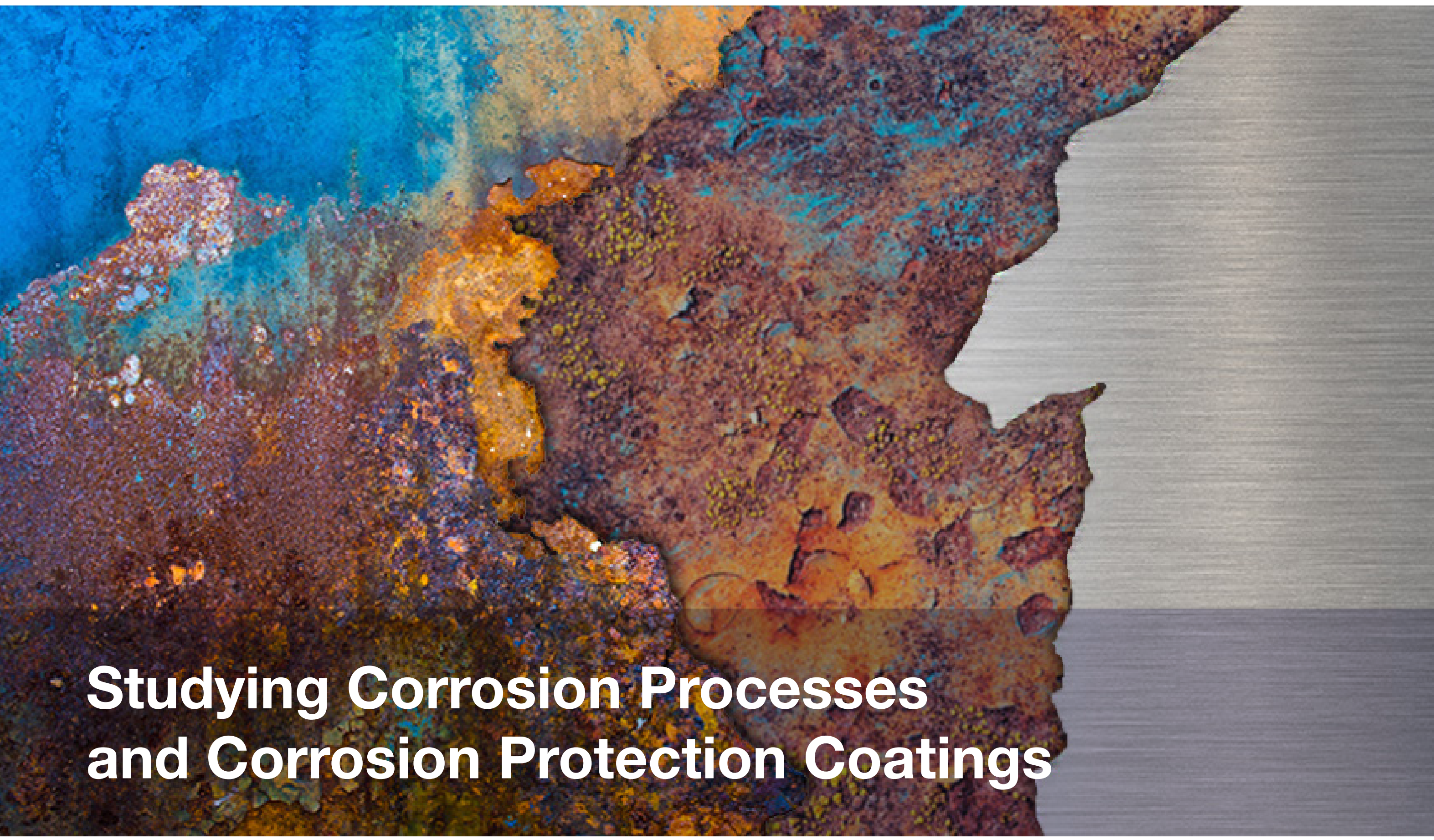
HORIBA



Studying Corrosion Processes and Corrosion Protection Coatings

www.horiba.com/corrosion

The study of Corrosion

Corrosion, a natural process, is a major issue in material choice and design, and a challenge for protection engineering.

