is dangerous and can have severe consequences.

High pressure TGA is a great tool to determine the stability of polymer seals under realistic operating conditions. The figure to the right shows the comparison of the thermal decomposition of an FKM seal for high pressure applications at 1, 40 and 80 bar. The temperature of decomposition at high pressure is reduced by 60 °C. This proves that the FKM seal can be applied only in a reduced temperature range under pressure without failing.





Foaming Agents

Foaming agents are chemical additives for polymers designed to decompose under the release of gases during a polymer production process. This way, polymer foams are created that can be used as packaging materials or as valuable soft and flexible polymer material in many consumer products. To optimize this production process, it is important to understand the generation of gases from foaming agents as a fuction of temperature and and pressure. HP-TGA can provide this data in the form of thermal decomposition profiles in the complete relevant pressure range.

Lubricants

The reliable performance of high quality motor oils and lubricants under pressure is of key importance for automotive engines and countless applications in the chemical, oil & gas and many other industries.

One example are rolling mills that are commonly used in the automotive or metal industry, but also for manufacturing construction products, flooring or furniture. These rolling processes need lubricants that can be used under pressures of 50 bar and above and it is important to understand the lifetime of these lubricants under process conditions.

The diagram to the left shows the thermal decomposition of two commercial lubricants at 3 and 80 bar. While the glycol-type lubricant (polyalkylenglycol oil) exhibits a thermal stability that is quite independent of the pressure applied, the PFPE lubricant (perfluorinated polyether oil) reacts differently: The thermal stability of the PFPE lubricant is clearly higher at 80 bar.

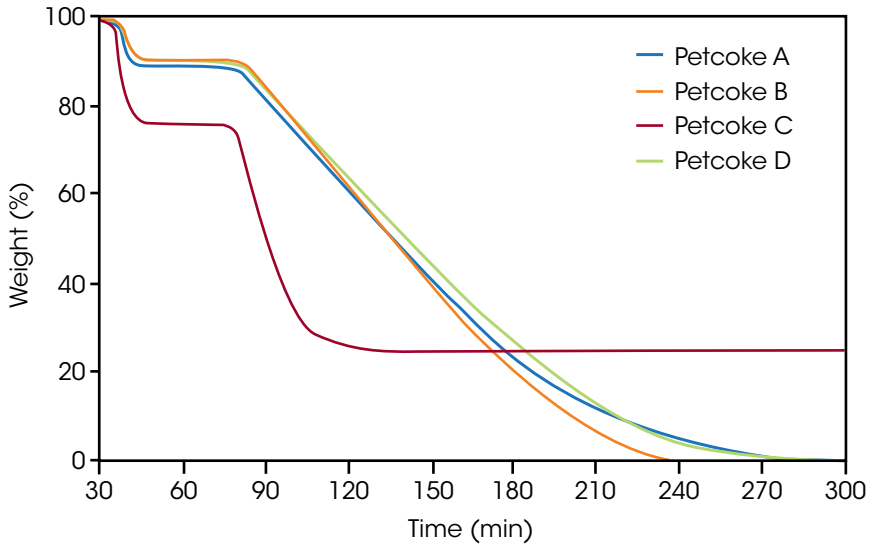
Gasification of Coal, Biomass and Waste

Many processes in the energy sector involve gas reactions under pressure. Gasification, the conversion of coal, biomass, or waste as feedstock into syngas, is a key step in a resource-saving circular economy or for the production of polymers and chemicals. This has been a key application for HP-TGA for many years. HP-TGA is a great tool to optimize gasification processes, because gasification plants usually operate in a pressure range between 10 and 30 bar where they are most energy efficient. In HP-TGA, the most economical and productive reaction conditions for the various feedstocks can be identified easily.

