MarqMetrix measurement products and solutions, widely deployed across multiple industries from oil and gas to food, allow companies to make faster, more informed decisions.

**MarqMetrix corporate focus:**
- **Process and product improvement** through customized optical measurement and control solutions
- **Multivariate data analysis** and cloud based tools for real-time monitoring, data fusion, visualization and control
- **Products and sensors**
  - Raman BallProbe™ uses patented spherical lens technology.
  - MOOS™ MarqMetrix Optical Oxygen Sensor performs equally well in jet fuel, wastewater, beer, blood, etc.
  - Wireless sensing platforms for system health management
Sensor Development & Deployment

- **Design** – instruments and sensors
- **Develop** – optimize for application, field or process
- **Optimize** – thoroughly assess performance in environment or application
- **Deploy** – apply in field or process applications

Example development and deployment of a sensitive and selective Raman instrument for measuring chemical signatures on the ocean floor at > 300 Bar and > 400°C
Applied Optical Sensor Applications

- Oil/fuels/petrochemicals
- Pharmaceuticals/chemicals
- Food quality and safety
- Polymers/coatings
- Fermentation/biotech
- Cellular/tissue
- Oceanography/environment
Applied & Process Raman Spectroscopy

Raman Capable of Measuring:
- Liquids
- Gases
- Solids
- Powders
- Mixed Composition (Slurries, Suspensions, Polymers)

Advantages:
- Little or no sample preparation is required
- Water is a weak scatterer
- Robust, stable and sensitive equipment
- Fiber optics enable remote analysis
- Excellent for chemical fingerprinting
MarqMetrix patented Raman Ballprobe™ technology enables effective process measurements due to the:

- Rigid and durable design: resistant to high temperature, pressure and thermal shock
- Excellent corrosion resistance thanks to the use of chemically inert materials
- Analysis being performed on the ball lens surface providing low sampling error, focus-free analysis and excellent performance in flow
- Non-fouling nature of the probe due to the round lens interface
- No moving parts, constant focal length and reproducible sample volume
- Probe is **ALWAYS** aligned when in contact with sample
- Effective sampling of liquids, slurries, powders, pastes, gasses and solids
MarqMetrix BallProbe™ Product Line

- Outside Diameters: 0.5”, 0.25”, 0.125”
- Made with high purity UV-grade sapphire ball lenses
- Hastelloy or stainless steel housing
- Std. working distance:
  - 400 μm in air
  - 550 μm in water
- Compatible laser wavelengths: 400-1500 nm
- Operating Temperature:
  - > 300° C (> 600 ° F)
- Operating Pressure:
  - > 300 bar (> 4500 psi)
Custom BallProbes™

Probe Customization:
- Lengths, widths, diameters
- Materials
  - Metals
  - Ceramics
  - Plastics
- Specifications:
  - Temperature
  - Pressure
  - Corrosion
- Adaptors to fit any commercial fiber optic probe or handheld instrument
- Commercial or OEM offerings
Laser-Induced Breakdown Spectroscopy (LIBS)

- Remote elemental analysis with no sample preparation
- Fiber-optic delivery or long range delivery of laser by telescope for remote analysis
- Laser-induced plasma ablates and super heats samples to provide elemental composition of sample

Analysis of ibuprofen tablet
- Depth profiling of tablet allows analysis of coating and substrate
- Laser readily absorbed by tablet
MarqMetrix O & G LIBS Applications

- Analysis of raw crudes for vanadium, nickel and nitrogen content
- Analysis of catalyst beds for contamination and deactivation by metals or metal complexes
- Analysis of polymers and polymerization catalysts
- Assessment of corrosion in pipes, fittings and valves
Current Optical Sensors

- Oxygen
- Moisture
- Ammonia
- Hydrogen
- Common Solvents
  - Alcohols
  - Esters
  - Amines
- Chlorinated Organics
- Organic Hydrocarbons (BTEX)
- Carbon Dioxide (in development)
- Hydrogen Sulfide (in development)
- Custom chemical sensors
Fiber Optic Sensor Advantages

• Fast response
• Reversible
• Inexpensive
• Stable
• Low Power
• Sensitive
• Small foot print
• Chemically Robust
• Disposable sensing tips
• Wireless and USB comms.
• Tailored to different sensor requirements
MarqMetrix Optical Oxygen Sensor (MOOS™)

