

Gas Analysis with a Mass Spectrometry Twist



Eric S. Oxley, Ph.D.

Innovation...



with Integrity



Gas Analysis with a Mass Spectrometry Twist



General Topics

- Hydrogen...a pesky little element
- Automotive industry...driving technology
- Limitations of existing technology
- Bruker's advancement of the industry



Dr. Eric S. Oxley

Bruker AXS

Product Manager, North America – Gas Analysis

Bruker Gas Analysis

Primary Portfolio



G4 PHOENIX DH



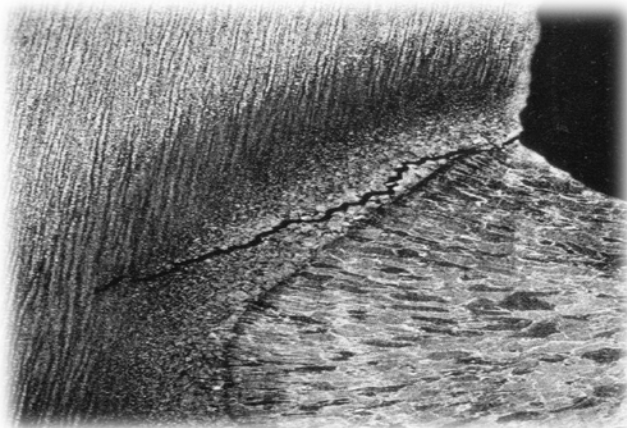
G8 GALILEO ON/H

G4 ICARUS CS HF



Bruker Gas Analysis

Hydrogen-Induced Failure



Controlling hydrogen content is paramount...

- Hydrogen has a negative impact on the physical properties of metals
- Any form of hydrogen can be detrimental
 - Trapped hydrogen in lattice
 - Mobile diffusible hydrogen
- Leads to weakening of the workpiece and the formation of cracks and pores
- Companies are investing in Bruker technology to help prevent these defects
- Instruments are being incorporated into:
 - Material Development
 - Process Control
 - Quality Assurance

Bruker Gas Analysis

Diffusible Hydrogen



Hydrogen-induced embrittlement
Hydrogen-assisted cracking
Flake formation
Pickling/blistering

Such a pesky little element...

- Small atomic diameter of hydrogen allows easy diffusion within metal lattice
- Introduced during fabrication, processing, and even after production is complete
 - Melting
 - Casting
 - Forging
 - Welding
 - Corrosion
- Once within lattice it has great mobility via interstitial diffusion
- Large pockets of high-pressure molecular hydrogen collect in metal, especially within grain irregularities
- Hydrogen not bound to lattice (diffusible hydrogen) can liberate and leave voids

Bruker Gas Analysis

High-Strength Steel



Automotive industry "drives" new tech...

- Auto companies, and suppliers of high-strength steel, are investing in cutting-edge hydrogen assessment technology
- Emphasis on minimizing fuel consumption while maintaining structural integrity
- Pushes development of high-strength low-alloyed steel to reduce vehicle weight and maximize fuel economy
- Especially susceptible to hydrogen-induced failure because it shows a high level of residual stress after cold forming
- *Example:* When steel is shaped to form contour of auto body

Bruker Gas Analysis

Diffusible Hydrogen Assessment



G4 PHOENIX DH

- Dedicated **Diffusible Hydrogen** analyzer
- Analyzes steel sheets, weld coupons and many other sample configurations
- Rapid-heating/cooling, large infrared (IR) furnace for samples up to 30mm
- Utilizes a stable thermal conductivity detector (TCD) for measuring hydrogen
- Features direct sample analysis
- Conforms to *AWS A4.3* and *ISO 3690*
- Rapid, automatic 10-pt gas calibration

Bruker Gas Analysis

Outstanding Versatility



The G4 **PHOENIX** DH allows you to choose a sampling method...