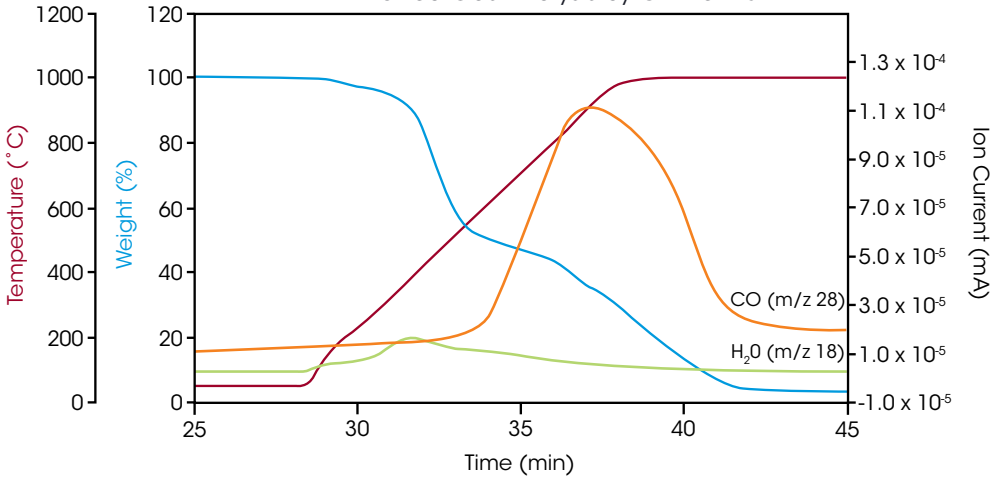
The diagram to the right shows the gasification of 4 different petroleum coke samples at 40 bar. Petroleum coke is a waste product in crude oil refineries and gasification is the only way to use the precious hydrocarbon content rather than simply burning it. Initially, the samples were pyrolyzed with a heating rate of 100K/min to 1100 °C, then 30% of CO_2 were introduced as gasification agent. The reaction follows the Boudouard reaction $CO_2 + C = 2\ CO$ and generates carbon monoxide rich gas. Obviously, sample C reacts quite differently. The much higher weight loss in the initial part of the weight curve indicates a higher content of volatile matter which is released during pyrolysis. Additionally, the residual weight is higher compared to the other samples which is characteristic for the higher ash content of sample C. Hence, the gasification process - which is the main weight change step for the other samples - is much smaller for sample C. This proves that sample C produces a substantially smaller amount of syngas than samples A, B and D.

While the weight change data from the HP-TGA experiment already provides very valuable information about the amount of organic matter transferred into the gasphase and thus, quantifies the syngas production, evolved gas analysis is another source for interesting information. FTIR, GC or online MS can be used to detect the product gases generated in the gasification process. In the graph to the right, online mass spectrometry was applied in a lignite gasification experiment with CO_2 as reactand gas. Two MS traces are shown here: m/z 18 indicates the release of water by drying of the lignite sample in the first section of the temperature gradient. The m/z 28 mass trace represents the generation of carbon monoxide and it can be seen that this signal increases as the reaction temperature reaches the setpoint of 1000 °C. The CO gas generation comes to an end when the carbon content of the lignite is fully consumed and the HP-TGA signal indicates that only the residual ash fraction is left in the crucible.

Gasification of Various Petroleum Coke Samples with CO_2



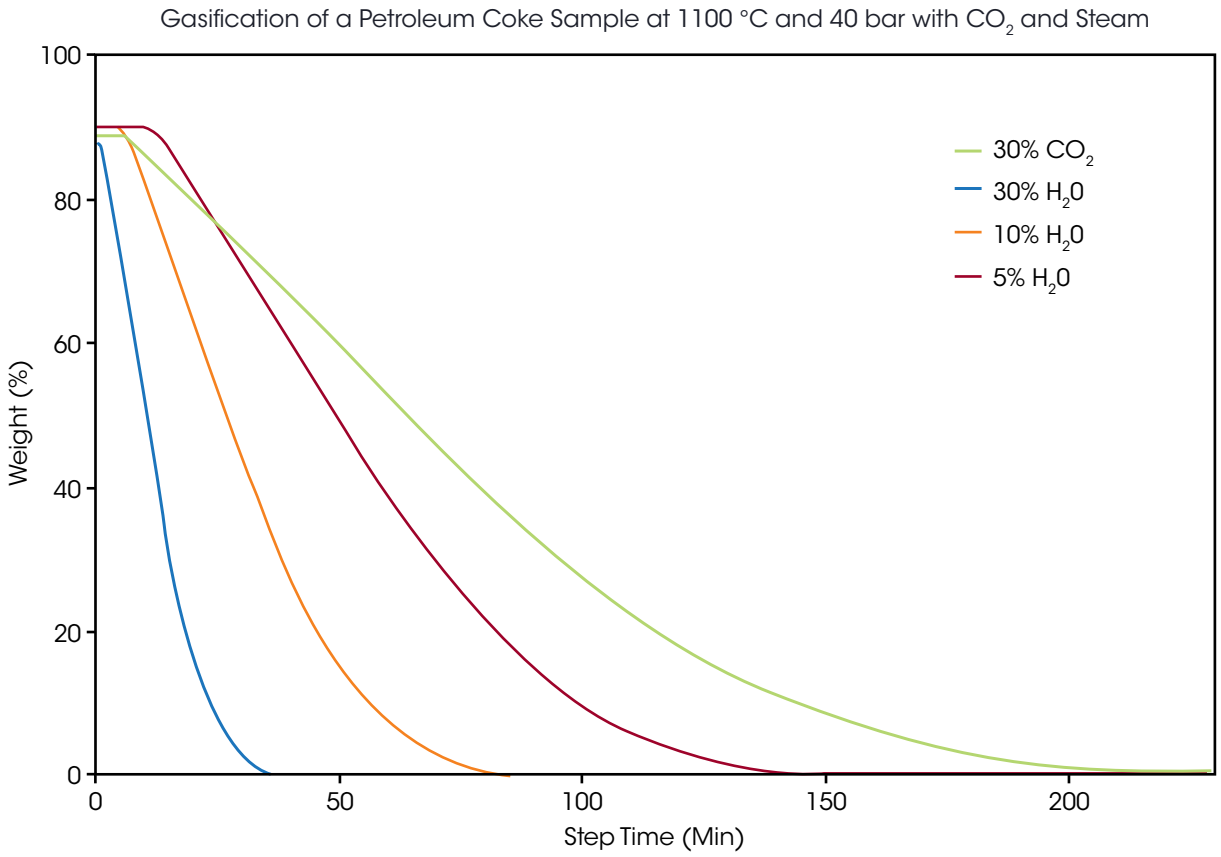
Gasification of Lignite Coal in 30% CO_2 Atmosphere with Evolved Gas Analysis by Online MS