Corrosion is the gradual deterioration of a material, usually metallic, due to chemical reactions with its environment. This results in material weakening, surface properties changes and performances degradation.

What causes corrosion and where does it happen?

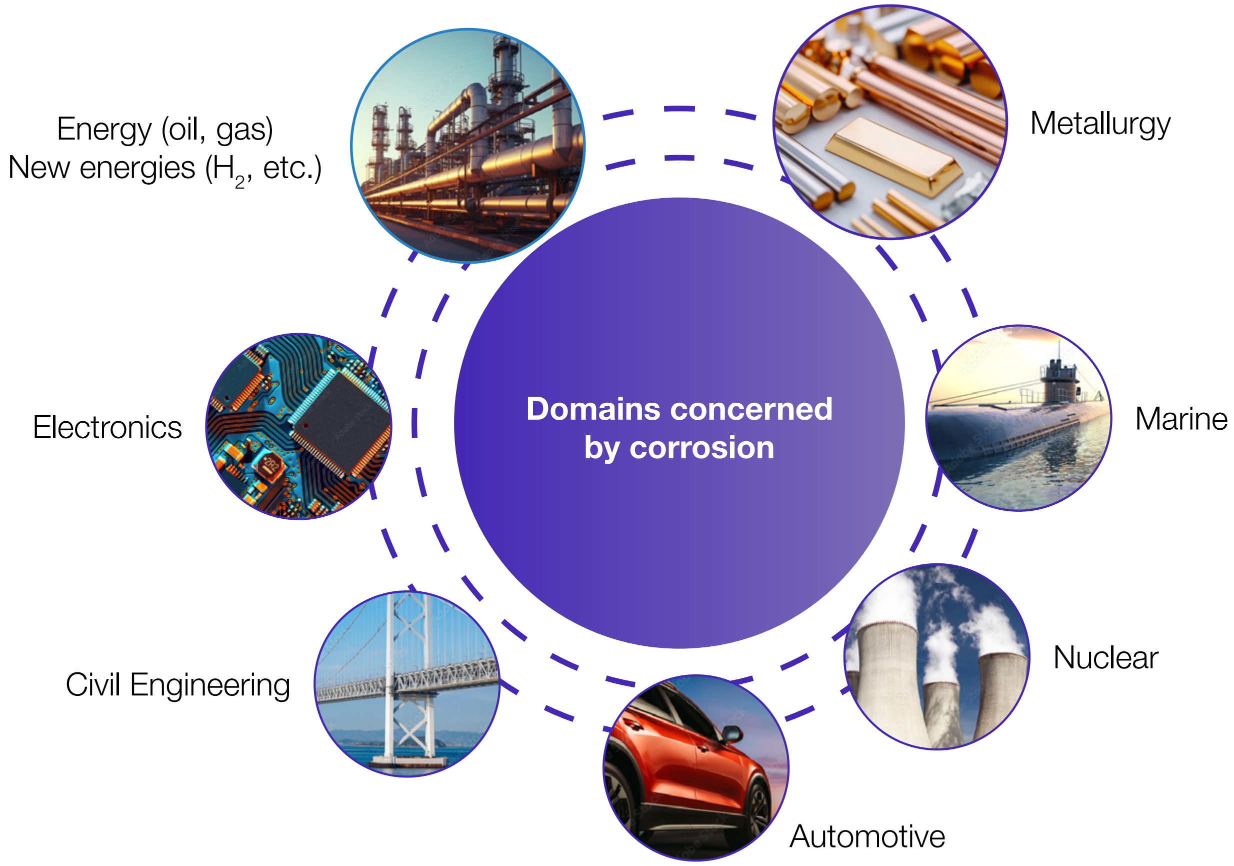
Corrosion (local or uniform) results from chemical reactions over the material due to environmental and mechanical factors.

Environmental Factors

Corrosion and its acceleration can be caused by **environment, pH**, **temperature**, **chemicals**, or **radioactivity**, leading to material degradation and failures, impacting safety and longevity.