Analyze samples rapidly with integrated hot extraction furnace



*Collect DH with degassing canisters (Oerlikon/Yanaco) and introduce into the **G4 PHOENIX***



Bruker Gas Analysis

"Complete" Hydrogen Assessment



G8 GALILEO ON/H

- Rapid **O**xygen, **N**itrogen, and **H**ydrogen assessment
- Utilizes TCD for hydrogen measurement
- HTC (High Temperature Configuration)
- Full automation available
 - Crucible and Sample loading
 - Furnace cleaning
- All-in-one hydrogen assessment
 - Total Hydrogen (or Residual Hydrogen)
 - Diffusible Hydrogen
- Direct temperature control of sample analysis via optical pyrometer

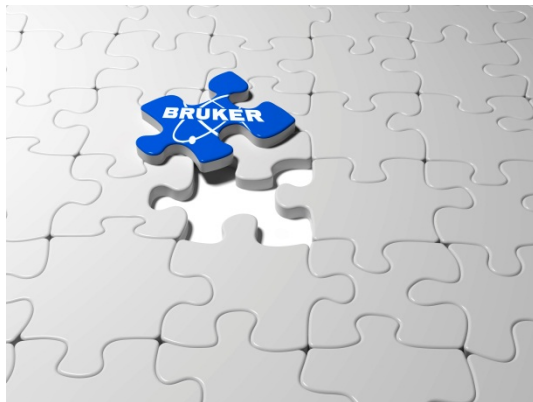
Bruker Gas Analysis

Conventional Techniques



Current technology shows limitations for some applications...

- Instruments with TC or IR detection are generally sensitive to the parts-per-million (ppm) range
- Thin nature of high-strength steel used in auto industry can be compromised by less than ppm-levels of hydrogen
- Instrumentation with better sensitivity is required
- Fortunately Bruker has the missing piece for this market...



Bruker Gas Analysis

Advancing the Industry



Bruker's exclusive solution...

- Bruker has broken the sensitivity barrier by expanding their portfolio
- Our **G4 PHOENIX** and **G8 GALILEO** analyzers have been coupled with external mass spectrometers
- Mass spectrometer acts as a secondary detector
- Improves hydrogen detection limits by about an order of magnitude compared to TCD and IR
- Maintains analysis procedures and other benefits of using the **G4 PHOENIX** and **G8 GALILEO**

Bruker Gas Analysis

Advancing the Industry



Bruker's new Thermal Desorption Mass Spectrometry (TDMS) product line...



G8 GALILEO ON/H MS



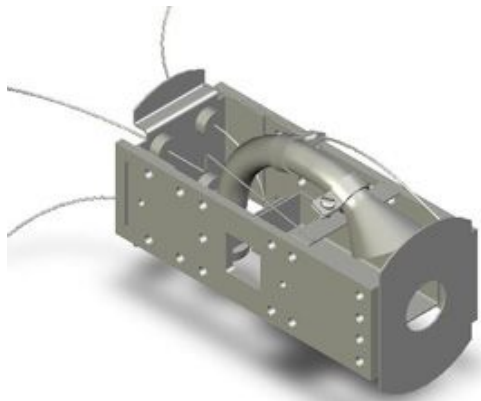
G4 PHOENIX DH MS

Bruker Gas Analysis

Advancing the Industry



Quadrupole Mass Analyzer



Channeltron Detector

Bruker's TDMS features...

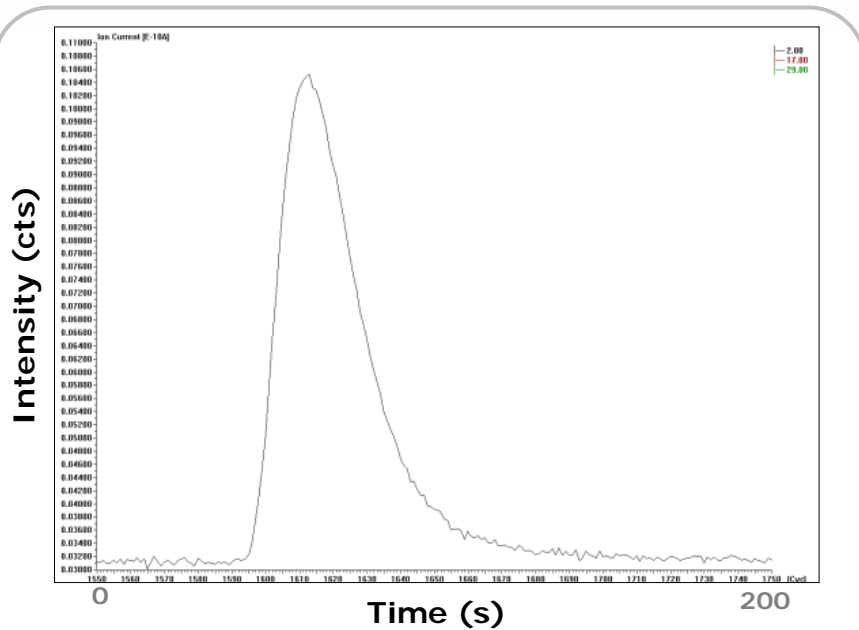
- **Quadrupole** mass analyzer tuned for selection of hydrogen ions (e.g., m/z 2)
- **Channeltron** detector optimized for hydrogen sensitivity
- Maintains **Oxygen & Nitrogen**, and **Hydrogen** via TCD, detection capabilities
- Measurement of all hydrogen forms:
 - **Diffusible Hydrogen**
 - **Total (or Residual) Hydrogen**