Gasification with Steam

A useful and often applied gasification agent is steam. Steam at high temperature reacts fast with the carbon content of the feedstock material and generates a product gas that contains not only carbon monoxide, but also hydrogen and various hydrocarbon gases depending on the process conditions. The hydrogen and hydrocarbons in the product gas can only be generated if water steam in the gasification reacts with the carbon as hydrogen source.

HP-TGA experiments allow the comparison of various gasification process conditions as can be seen in the graph below: A petroleum coke sample reacted with 30% CO_2 and varying concentrations of 5, 10 and 30% of steam at 1100 °C and 40 bar. Evidently, the highest steam concentration of 30% leads to the fastest gasification kinetics. Reducing the steam concentration in the reaction gas at the same temperature and pressure leads to slower reaction kinetics of the gasification. The slowest kinetics are observed for the gasification in dry reaction gas with 30% CO_2.



CATALYST REACTION STUDIES | APPLICATIONS

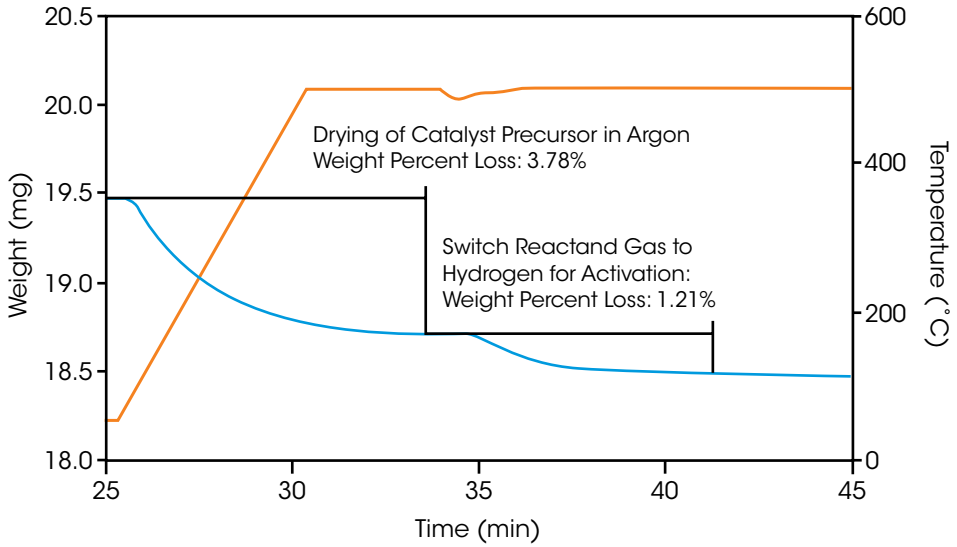
Gas/solid heterogenous catalysis comprises the bulk of catalytic processing: over 90% of chemicals worldwide are manufactured with the aid of solid catalysts. Typically, the gaseous reactants are fed over the catalyst bed, usually at high temperatures and often at high pressures. About 800,000 tons of solid catalysts are prepared and used every year worldwide, but this does not mean that we understand how they work*.