Mechanical Factors

Stress and **wear** can also expose metals to corrosion through degradation of the surface, leading to material degradation in stressed and friction-exposed components.



Why do we study corrosion?

The complexity of corrosion processes and coatings presents significant challenges that need to be addressed and require a large range of adequate measurement techniques.

- Accurate prediction and detection of corrosion through advanced monitoring and diagnostic technologies.
- Development of advanced materials and protective coatings to resist corrosion.
- Compliance with environmental regulations, addressing sustainability concerns, and promotion of recycling initiatives.

HORIBA portfolio of instruments support corrosion and corrosion protection studies at **macro, micro, and nanoscales** addressing among other the following topics:

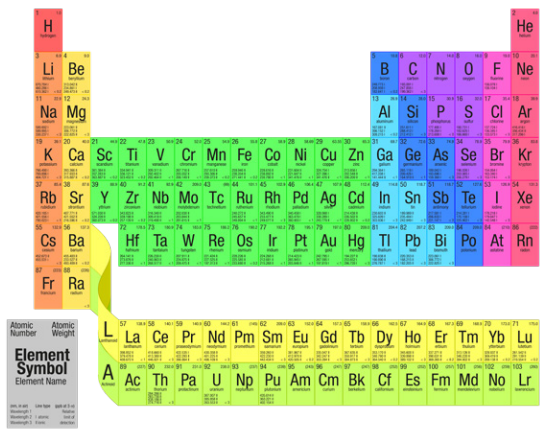
- **Measuring hydrogen in metals** using Elemental Analyzers.
- **Checking surface reactivities in operando** with Atomic Emission Spectroelectrochemistry.
- **Assessing composition, thickness and degradation of passivation films or multi-layer protective coatings** using Glow Discharge Optical Emission Spectroscopy (GDOES) and Raman Spectroscopy.
- **Controlling plating efficiency and detecting plating bath contamination** with X-Ray Fluorescence (XRF) and Inductively Coupled Plasma (ICP).
- **Mapping surfaces to detect local corrosion** using Atomic Force Microscopy (AFM) and Raman Spectroscopy.
- **Analyzing formulations of conversion coatings, organic coatings, and paints** through Particle Characterization Analyzer (PCA), Molecular Fluorescence, Raman Spectroscopy, and GDOES.
- **Investigating root causes of corrosion**.

Our advanced instruments are designed to answer these crucial questions, characterizing materials, looking at surfaces and interfaces, and ensuring the optimal design of materials, coatings, processes, and products.

Analytical needs in corrosion

Elemental analysis for material selection

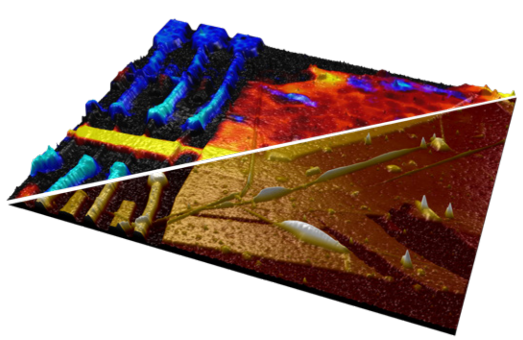
To assess the elemental composition of all materials facing corrosion, HORIBA offers techniques such as **Inductively Coupled Plasma (ICP)** or **X-ray Fluorescence (XRF)**. In this domain, norms and standards are extremely strict.



Evolution of materials should also be addressed. When facing corrosive environments, elements could migrate towards the surfaces, so compositional elemental analysis may drastically change with depth, which could be seen, for instance, with **Glow Discharge Optical Emission Spectroscopy (GDOES)**.

Coatings and protection layers are essential in the prevention of corrosion and can range from nanoscale to several tens of micrometers, and their elemental compositions should also be characterized.

Molecular and structural investigations



In material studies, **Raman Spectrometry** is a key analytical tool. Non-destructive molecular and structural information can be obtained down to microscale using Raman microscopes and on-line observation of corrosion processes can be done remotely with Raman probes.