Sensor Applications

- Petroleum production
- Chemical industrial processes
- Biological processes
- Ocean environmental monitoring
- Environmental monitoring
- Atmospheric monitoring
- Medical O₂ blood and respiration
- Pharmaceutical production
- Food production and preservation
- Industrial water processing
- Fuel O₂ intake for engine performance
- Anaerobic environment monitoring
Low Concentration O₂ Sensor in Water

- $R^2 = 0.99964$
- 3 Latent Variables
- RMSEC = 0.27879
- RMSEP = 0.29719
- Calibration Bias = -3.187e-015
- Prediction Bias = -0.068453

5 replicates at each concentration
Concentration range: 1 - 38 μmol/L

1 μmol/L = 32.5 ppb
Oxygen Analysis in Jet Fuel A Vapor

5 replicates at each concentration
Range: 0 – 0.25 mole fraction O₂

$R^2 = 0.999$
3 Latent Variables
RMSEC = 0.0019956
RMSECV = 0.0025969
Calibration Bias = 4.1633e-16
CV Bias = -0.0001148

Measured Oxygen Mole Fraction
Predicted Oxygen Mole Fraction
Chemical Sensor Problems:

• Physical Destruction
  – Membranes are dissolved or delaminated in harsh solvent conditions

• Chemical Destruction
  – The chemistry of the sensor is altered by exposure to solvent and no longer performs as expected

• Leaching
  – The sensing compound leaches out of the sensing membrane

MarqMetrix Solution:

• Sensing compound can now be encapsulated in nanoparticles:
  – Several synthesis methods for nanoparticles allow control of particle size and composition
  – Nanoparticle structure allows diffusion of gas and inhibits solvent access to sensing compound in both gases and liquids

• Method is highly reproducible and scalable

• Optical oxygen and hydrogen sulfide sensors can operate in pure hydrocarbons for extended periods
Nano-encapsulation Protects Sensors

Without Encapsulation:
Sensors last less than a minute in acetone

sor Destruction
$T_{1/2} = 3$ Seconds!

With Encapsulation:
Sensors last for weeks in acetone

Refractive Index Change
Multivariate Data Analysis & Data Fusion

**Concept:**

- **Surround a chemical problem or process with complimentary and orthogonal tools to extract a greater quantity of information than each tool individually provides**

- In most cases the complimentary and orthogonal measurements are already collected throughout a production cycle

- Multi-instrument analysis also allows for inferential modeling of attributes not directly measured by the instrumentation
  - Physical properties (density, viscosity,...)

- Use of data fusion can increase the information extracted from these measurements and therefore increase the value of the measurement
Applications to O & G

- Analysis of crude samples from around the globe to assess quality and value
- Analysis of distillates for product quality, physical attributes and process control
- Application of specified sensor/instrument suites to determine chemical and physical properties of O & G samples
- Developed multivariate data fusion algorithms to accurately quantify chemical and physical properties
Data Fusion Procedure

Data Fusion Model Results

Comparison of Individual Models to Fused Model

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Raman</th>
<th>IR</th>
<th>NMR</th>
<th>Fused</th>
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</thead>
<tbody>
<tr>
<td>°API</td>
<td>1.96%</td>
<td>1.85%</td>
<td>0.477%</td>
<td>0.237%</td>
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<tr>
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<tr>
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<td>0.708%</td>
<td>0.463%</td>
<td>0.063%</td>
<td>0.03%</td>
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</tbody>
</table>
Prediction of Cloud Point in ULS Diesel

- A series of Ultra Low Sulfur Diesel samples were analyzed using online Raman spectroscopy in a processing facility.
- 13 quality assurance assays of the diesel samples were collected, these included values such as density and cetane number.
- Without data fusion the model error was 1.97°C for cloud point.
- After application of the data fusion algorithms developed at MarqMetrix the error was reduced to 1.24°C a reduction of 37%.
Cloud Point Modeling Results

Predictions of Cloud Point from Medium Level Data Fusion

$R^2 = 0.964$

2 Latent Variables

RMSEC = 0.9693°C

RMSECV = 1.2442°C
Data Fusion Value Proposition

• The use of data fusion within petrochemical applications has lead to:
  – Characterization of chemical and physical quantities Crude Oil
  – Determination of value based properties of Crude Oil distillates
  – Prediction of the cloud point and other metrics of ULSD

• Higher order data fusion allows for the combination of multivariate (instruments) and univariate (sensors) for increased model performance

• Due to the combinatorial advantage, higher order data fusion opens the doors to a massive number of potential applications including
  – Process control
  – Quality assurance
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