Bruker Gas Analysis

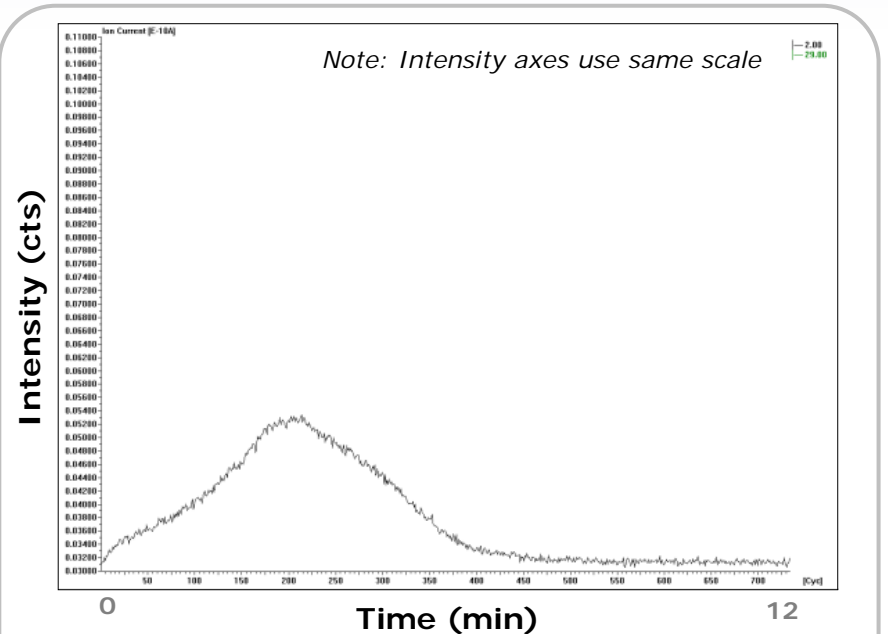
Mass Spectrometer Signals



Typical signals with G4 PHOENIX DH MS:



- Gas dose aliquot of 5% H₂ in N₂ from gas calibration unit
- Approx. 0.5021 mL H₂
- Absolute H₂ content: **2.1 µg**



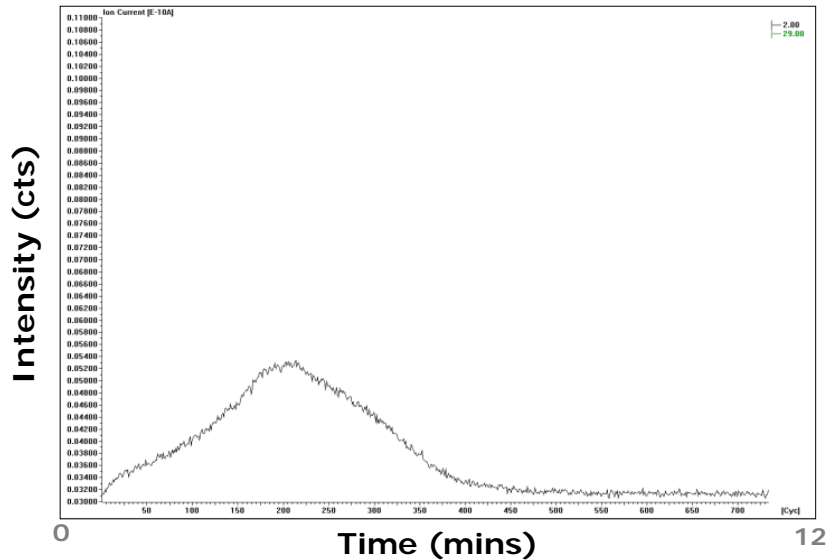
- Steel sample (50mm x 20mm x 1.3mm)
- Temperature ramping: 25°C – 900°C, 60min
- Sample weight: 9.7214g
- H₂ concentration: **0.43 µg/g (0.43 ppm)**