Topography of surfaces by multimodal **Atomic Force Microscopy (AFM)** will show local non-uniformities where corrosion processes could initiate making it also a decisive asset.

Analysis of particles (powder) is also crucially important when considering susceptibility to and protection from corrosion. Particle size distribution, surface potential and area can be used to analyze and control risks.

Interactions with the environment

Study of surface properties and coatings effectiveness in relation to the environment.

HORIBA offers fast and easy measurement capabilities which generate a wealth of information crucial in understanding the phenomena.

Examples of solutions:

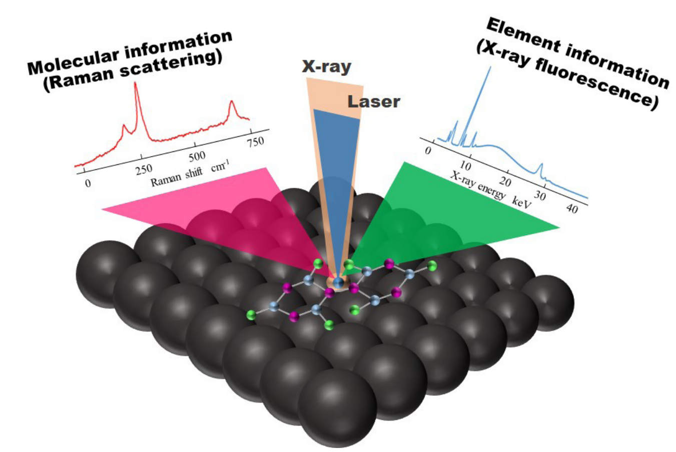
- Measure in operando of surfaces changes exposed to flowing electrolytes.
- Chemical analysis of dissolution products.
- Off-line studies varying corrosion parameters (time, temperature, pH, pressure, etc.).

Coupling techniques to go beyond

Obtained information from any analytical technique is always partial, resulting from interaction of the technique of choice with the material of interest.

Combination of techniques offering a multidimensional approach is therefore crucially important and our analytical techniques can easily be combined with other important surface techniques such as Scanning Electron Microscopy (SEM) or X-ray Photoelectron Spectroscopy (XPS).

For example, Raman measurements can be done at different depths within a GD crater, combining elemental and molecular depth profile analysis. **Correlative measurements** are also performed with accurate repositioning of the points of interest between multiple techniques, as particle analysis with µ-XRF, microRaman and a navYX repositioning system.



Analytical solutions for the study of corrosion

Atomic Emission Spectroelectrochemistry (AESEC)

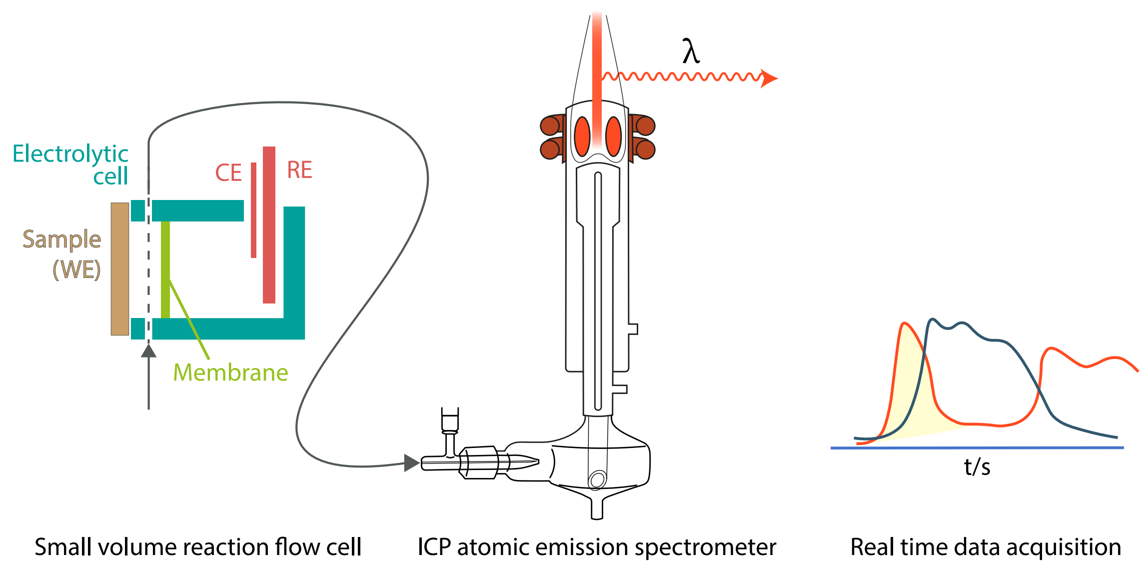
AESEC combines ICP with Electrochemistry. This analytical technique studies the behavior of elements during electrochemical reactions.