HP-TGA is a great new tool to investigate gas/solid catalytic reactions. With the solid catalyst as sample in the crucible of a HP-TGA system, the reactand gas mixture can be applied under varying conditions of temperature, pressure, gas flow rate or reactand concentration. The reaction yield can be monitored with EGA analysis (online MS is often used) and the catalyst weight is an important indicator for the catalytic reaction process.

Catalyst Activation

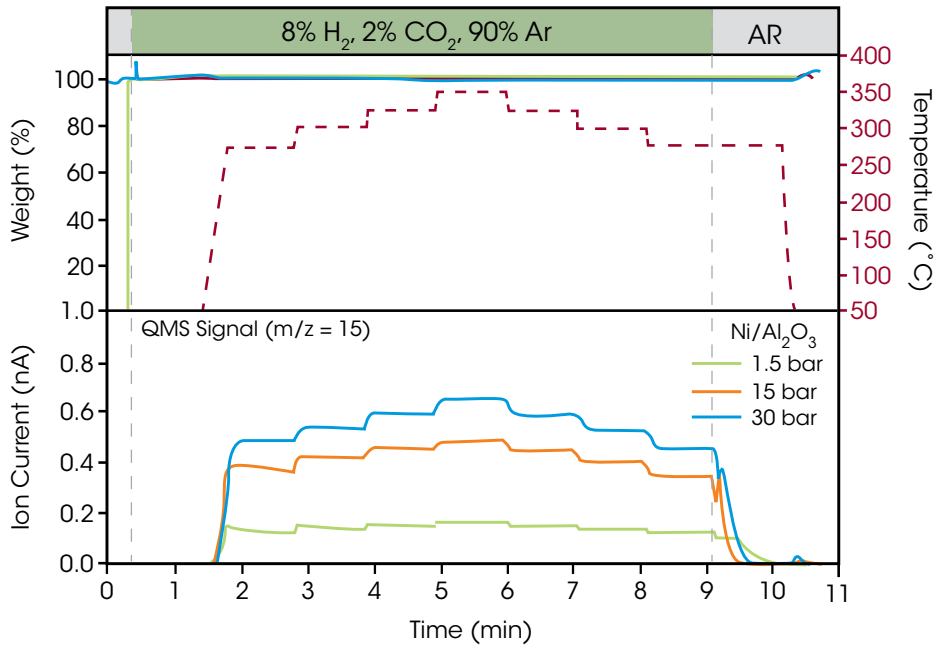
The weight of a catalyst can change during an experiment for many reasons. Catalysts precursors are usually produced from inert carrier materials and metal oxides. During an activation process, the catalyst precursor is dried by heating and then the metal oxide is reduced to generate the active metal. In the diagram to the right, this two step process has been performed in the HP-TGA 75 instrument: a catalyst precursor material with 9% nickel oxide content was dried to constant weight at 500 °C. Then, hydrogen gas was used for reduction to create the active nickel catalyst and the observed weight loss of 1.2% corresponds well with the nickel oxide percentage to indicate complete conversion.