Bruker Gas Analysis

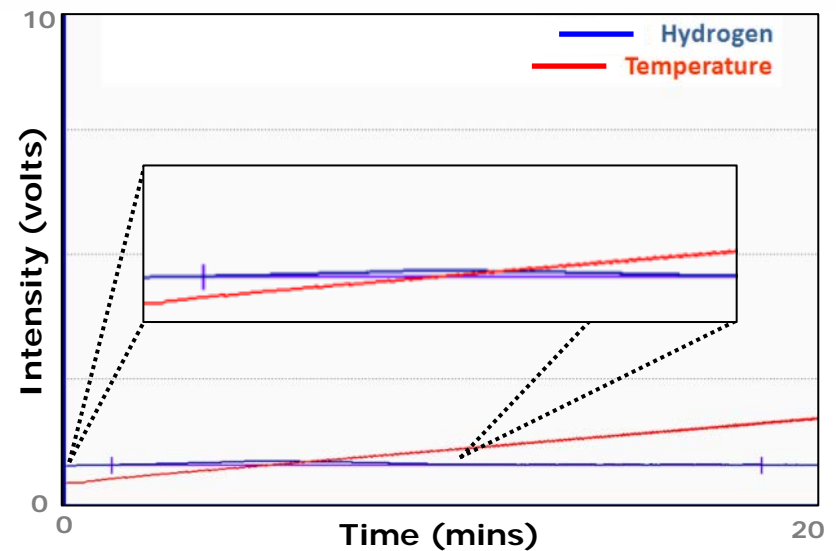
Thermal Desorption Comparison



MS output from G4 PHOENIX DH-MS analysis



TCD output from G4 PHOENIX DH-MS analysis



- Signals collected from same analysis
- Steel sample (50mm x 20mm x 1.3mm)
- Temperature ramping: 25°C – 900°C, 60min
- Sample weight: 9.7214g
- H₂ concentration: **0.43 µg/g (0.43 ppm)**