- Real-time monitoring of elemental changes during electrochemical reactions.
- Ultra-Fast, high resolution, high dynamic measurement technologies.
- Highly sensitive to detect trace amounts of elements.
- Specifically identify and quantify different elements in a complex mixture.

AESEC can be used to study the corrosion behavior of metals and alloys by monitoring the release of metal ions during the corrosion process and to analyze the deposition of metals onto electrodes.

It can give answers to:

- How do metals and alloys (Cu, Fe, Al, Ni, Ti, Zr, Cr, Mo, etc.) react?
- How do alloy components selectively dissolve?
- What are the stoichiometries of dissolution and film formation?



Conceptual block diagram of AESEC showing three major components of the method: (a) the reaction flow cell. WE: Working Electrode. CE: Counter Electrode. RE: Reference Electrode (b) the ICP torch and aspiration system, and (c) the data acquisition and quantification, illustrated for Zn and Mg.
CORROSION. 2019;75(12):1398-1419. doi:10.5006/3336

Glow Discharge Optical Emission Spectroscopy (GDOES)

GD-Profiler 2™

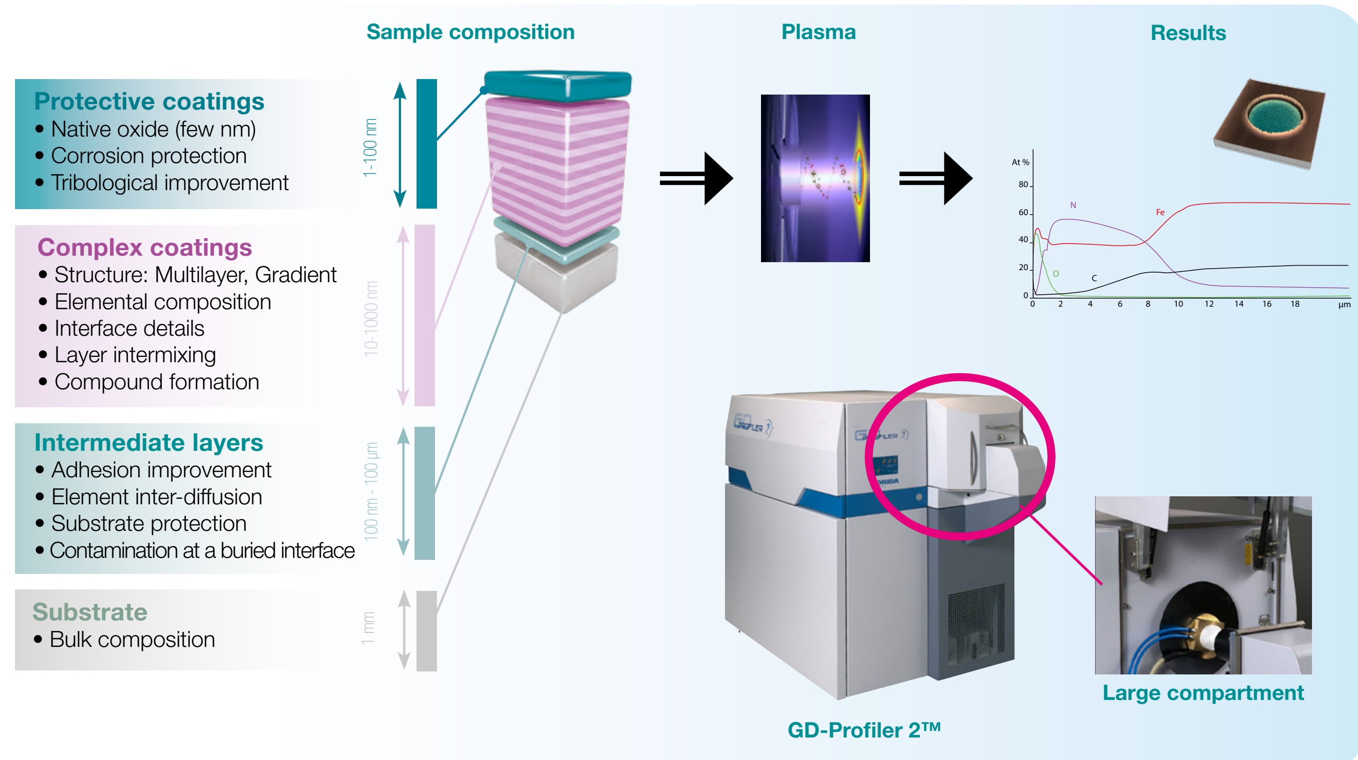
GDOES can provide detailed information about the elemental composition of a material's surface and subsurface layers.