Activation of a Nickel Catalyst with Hydrogen Gas
in a Discovery HP-TGA 75



* Gadi Rothenberg, Catalysis: Concepts and Green Applications, 2017, p 132

Methanation Reaction in HP-TGA with EGA Analysis by Online MS

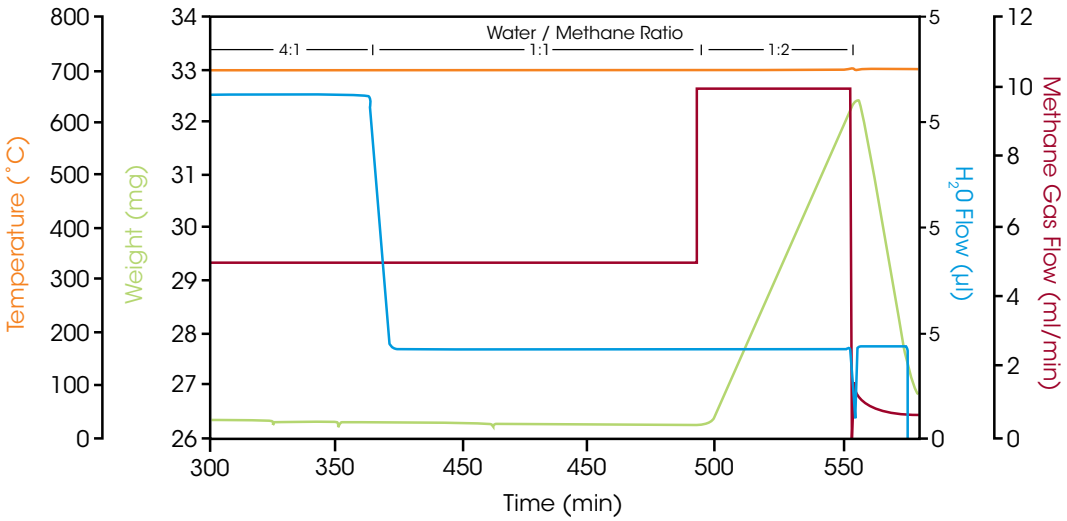


The reaction yield of Methane detected as m/z 15 by the MS changes with temperature between 275 and 350 °C and pressures of 1.5, 15 and 30 bar.

Reaction Yield by EGA Analysis

The activated catalyst was then used for a methanation reaction: 8% of Hydrogen and 2% of CO_2 in the reactand gas were converted by catalytic reaction to form methane and water as reaction products. The upper part of the figure to the left shows how the reaction temperature was adjusted stepwise from 275 to 350 °C. The reaction turnover was measured by online quadrupole mass spectrometry, for three different pressures of 1.5, 15 and 30 bar. The m/z trace 15 shown in the lower part of the diagram indicates the production of methane. This data shows how the reaction yield changes with temperature and pressure. The weight of the catalyst sample was recorded by the HP-TGA and is shown as weight% in the upper part of the diagram. The catalyst weight remained stable over the whole experiment. This indicates that the catalyst is neither deactivated nor are carbon or other residues formed on it.