Bruker Gas Analysis

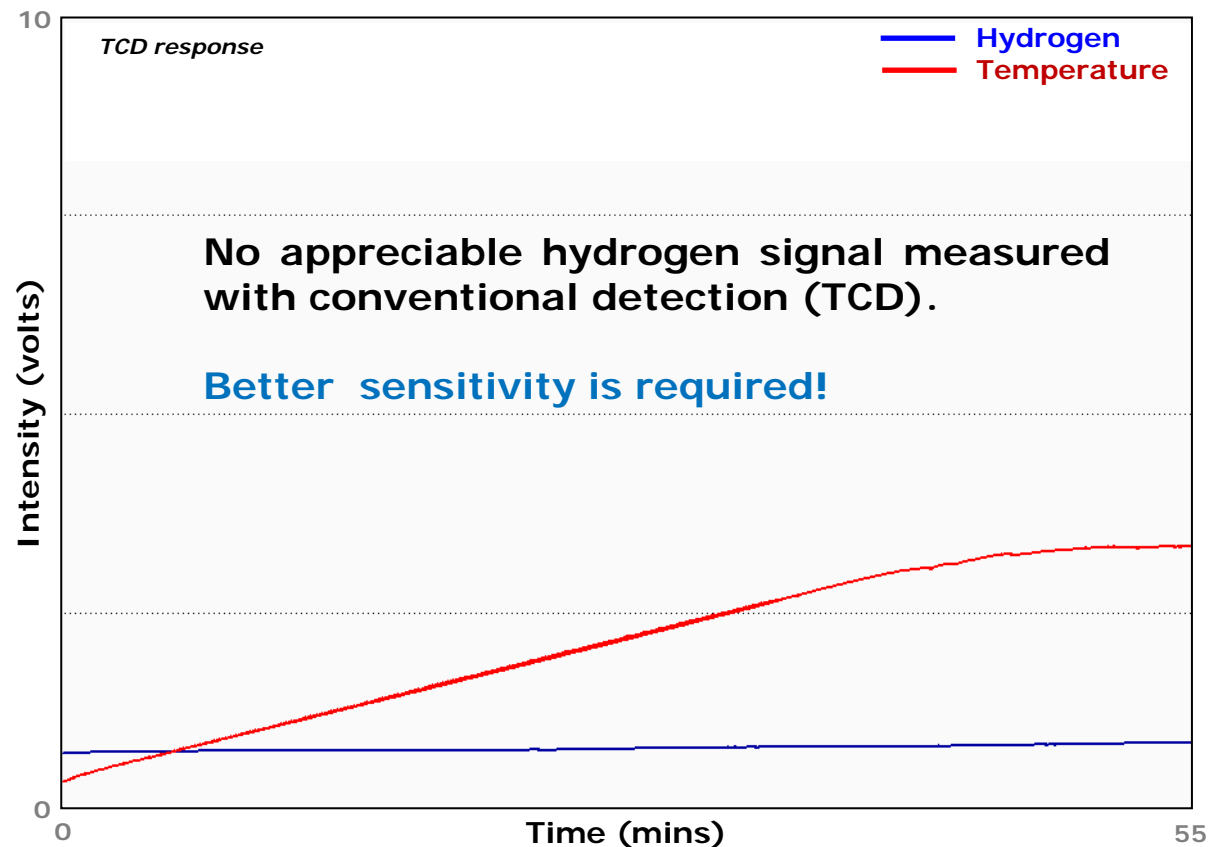
Detection Limits



Finding the limits of hydrogen detection with conventional detection...

Analysis Parameters

- Steel sample after galvanization and dezincification
- 50mm x 20mm x 1.3mm
- Temperature ramping: 25°C – 900°C, 60min
- Sample weight: 12.8433g
- H₂ concentration: **0.043 µg/g (43 ppb!)**