- Can detect all elements including O, H, D, Cl, S, etc.
- Ultra-Fast Elemental depth profile.
- Patented Real Time Depth Measurement DIP.
- Patented Ultra-Fast Sputtering mode for polymeric and carbon layers.

GDOES is advantageous for studying corrosion due to its ability to provide detailed depth profiles of all materials and coatings, rapid and sensitive analysis, with almost no sample preparation, and the capability to enhance the understanding of corrosion mechanisms.

It can give answers to:

- What is the composition and thickness of an oxide layer?
- How to run many samples in short time to statistically assess a process?
- How elements migrate in a coating due to environment?



Analytical solutions for the study of corrosion

Raman spectroscopy

Raman spectroscopy relies on laser/material interaction to study corrosion and can provide detailed analysis about materials without damaging the sample.

- Structural and molecular composition of corroded films down to the micrometric scale.
- In situ characterization.
- Remote operation is possible with fibered SuperHead.

Raman spectroscopy allows for high-resolution spatial mapping of corrosion compounds on complex surfaces, providing detailed insights into the chemical composition and structural changes occurring at different stages of corrosion.

LabRAM Soleil

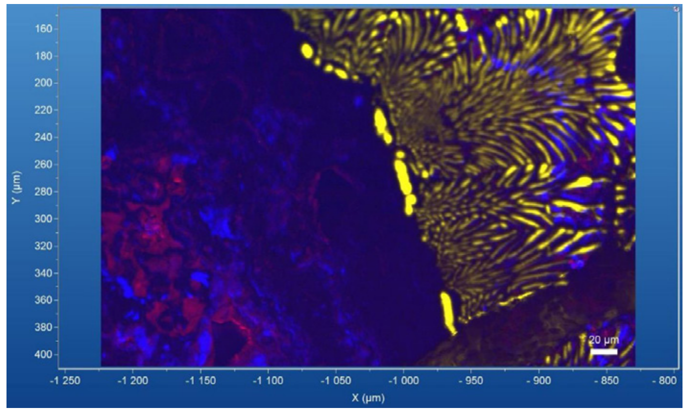
Photoluminescence (PL) is also directly obtained in the Raman instrument, enabling non-destructive, real-time detection and mapping of corrosive species and sites, monitoring protective coatings, and understanding corrosion mechanisms through changes in luminescent properties.

Remote or on-line observation of corrosion process can be checked with the use of a Superhead or flow cell connected to the Raman instrument.

SuperHead

Raman can give answers to:

- Is the material composition consistent with its specification?
- What are the corrosion products formed on the material surface?
- Are there any phase transitions occurring at the interface between materials and in coatings?
- How does the corrosion rate change over time?