Steam Reforming Reaction at 10 bar and 700 °C with Catalyst Coking

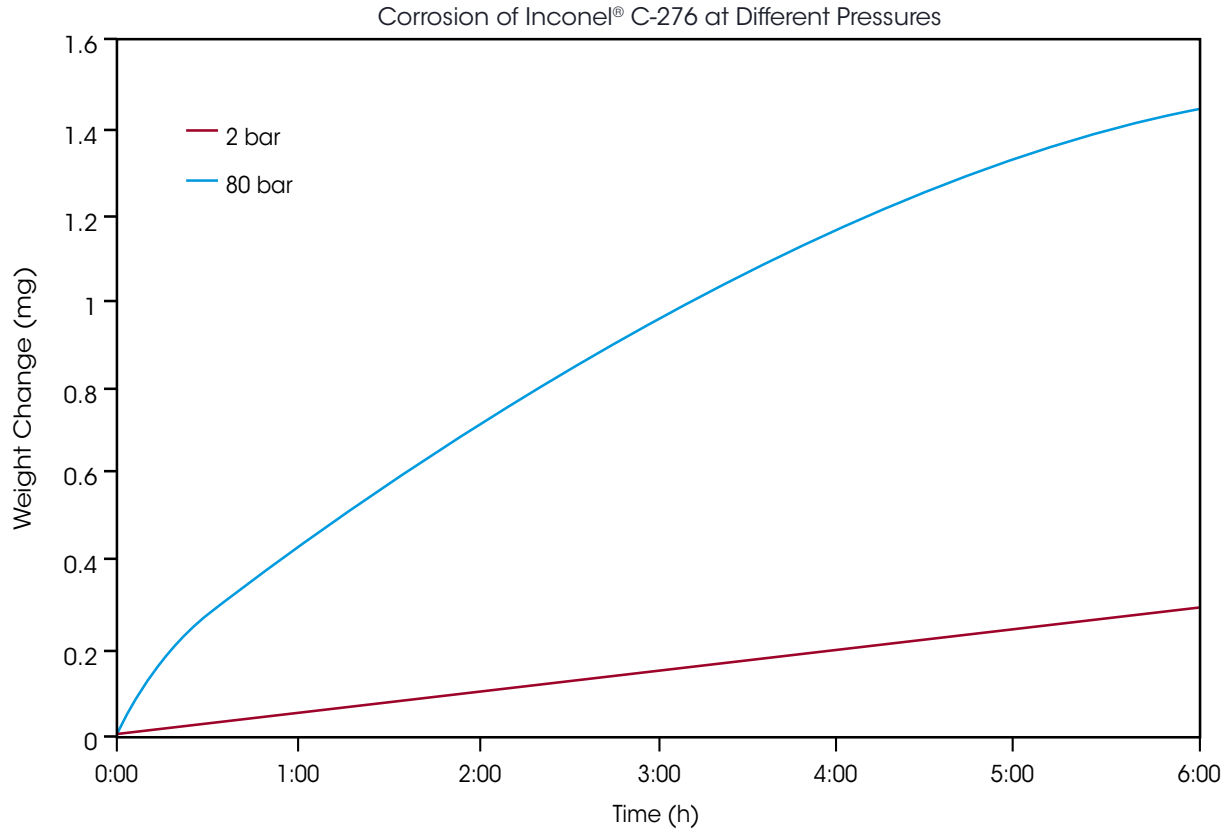


Reaction with Steam and Catalyst Coking

In a steam reforming reaction, a nickel catalyst was used for the generation of hydrogen and carbon monoxide from methane and steam ($CH_4 + H_20 = 3\ H_2 + CO$). In this experiment, pressure and temperature were held constant at 10 bar and 700 °C while the steam to methane ratio was at the beginning. Primarily, the steam to methane ratio was 4:1 and the catalyst weight was approaching a constant value. The weight remained stable even when the ratio was changed to 1:1 by reducing the steam flowrate. Only when the ratio is changed to 1:2 by increasing the methane flowrate, the catalyst weight rapidly increases due to the formation of coke on the catalyst surface. When the methane flow is switched off, the coking process proves to be reversible. This is indicated by the decreasing weight of the catalyst. The weight loss is caused by the oxidation of the coke which was formed on the catalyst by the steam in the reaction gas.

High Temperature Corrosion

Understanding the corrosion resistance of a material is critical for improving technical processes and increasing efficiency. For example, the efficiency of gas or steam turbines and jet engines is directly related to their maximum operation temperature. The maximum temperature is limited by the high-temperature corrosion of the metals and other materials used in the hot zone of the turbine. The mass change of a metal or other material caused by corrosion is generally very small. Additionally, even high temperature corrosion is usually a slow process. The Discovery HP-TGA is ideally suited for such measurements because the exceptional high resolution and accuracy. This allows measurements of small changes in sample mass to be performed in a comparably short period of time. The diagram below compares the mass increase of a Inconel®* C-276 alloy in air at 1000 °C at 3 bar and at 80 bar. The observed weight gain is caused by oxidation of the alloy's surface. The total mass change here is about 287 µg at 3 bar and 1444 µg at 80 bar. As expected, the pressure of the corrosive atmosphere has an influence on the kinetics of, and amount of, corrosion.



* INCONEL® is a trademark of Huntington Alloys Corporation, Huntington, WV 25705, United States of America

TA INSTRUMENTS | COMPLEMENTARY ANALYTICAL INSTRUMENTS

High Temperature Analyzers

TA Instruments is the market leader in thermal analysis and rheology with a broad portfolio of complementary measurement technologies. Some of the instruments which are especially relevant to the high pressure TGA are listed here. These can be applied for measuring material properties in the same applications and workflows.

Discovery SDT 650 – Simultaneous Thermal Analyzer

The combined DSC/TGA instrument simultaneously provides heat flow and weight data at temperatures up to 1500 °C. It is the ideal tool to analyze phase changes like glass transition and melting as well as reactions and decomposition. With its large temperature range and controlled atmosphere capability it provides complementary material data.

DLF 1600 – Laser Flash Analyzer

The Discovery Laser Flash DLF 1600 is an advanced instrument for the measurement of thermal diffusivity and specific heat capacity of materials from room temperature to 1600 °C. With the ability to be operated in a variety of atmospheric conditions, including air, inert gas, or under vacuum, the DLF 1600 can characterize a wide variety of materials including ceramics, carbons, composites, glasses and metals.

DIL - Push Rod Dilatometers

DIL800 series dilatometers measure dimensional changes of materials as a function of temperature in the range up to 1700 °C. They can be used to test a wide range of materials including ceramics, glasses and metals. These dilatometers provide measurements of a wide variety of properties including thermal expansion, sintering, phase transitions, softening point and glass transition temperature.

VIS 413 – High Temperature Viscometer

The VIS 413 rotational viscometer measures the viscosity of melts at high temperatures up to 1750 °C. The unique capability to be operated in vacuum and inert as well as reactive gas atmospheres allows analysis of the flow behavior of oxygen sensitive sample materials. Applications include viscosity measurements of molten glass, ceramics, metals, coal ash and slag.

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