Bruker Gas Analysis

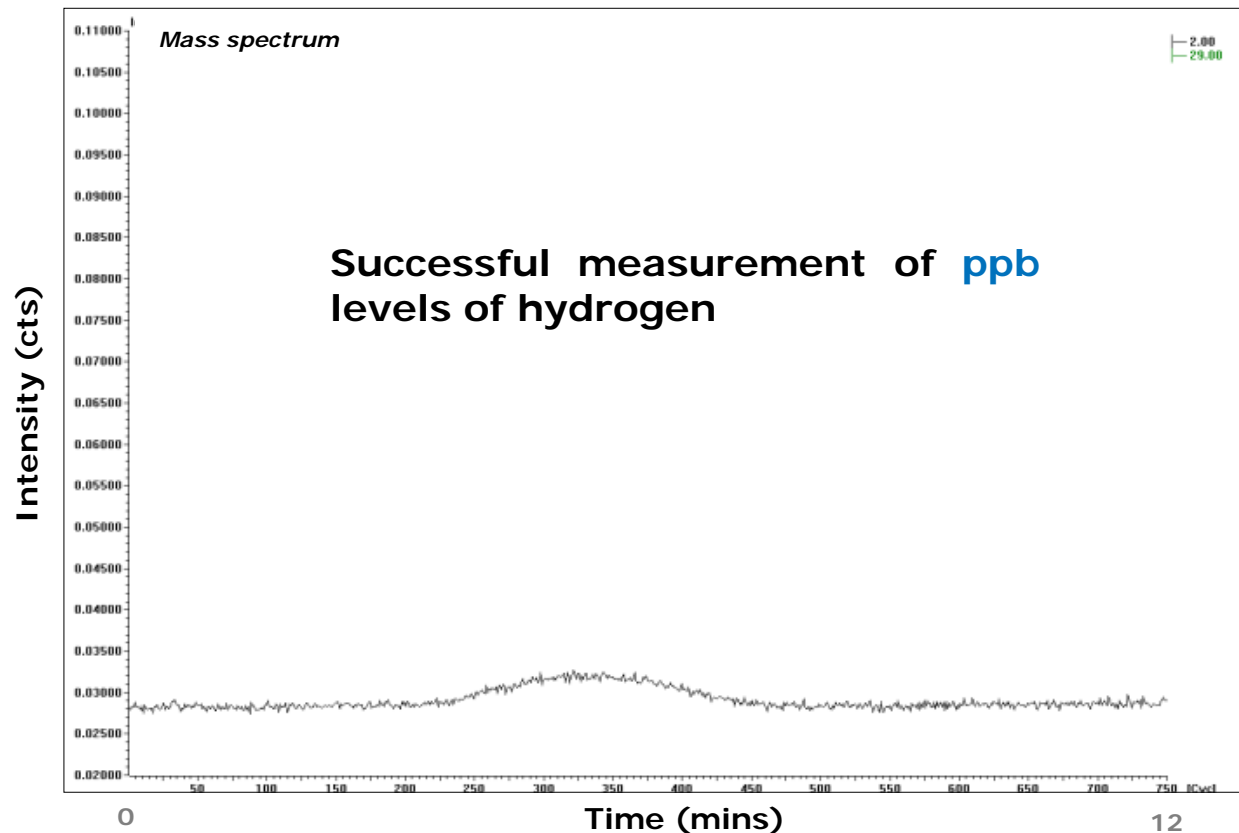
Outstanding Detection Limits



Discovering the superior sensitivity of Bruker's TDMS...

Analysis Parameters

- Same analysis as previous example
- Steel sample after galvanization and dezincification
- 50mm x 20mm x 1.3mm
- Temperature ramping: 25°C – 900°C, 60min
- Sample weight: 12.8433g
- H₂ concentration: **0.043 µg/g (43 ppb!)**



Bruker Gas Analysis

Additional Literature



FIRST Newsletter

May 2012

Ultra-low Hydrogen Detection in Steel: Utilizing Mass Spectrometry to Extend the Boundaries of Traditional Gas Analyzers

By Dr. Eric S. Oxley¹, Dr. Heinrich Stremming² and Dr. Peter Paplewski²

¹ Bruker Elemental, Billerica, MA USA

² Bruker Elemental, Kalkar, Germany

Overview

The principles and applications of gas analysis, including the use of oxygen-assisted combustion for carbon/sulfur assessment and inert gas fusion (IGF) for oxygen/nitrogen/hydrogen determination, date back many years. While improvements in these techniques are routinely made with each new product cycle, typically these are incremental advancements such as a slight reduction in analysis time. Bruker, however, has made a substantial step forward with their introduction of "hybrid" gas analyzers that utilize mass spectrometry to extend the detection limits of "traditional" gas analysis down to parts-per-billion levels.

Hydrogen-induced Failure in Steels

Hydrogen is known to have a considerable negative impact on the physical properties of steel, sometimes resulting in the complete failure of crucial mechanical components. As such, many companies invest in Bruker's gas analyzer technology that can provide information on the hydrogen content (in addition to oxygen/nitrogen, and carbon and sulfur analyzers, if needed) for incorporation into their material development, process control and quality assurance departments.

One particular sector that places emphasis on the assessment and control of hydrogen content is the automotive industry. The initiative to minimize fuel consumption by weight reduction has forced automakers to utilize thin, high-strength steel to

reduce the overall vehicle weight. Unfortunately the very nature of this low-alloyed, high-tensile strength material makes it susceptible to residual stresses and cracking.

The primary reason for the stress and cracking can be attributed to hydrogen embrittlement. Because hydrogen atoms are so small they can easily diffuse into the metal lattice during fabrication and processing. After penetrating the surface hydrogen atoms can combine and accumulate within the voids of the lattice and form "large" pockets of molecular hydrogen with a high internal pressure. If the accumulated hydrogen is significant enough the metal can crack at these locations when sufficient stress is applied (Figure 1), such as when it is formed into the contour of the automotive body.

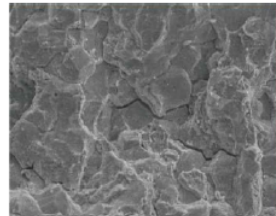


Figure 1: Embrittlement of steel microstructure as a result of exposure to hydrogen.

Traditional Bruker Gas Analyzers

Much to the delight of companies throughout the world Bruker offers instrumentation to accurately and rapidly assess the hydrogen content in steels (along with many other metal-based samples). Even different forms of hydrogen can be independently evaluated and reported, including both diffusible and total hydrogen.