Example of PL measurement:
Identical chemical phases of metal oxides can have different luminescence properties associated to the oxidation degree of the metal, linked to the kind of corrosion occurring.

Yellow: eutectic cuprite
Blue: eutectic cuprite corroded
Red: cuprite corroded

EMGA series, Oxygen/Nitrogen/Hydrogen Analyzer

EMGA-Expert

The EMGA analyzer is a specialized instrument used for the precise measurement of Oxygen, Nitrogen, and Hydrogen content in various materials.

- Reference technique for accurate O/H measurement in materials.
- Highly accurate analyses from sub ppm to tens of % in wide measurement range.
- Rapid analysis and automated sample handling to save time.

The EMGA NOH analyzer relies on the technique of fusion in inert gas to provide precise and accurate measurements of Oxygen and Hydrogen content, which are critical to understand corrosion mechanisms, identify corrosion products, and assess material resistance, thereby aiding in the development of more durable materials and coatings. All kind of inorganic materials in chips, pins and powders can be easily analyzed with minimized sample preparation.

EMGA can give answers to:

- How much O is present and so which type of oxide is formed?
- Are there different phases in the material when fusion temperature ramps up?
- What is the level of H and is there any risk of embrittlement?

AR-637	Sample weight (g)	Hydrogen (ppm)
1	0.1016	21.6
2	0.1015	20.6
3	0.1019	23.4
4	0.1008	21.5
5	0.1007	21.7
6	0.1016	22.8
7	0.1004	22.5
8	0.1013	21.0
9	0.1014	22.3
10	0.1015	20.7
	Average (ppm)	**21.81**

Result of Hydrogen amount in Titanium alloys
Reference value of AR-637 25 ± 4 ppm

Analytical solutions for the study of corrosion

AFM-Raman

Atomic Force Microscopy (AFM) provides high-resolution surface imaging of surfaces, giving insights on the initiation and progression of corrosion, surface morphology, roughness, and structural integrity. Combining AFM with Raman spectroscopy significantly enhances the study of corrosion and corrosion protection coatings by providing a comprehensive understanding of corrosion mechanisms and the effectiveness of protective coatings.

SignatureSPM

SignatureSPM is the first multimodal characterization system built on an automated AFM platform and integrated with a Raman/photoluminescence spectrometer.

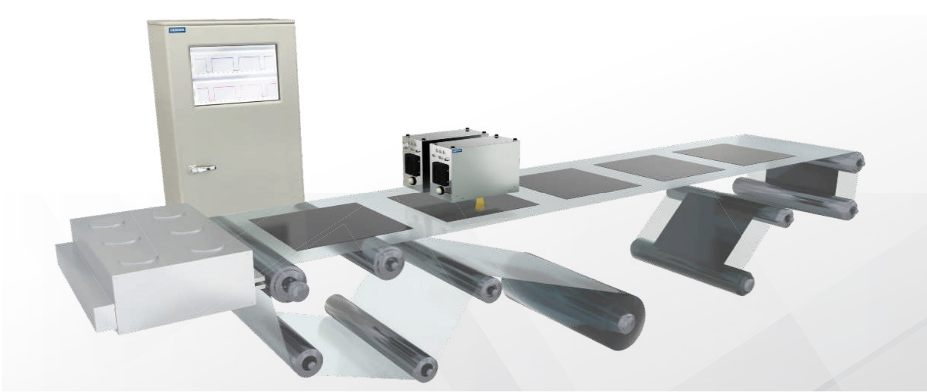
- Surface topography with nanometric chemical information.
- True colocalized measurements of physical and chemical properties.

Micro-X-ray and in-line X-ray fluorescence spectroscopy

X-ray fluorescence (XRF, micro-XRF) is used to provide detailed elemental maps and thickness of materials.

- Non-destructive elemental chemical analysis.
- Real-time and continuous monitoring of samples and coatings.
- Lateral resolution down to 10 µm with XGT9000.

XGT9000



HORIBA inline XRF Monitor

Ellipsometry

Ellipsometry is a powerful tool in corrosion studies due to its high sensitivity and ability to study thin film properties in a liquid environment.