Application Note

Hydrogen Determination in High Strength Steel



G8 GALILEO ON/H



G4 PHOENIX DH

Carrier Gas Fusion and Hot Extraction Method
with Thermal Conductivity Detection and
Mass Spectrometer

Bruker Gas Analysis

Product Support



Full Demo Laboratory

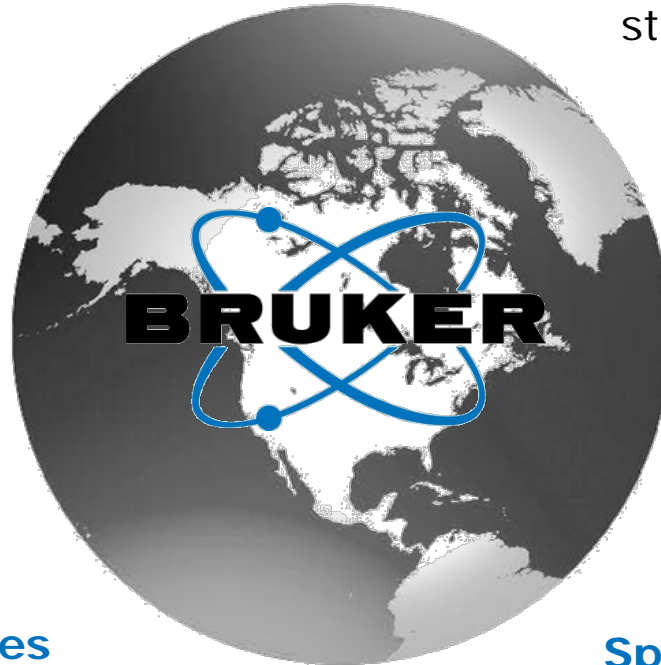
Hands-on demonstrations and training

Consumables

Compatibility with industry-standard consumables

Product Specialists

Sample application support



Service

Multiple service partners distributed throughout US, Canada and Mexico

Application Notes

Specific guidelines for many applications

Spare Parts

Ship from North American Bruker distribution centers

Bruker Gas Analysis

For Additional Information



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Bruker Gas Analysis

Q&A Session



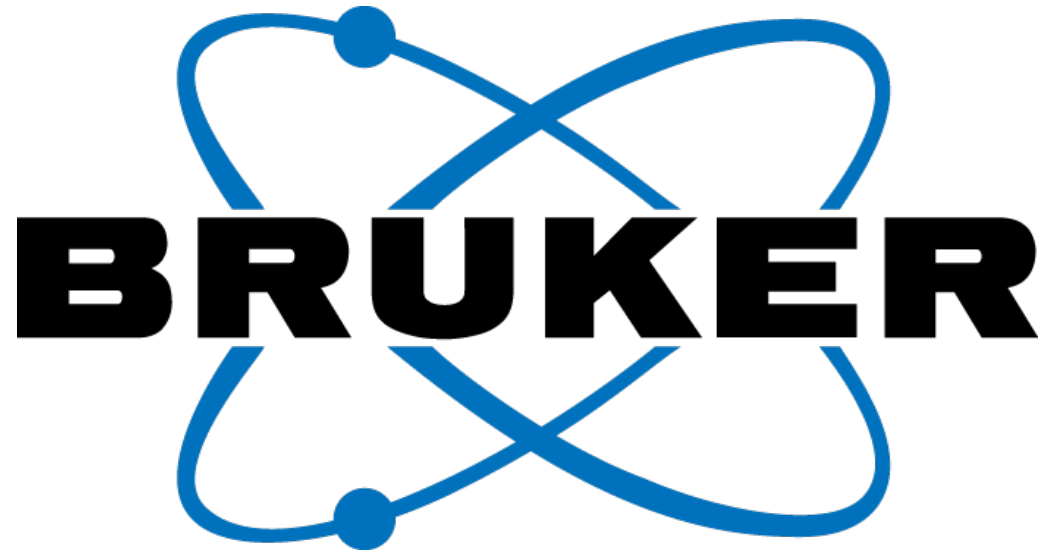
Thank you for participating!

If you have any questions, please submit them using the "Q&A" window on the right side of your WebEx viewer.

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