- Reference technique for ultra-thin films.
- Passivation layers and lubricating films studies.

UVISEL Plus

Particle Characterization Analyzer

Partica LA-960V2

Partica LA-960V2 provides insights into the corrosiveness of the environment and the effectiveness of corrosion inhibitors by analyzing the size distribution, surface potential, and surface area of particles.

- Formulation of coatings.
- Study of degradation products.
- Links with surface areas and reactivity.

Fluorescence Spectroscopy

Fluorescence spectroscopy is a non-destructive technique used to characterize corrosion at molecular level by detecting, identifying, and analyzing corrosion products and processes.

- Identify corrosion products by their unique emission spectra and characterize protective coatings.
- Study environmental impacts and monitor corrosion progression over time.
- Detect and track corrosion inhibitors tagged with fluorescent markers.

Fluorolog-QM

Analytical Solution Plaza

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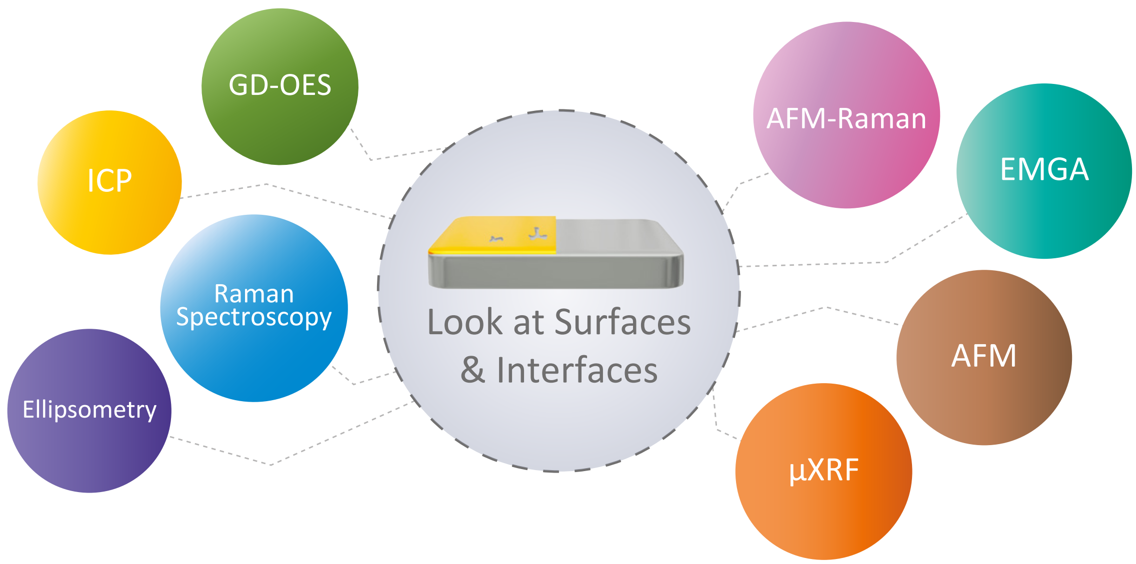
HORIBA Analytical Solutions Plaza has areas for each of HORIBA's focus markets such as "Energy & Environment", "Advanced Materials & Semiconductors", and "Biotechnology & Healthcare".

For corrosion studies, HORIBA promotes application proposals, contract analysis, and joint development tailored to customer needs. As a solution partner for our customers, we aim to provide high value-added services.



HORIBA also offers testing facilities with multiple other equipment for automotive or H_2 energies. Our centers in Venissieux France (for H_2) or Nuneaton UK (Mira —for Automotive) can do corrosion studies of automotive and automotive components.

More about HORIBA

The HORIBA Group, made up of 49 companies in 27 countries, is a leading company that provides **analytical and measurement systems** throughout the world. HORIBA business is evolving in the markets of automotive, process and environmental instruments, medical diagnostics, semiconductor instruments and scientific instruments. It is our continual source of joy and pride that our analytical and measurement business can contribute to **global environmental conservation, safety and health, and moreover, to mitigating energy problems**.

HORIBA

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